THE FEASIBILITY OF A UNITISED REGENERATIVE FUEL CELL WITH A REVERSIBLE CARBON-BASED HYDROGEN STORAGE ELECTRODE

A thesis submitted in fulfillment of the requirements for the degree of Master of Engineering by Research

Mohammad Javad Jazaeri
B.Sc.

School of Aerospace, Mechanical and Manufacturing Engineering
College of Science, Engineering and Health
RMIT University
August 2013
ACKNOWLEDGMENTS

I would like to thank my supervisor, Associate Professor John Andrews, for sharing his ideas, knowledge, and insights. I am very grateful for his tireless efforts in providing guidance, feedback and constant motivation during this program. I would like to express my gratitude to Dr Fugen Daver (RMIT University) for suggesting saturated salt solutions in obtaining constant relative humidities and also for granting me access to the chemistry lab, the BET measurement analyser, and the hot-press machine. I would also like to thank Dr Anthony O'Mullane (RMIT University) for sharing his knowledge in electrochemical impedance spectroscopy (EIS) and for spending his valuable time to help me with the EIS measurements.

I would like to thank Professor Aliakbar Akbarzadeh (RMIT University) for his encouragement and financial support in the duration of this program. I truly appreciate the opportunities that Dr Abhijit Date and Dr Asintha Nanayakkara from RMIT University have given me to experience teaching and tutoring.

Many thanks go to Mr Saeed Seif Mohammadi (MEng graduate, RMIT University) who selflessly shared his experience on the URFC set-ups. I would like to thank Mr Amandeep Oberoi (PhD candidate, RMIT University) for being my lab-mate. I also would like to thank many good friends in the Energy CARE group who shared good times and bad times with me. If I wanted to name everybody who has inspired, taught and encouraged me along the way, this section would have been several pages long.

I would like to thank Ms Zahra Homan from School of Applied Sciences (RMIT University) for her technical assistance in the chemistry lab. I also would like to acknowledge Professor Alan Chaffee (Monash University) and Mr Lachlan Ciddor (PhD candidate, Monash University) for providing a number of activated carbons.

I would like to acknowledge the facilities, and the scientific and technical assistance, of the Australian Microscopy & Microanalysis Research Facility at the RMIT Microscopy &
Microanalysis Facility. In particular, I would like to thank Mr Phil Francis and Mr Peter Rummel.

I would like to thank Mr Patrick Wilkins and Mr David Goodie from the School of Aerospace, Mechanical, and Manufacturing Engineering workshop at RMIT University for manufacturing the experimental cell and guiding me in modifying the designs.

I would like to express my gratitude to Ms Lina Bubic and Ms Emilija Simic from RMIT University for their administrative assistance throughout this program. I would like to thank Ms Wendy Haszler from RMIT University library for her assistance in finding some of the references. I also would like to acknowledge the generous International Conference Grant from the School of Graduate Research, RMIT University.

I heartily thank my family for their never-ending love, encouragement, and for always being there for me. I would like to dedicate whatever I have achieved in the past two years to them.
DECLARATION

I, Mohammad Javad Jazaeri, hereby submit the thesis entitled “The Feasibility of a Unitised Regenerative Fuel Cell with a Reversible Carbon-Based Hydrogen Storage Electrode” for the degree of Master of Engineering by Research and certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, for any other academic award and that the content of the thesis is the result of work that has been carried out since the official commencement of the program.

Mohammad Javad Jazaeri
30 August 2013
# TABLE OF CONTENTS

## 1 INTRODUCTION
1.1 ROLE OF HYDROGEN IN A SUSTAINABLE ENERGY STRATEGY 1  
1.2 HYDROGEN STORAGE TECHNOLOGIES 3  
1.3 ELECTROCHEMICAL STORAGE OF HYDROGEN 6  
1.4 THE PROTON FLOW BATTERY CONCEPT 7  
1.5 SIGNIFICANCE OF THE RESEARCH 8  
1.6 OBJECTIVES OF THE PROJECT 9  
1.7 RESEARCH QUESTIONS 10  
1.8 SCOPE 10  
1.9 EXPECTED OUTCOMES 11  
1.10 NOVELTY OF THE PROJECT 11  
1.11 STRUCTURE OF THE THESIS 12

## 2. RESEARCH DESIGN AND METHOD
2.1 OVERVIEW 14  
2.2 GENERAL METHODOLOGICAL APPROACH 14  
2.3 EXPERIMENTAL PROCEDURES 14  
2.4 INSTRUMENTATION AND COLLECTING DATA 16  
2.5 ACTIVITIES 17

## 3. THE CONCEPT OF A REVERSIBLE URFC WITH AN INTEGRATED CARBON HYDROGEN STORAGE ELECTRODE
3.1 COMPONENTS OF A HYDROGEN SYSTEM 20  
3.1.1 PEM electrolyzers 20  
3.1.2 Methods of hydrogen storage 22  
  3.1.2.1 High-pressure hydrogen storage 22  
  3.1.2.2 Liquid hydrogen 24  
  3.1.2.3 Hydrogen sorption in solid state 25  
  3.1.2.4 Chemically bonded hydrogen storage liquids 26  
3.1.3 PEM fuel cell 26  
3.1.4 Structure and principles of a PEM URFC 27  
3.2 CONVENTIONAL HYDROGEN SYSTEMS 30  
3.2.1 A hydrogen system employing an electrolyser, storage unit, and fuel cell 30  
3.2.2 A hydrogen system employing a URFC and storage unit 32  
3.3 INTEGRATED HYDROGEN STORAGE IN A PEM URFC 34  
3.3.1 The concept of the proton flow battery 34  
3.3.2 Benefits and potential applications of a proton flow battery 35  
3.4 PREVIOUS WORK ON THE CONCEPT OF INTEGRATING HYDROGEN STORAGE ELECTRODE IN URFC 36  
3.4.1 History of the concept 36  
3.4.2 General Electric Company and a rechargeable fuel cell 45  
3.4.3 Electrochemical storage of hydrogen in activated carbon 51  
3.4.4 Recent work on the concept of proton flow battery at RMIT University 57
# 3.5 SOLID STATE HYDROGEN STORAGE IN ACTIVATED CARBON

3.5.1 Activated carbon as the medium for hydrogen storage 58  
3.5.2 Mechanism of electrochemical storage of hydrogen in activated carbon 59

# 3.6 Conclusions

3.6.1 Limitations of previous studies and areas requiring R&D 60  
3.6.2 Towards realisation of the concept of a proton flow battery with activated carbon electrode 61

# 4. FABRICATION AND CHARACTERISATION OF ACTIVATED CARBON-NAFION COMPOSITE MATERIALS

## 4.1 FABRICATING ACTIVATED CARBON

4.1.1 Preparation and characterisation of precursors 62  
4.1.1.1 Precursors 62  
4.1.1.2 Morphology of precursors 64  
4.1.1.3 Elemental analysis of precursors 68  
4.1.2 Activation techniques 72  
4.1.2.1 Physical activation 72  
4.1.2.2 Chemical activation 73  
4.1.2.3 Replica technique 75  
4.1.2.4 Selecting the activation technique 75  
4.1.3 Activating precursors with chemical activation technique 76  
4.1.3.1 Carbonisation 76  
4.1.3.2 Impregnation 77  
4.1.3.3 Activation 78  
4.1.3.4 Washing 79  
4.1.3.5 Drying 80  
4.1.3.6 Summary of the KOH activation procedures 81  
4.1.4 Activated carbons from Monash University 83

## 4.2 CHARACTERISTICS OF ACTIVATED CARBONS AND SELECTING SAMPLES FOR COMPOSITE MATERIALS

4.2.1 Porosity measurement 83  
4.2.1.1 Models of activated carbon and the concept of porosity 83  
4.2.1.2 Adsorption isotherm analysis method 85  
4.2.1.3 CO2 and N2 adsorption isotherms 90  
4.2.1.4 Summary of porosity tests on the activated carbons 92  
4.2.2 Selecting samples for fabricating composite material 94  
4.2.2.1 Influential factors in selecting samples 94  
4.2.2.2 Selecting samples for fabrication of composite electrodes 94

## 4.3 FABRICATION OF COMPOSITE MATERIALS

4.3.1 Ingredients for composite materials 95  
4.3.1.1 Nafion solution 95  
4.3.1.2 Activated carbons 97  
4.3.2 Mixing nafion and selected activated carbon samples 97  
4.3.3 Fabricating of the composite materials 99  
4.3.3.1 Solution casting of the composite materials 99  
4.3.3.2 Size and number of the composite samples 100  
4.3.4 Protonation of composite materials 101  
4.3.5 Investigation of proper dispersion of activated carbon in nafion 101
# TABLE OF CONTENTS

4.4 SETTING UP DIFFERENT RELATIVE HUMIDITY ENVIRONMENTS 107

4.4.1 Design and manufacturing of a relative humidity chamber 107

4.4.2 Test points in environments at various relative humidities 109

4.5 PHYSICAL BEHAVIOUR OF THE COMPOSITE MATERIALS IN DIFFERENT RELATIVE HUMIDITY ENVIRONMENTS 109

4.5.1 Measurements of the composites in different relative humidity environments 109

4.5.2 Water uptake of the composite materials 111

4.5.3 Swelling of the composite materials 115

4.6 MEASUREMENT OF ELECTRON AND PROTON CONDUCTIVITY OF THE COMPOSITE MATERIALS 117

4.6.1 Electrochemical impedance spectroscopy 117

4.6.2 Design and manufacturing the test cell for EIS method 119

4.6.3 Equivalent circuit
   - 4.6.3.1 Equivalent circuit of nafion membrane 120
   - 4.6.3.2 Equivalent circuit of composite material 122

4.6.4 Electrochemical characterisation of the test set-up 125
   - 4.6.4.1 Identifying values of EIS test rig 125
   - 4.6.4.2 Proton conductivity of Nafion 115 membrane 126

4.6.5 Proton conductivity of the composite materials 127

4.6.6 Electron conductivity of the composite materials 129

4.7 SELECTING THE COMPOSITE MATERIALS FOR FABRICATING FULL-SIZE COMPOSITE ELECTRODES 132

4.7.1 Overview of electron and proton conductivity of the composite materials 132

4.7.2 Selection of materials for test electrodes 133

4.8 ANALYSIS OF THE PHYSICAL AND ELECTROCHEMICAL CHARACTERISTICS OF THE COMPOSITE MATERIALS 135

4.8.1 Water uptake of the composite materials in different relative humidity environments 135

4.8.2 Volumetric swelling of the composite materials in different relative humidity environments 136

4.8.3 Proton conductivity of the composite materials in different relative humidity environments 137

4.8.4 Electron conductivity of the composite materials in different relative humidity environments 138

4.9 OTHER APPLICATIONS FOR THE FABRICATED COMPOSITE MATERIALS 139

5. TESTS ON THE COMPOSITE ELECTRODES IN THE EXPERIMENTAL REVERSIBLE FUEL CELL 141

5.1 FABRICATION OF THE FULL-SIZE COMPOSITE ELECTRODES 141

5.1.1 Employing a backing layer in the composite electrodes 141

5.1.2 Casting the full-size composite electrodes 145

5.1.3 Protonation of the casted composite electrodes 147

5.1.4 The specifications of the composite electrodes 148

5.2 FABRICATION OF THE MEMBRANE ELECTRODE ASSEMBLIES 149

5.2.1 The catalysts for the oxygen electrode 149

5.2.2 Nafion membrane protonation 150

5.2.3 Hot pressing the electrodes and membranes 151
5.3 DESIGN AND CONSTRUCTION OF THE EXPERIMENTAL PEM URFC CELL 154
5.3.1 Material of the end-plates 154
5.3.2 Design of the flow channels 155
5.4 THE CONSTRUCTION OF THE EXPERIMENTAL PROTON FLOW BATTERIES 158
5.4.1 The structure of the proton flow battery 158
5.4.2 The components of the cell
   5.4.2.1 membrane-electrode-assembly 159
   5.4.2.2 The end-plates and the flow channel 160
   5.4.2.3 The sealing of the cell 160
5.5 THE EXPERIMENTAL SETUP 162
5.5.1 Components of the experimental setup 162
   5.5.1.1 Gas storage tanks 162
   5.5.1.2 Power supply 163
   5.5.1.3 Hydrogen extraction cabinet 163
5.5.2 The experimental setup 164
5.6 EXPERIMENTAL PROCEDURE 167
5.6.1 Electrolyser mode 167
5.6.2 Fuel cell mode 167
5.7 EXPERIMENTAL RESULTS 169
5.7.1 Voltage-current characteristics 169
5.7.2 Charging with constant current 177
5.8 DISCUSSIONS 184
6. DISCUSSIONS OF THE RESULTS 188
6.1 POSSIBLE EXPLANATIONS FOR THE EXPERIMENTAL RESULTS 188
   6.1.1 Summary of the key findings 188
   6.1.2 Limited nafion penetration into activated carbons 189
   6.1.3 Existence of oxygen groups on the activated carbon surfaces 192
   6.1.4 Competitive reactions that prevent hydrogen storage 195
   6.1.5 Possible irreversible hydrogen storage 194
6.2 FINDINGS 198
7. CONCLUSIONS AND RECOMMENDATIONS 199
7.1 RESPONSES TO THE RESEARCH QUESTIONS 199
   7.1.1 What types of carbon materials have been used in reversible and direct hydrogen storage? 199
   7.1.2 What is the proper procedure to fabricate activated carbon samples, the composite materials and the composite electrodes for this application? 200
   7.1.3 What would be the performance of composite materials of carbon and proton conducting media in different levels of hydration? 201
   7.1.4 How does the performance of the URFCs with composite electrodes compare with that of typical standard URFCs? 203
   7.1.5 Is it feasible to incorporate the fabricated composite electrodes into URFCs for direct reversible hydrogen storage? 203
7.2 THE KEY CONTRIBUTIONS OF THIS THESIS 204
   7.2.1 Activating carbon with KOH chemical activation method 204
   7.2.2 Fabricating composite materials from activated carbon and nafion 205
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2.3</td>
<td>Characterising the composite materials under various relative humidities</td>
<td>206</td>
</tr>
<tr>
<td>7.2.4</td>
<td>Dual proton and electron conductivity of the fabricated composite materials</td>
<td>206</td>
</tr>
<tr>
<td>7.2.5</td>
<td>Casting of full-size composite electrodes</td>
<td>207</td>
</tr>
<tr>
<td>7.2.6</td>
<td>Testing the composite electrodes in a PEM URFC experimental cell</td>
<td>208</td>
</tr>
<tr>
<td>7.3</td>
<td>CONCLUSIONS</td>
<td>209</td>
</tr>
<tr>
<td>7.4</td>
<td>RECOMMENDATIONS</td>
<td>211</td>
</tr>
<tr>
<td>7.4.1</td>
<td>Computer simulation on proton conductivity within the composite materials and rate of sorption and desorption reactions in various conditions</td>
<td>211</td>
</tr>
<tr>
<td>7.4.2</td>
<td>The relationship between water uptake of composite materials and mesoporosity</td>
<td>212</td>
</tr>
<tr>
<td>7.4.3</td>
<td>New composite materials with different carbon to nafion ratio</td>
<td>212</td>
</tr>
<tr>
<td>7.4.4</td>
<td>Investigating irreversible hydrogen storage in the composite electrodes</td>
<td>212</td>
</tr>
<tr>
<td>7.4.5</td>
<td>Doping activated carbon to encourage sorption reaction in the electrolyser mode</td>
<td>213</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>Schematic of a PEM electrolyser</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>Polarisation curve for PEM electrolysers</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>Schematic of constant Electrode PEM URFC</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>Schematic of a conventional hydrogen system</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>Schematic of a hydrogen system with URFC</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>Schematic of Integrated hydrogen storage in PEM URFC</td>
<td>34</td>
</tr>
<tr>
<td>7</td>
<td>The exploded view of Folonari et al.’s cell</td>
<td>37</td>
</tr>
<tr>
<td>8</td>
<td>Schematic of the hydrogen charging of metals using proton conducting ceramics proposed by Condon and Schober (1995)</td>
<td>39</td>
</tr>
<tr>
<td>9</td>
<td>Schematic of the proposed system with proton conducting ceramic</td>
<td>39</td>
</tr>
<tr>
<td>10</td>
<td>Potential of the metal hydride electrode versus the reference electrode</td>
<td>41</td>
</tr>
<tr>
<td>11</td>
<td>A schematic of an electrode from Sanders (2007)</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>A schematic of the complete cell suggested by Sanders (2007)</td>
<td>43</td>
</tr>
<tr>
<td>13</td>
<td>The schematic of the fuel cell/battery concept of Choi et al (2010)</td>
<td>44</td>
</tr>
<tr>
<td>14</td>
<td>Simplified schematic of the device proposed by Wang and Wei (2007)</td>
<td>46</td>
</tr>
<tr>
<td>15</td>
<td>Schematic of the new configuration for the concept of rechargeable fuel cell</td>
<td>47</td>
</tr>
<tr>
<td>16</td>
<td>Schematic of the full cell of a rechargeable fuel cell</td>
<td>49</td>
</tr>
<tr>
<td>17</td>
<td>Schematic of a rechargeable metal air battery</td>
<td>50</td>
</tr>
<tr>
<td>18</td>
<td>Schematic representation of the rechargeable fuel cell</td>
<td>55</td>
</tr>
<tr>
<td>19</td>
<td>The different morphologies of the outer and inner (fractured) surfaces of black coal pieces</td>
<td>63</td>
</tr>
<tr>
<td>20</td>
<td>The morphologies of charcoal samples</td>
<td>64</td>
</tr>
<tr>
<td>21</td>
<td>SEM picture of the charcoal powder before activation using Philips XL30 SEM</td>
<td>65</td>
</tr>
</tbody>
</table>
Figure 22: Different structures in the charcoal powder using Philips XL30 SEM

Figure 23: SEM picture of the black coal powder before activation using an FEI Quanta 200 ESEM

Figure 24: A particle of the coal sample in high magnification using FEI Quanta 200 ESEM

Figure 25: Schematic of an EDX apparatus

Figure 26: EDS result for the charcoal sample before activation using Philips XL30 SEM with Oxford Si (Li) detector

Figure 27: EDS for black coal sample before activation

Figure 28: Schematic of the horizontal tube furnace used in the present project (modified from Agirre et al. 2013)

Figure 29: The horizontal tube furnace at RMIT University used in KOH chemical activation

Figure 30: Washing apparatuses of activated carbon

Figure 31: EDS elemental analysis of an activated carbon sample after washing step

Figure 32: Computer-generated model of activated carbon

Figure 33: McBain balance for adsorption isotherm

Figure 34: Typical adsorption isotherms for a porous sample

Figure 35: BET plot generated from an adsorption isotherm results

Figure 36: Comparison of CO2 and N2 adsorption isotherm data in DR plot

Figure 37: Structure of nafion.

Figure 38: A mixture of nafion and activated carbon in the beaker

Figure 39: Casting the composite materials in the mould.

Figure 40: Surface of the EIS samples

Figure 41: Low magnified images of cross section of the composite materials

Figure 42: Higher magnified images of cross section of the composite material of AC3

Figure 43: The cross sectional of AC4 at different magnifications

XIII
Figure 44: The variable relative humidity chamber used to vary the level of hydration of the sample composite materials.

Figure 45: Water pathways in Nafion

Figure 46: Water uptake of the aC-nafion composite materials in various relative humidity environments.

Figure 46: Water uptake per SO3$^-$ group ($\lambda$) of the aC-nafion composite materials in various relative humidity environments.

Figure 48: Nafion intrusion into the gas diffusion layer

Figure 49: Swelling of the aC-nafion composite materials in various relative humidity environments.

Figure 50: EIS cell designs for (a) in-plane and (b) through plane arrangement

Figure 51: EIS test cell used to measure proton and electron conductivity of the ac-nafion composite materials

Figure 52: Equivalent circuit for nafion membrane and test configuration

Figure 53: Equivalent circuit and Nyquist plot for mixed conductive material at different temperatures

Figure 54: Equivalent circuit and test configuration for measuring proton conductivity of the aC-nafion composite materials

Figure 55: Electric resistance of the EIS set-up and the result of measuring electric resistance of the EIS set-up

Figure 56: Nyquist plot of Nafion 115 soaked in water

Figure 57: Experimentally-measured proton conductivities of the aC-nafion composite materials in various relative humidity environments.

Figure 58: Electron conductivity of the aC-nafion composite materials in various relative humidity environments.

Figure 59: Electron and proton resistance of the composite materials in various relative humidity environments.

Figure 60: Photocatalytic system using a dual proton and electron conductive material

Figure 61: The backing layer beneath the composite material

Figure 62: SEM image of carbon cloth by using Philips XL30 SEM
Figure 63: The composite electrode made without backing layer 143
Figure 64: The aluminium foil backing of an electrode before and after being tested in the experimental PEM URFC 144
Figure 65: Delamination of the activated carbon electrode from the membrane 144
Figure 66: The first try to make a composite aC-nafion electrode with carbon cloth as backing layer 146
Figure 67: A fully hydrated composite aC-nafion electrode twice coated with aC-nafion slurry 147
Figure 68: The protonation of composite electrodes, left: the magnetic hot plate, right: washing the electrodes 148
Figure 69: Nafion membrane with and without treatment with hydrogen peroxide and sulphuric acid. 151
Figure 70: MEA fabrication techniques 152
Figure 71: Hot-press machine at RMIT University 153
Figure 72: Hot pressing machine for fabricating the MEAs 154
Figure 73: Flow field patterns 155
Figure 74: The designed URFC cell in this thesis 157
Figure 75: Components of a proton flow battery 159
Figure 76: The position of the seal in a PEM URFC 161
Figure 77: The silicone rubber seals on the end-plates of the experimental URFC 161
Figure 78: The storage tank used for hydrogen and oxygen gases in the experimental URFC system 162
Figure 79: The DC power supply used in the electrolyser mode 163
Figure 80: The hydrogen cabinet at RMIT University 164
Figure 81: The schematic of the experimental set up 165
Figure 82: The experimental setup in electrolyser mode 166
Figure 83: The experimental setup in fuel cell mode 166
Figure 84: The electric circuit in the electrolyser mode 167
Figure 85: The electric circuit in the fuel cell mode 168
Figure 86: The measured polarisation curves for the ACN1 170
Figure 87: The measured polarisation curves for the ACN2 171
Figure 88: The measured polarisation curves for the ACS1  172
Figure 89: The measured polarisation curves for the ACS2  173
Figure 90: The PEM URFC polarisation curves for MEAs with various  175
catalyst loadings on O-side and H-side
Figure 91: The performance of the fabricated composite MEAs compared  176
to a normal MEA with same catalyst types and loading on oxygen electrode in the electrolyser mode
Figure 92: The performance of the fabricated composite MEAs compared  177
to a normal MEA with same catalyst types and loading on oxygen electrode in the fuel cell mode
Figure 93: The discharge mode of the ACN1 electrode after charging at a  178
constant current of 32 mA/g of activated carbon
Figure 94: The discharge mode of the ACN2 electrode after charging at a  179
constant current of 18 mA/g of activated carbon
Figure 95: The discharge mode of the ACS1 electrode after charging at a  180
constant current of 30 mA/g of activated carbon
Figure 96: The discharge mode of the ACS2 electrode after charging at a  181
constant current of 29 mA/g of activated carbon
Figure 97: The schematic of role of bulk water in defusing protons into a  191
activated carbon particle
LIST OF TABLES

Table 1: DOE targets for on-board hydrogen storage in light-duty vehicles 4
Table 2: Activities conducted in this research project 18
Table 3: The composition of the charcoal and coal 71
Table 4: Ranking the activating techniques for the application of this thesis 75
Table 5: Summary of the activation methods for the activated carbon samples prepared at RMIT in this project 82
Table 6: Porosity of the activated carbon samples 93
Table 7: Composition of the nafion solution 96
Table 8: Equilibrium relative humidities for selected saturated salt solutions at 20, 25, and 30°C (ATSM 2012) 107
Table 9: Specification of the hygrometer of the humidity chamber 109
Table 10: Measurements of the samples before and after RH 110
Table 11: Summary of proton and electron conductivity of composite materials 132
Table 12: Dual proton and electron conduction at full hydration 140
Table 13: The mass and the dimensions of the composite electrodes 149
Table 14: Dimensions of the experimental cell 158
Table 15: The summary of the performance of the composite electrodes with constant-current charge at 0.01 A 183
EXECUTIVE SUMMARY

The limited number of oil and gas resources and the irreversible environmental effects of using fossil fuels, such as global warming, require increasing the share of renewable energy sources, in particular solar and wind, to meet the increasing global energy demand. However, an inherent characteristic of most renewable energy sources is their variability and intermittency. Hence, effective and economic energy storage technologies are needed to allow continuous energy supply from renewables. Hydrogen has been proposed as a storage medium with wide applications in grid storage systems and vehicular storage systems.

A conventional zero-emission hydrogen energy storage system consists of an electrolyser, a hydrogen storage, and a fuel cell. The electrolyser produces hydrogen gas usually by splitting water with electricity that has been produced by photovoltaic cells. The produced hydrogen gas is then stored in a separate hydrogen storage unit, in form of compressed gas or liquid, or stored in solid state storage materials like metal hydrides. When the electricity demand is higher than the electricity production from photovoltaic cells, hydrogen can be extracted from the hydrogen storage unit and transferred to a separate fuel cell. In the fuel cell, hydrogen and oxygen are recombined together to produce electricity and water. A more compact hydrogen system uses a unitised regenerative fuel cell that is a single device that is capable to operate as fuel cell and electrolyser. With this device the hydrogen system needs only a URFC and a separate hydrogen storage unit. Hydrogen gas is produced in the URFC during electrolyser mode. The produced hydrogen gas is stored in the hydrogen storage unit. When it is required, hydrogen is extracted from the hydrogen storage unit and goes back to the URFC to react with oxygen gas during the fuel cell mode of the URFC.

The new concept that has been investigated in this thesis, called a proton flow battery, is to integrate all the three components of a conventional hydrogen system, i.e. electrolyser, storage unit, and fuel cell, into a single device. In this concept, the hydrogen storage unit is integrated into a proton exchange membrane URFC. The hydrogen ions (protons) are produced in the electrolyser mode on the oxygen electrode. The protons are transferred
through the proton exchange membrane to the hydrogen electrode. The material of the hydrogen electrode is selected to reversibly store hydrogen. In this thesis, a number of composite materials of activated carbon and nafion have been used for fabrication of the hydrogen electrode. Nafion is a proton conducting polymer and is used in this thesis to facilitate the proton distribution and transport into the composite electrodes. The protons combine with electrons on the hydrogen electrode and electrochemically are stored in the hydrogen electrode. In the fuel cell mode, hydrogen is extracted from the hydrogen electrode in form of protons. The protons are transferred back to the oxygen electrode, where they react with oxygen and produce electricity and water.

The overall aim of this thesis was to investigate the feasibility of using activated carbon (aC) as a hydrogen storage material in realisation of the concept of integrating hydrogen storage unit in a PEM URFC. To achieve this aim, a set of in-house activated carbons were fabricated by the author, and several other forms of activated carbon were supplied by Monash University. A number of composite materials from the activated carbon and nafion were made, and the physical and electrochemical properties of the composite materials were determined at different relative humidities. The composite materials were scaled up to fabricate composite electrodes. These composite electrodes were tested in a specially designed PEM URFC to investigate the feasibility of the proton flow battery concept.

The research questions addressed in this thesis were as follows:

1. What types of carbon materials have been used in reversible and direct hydrogen storage?
2. What is the proper procedure to fabricate activated carbon samples, the composite materials and the composite electrodes for this application?
3. What would be the performance of composite materials of carbon and proton conducting media in different levels of hydration?
4. How does the performance of the URFC with composite electrodes compare with that of typical standard URFC?
5. Is it feasible to corporate the fabricated composites for direct reversible hydrogen storage in URFCs?
The outcomes of this thesis are:

- Activation of five carbon samples from charcoal and black coal precursors with KOH chemical activation
- Characterisation of the activated carbons including porosity with CO₂ adsorption isotherm at 273 K and N₂ adsorption isotherm at 77 K, elemental composition with energy-dispersive electron spectroscopy (EDS), morphology and particle size with scanning electron microscopy
- Fabrication of six composite materials from Nafion and activated carbon samples with solution casting that have dual proton and electron conductivity
- Measurement of the properties of the composite materials at five different relative humidities, including:
  - Physical characterisation, water uptake and volumetric swelling. The cross-sectional structures of the composite materials were obtained by scanning electron microscopy.
  - Electrochemical characterisation, namely proton conductivity and electron conductivity.
- Development of a new method to measure proton conductivity of high carbon content composite aC-Nafion materials with electrochemical impedance spectroscopy
- Fabrication of full-size composite electrodes of Nafion and activated carbons and fabricating membrane-electro-assemblies (MEAs) by hot-pressing
- Design and construction of a special cell for testing the concept and testing the MEAs in the experimental PEM URFC sell
- Identification of the limitations of the concept and proposing a set of specific recommendations for future work

A comprehensive review of the literature on the concept of the proton flow battery revealed that a concept with some similarities to the one investigated in the present thesis has been patented by General Electrics in 2007. However, no experimental results on the performance of an actual system have so far been published. The literature review on the use of activated carbon revealed that a considerable amount of hydrogen has been stored directly in activated carbon electrodes in cells with an alkaline electrolyte. The reversible hydrogen storage as high as 2 wt% have been reported in KOH electrolyte. The feasibility
of storing hydrogen in activated carbon in acidic electrolyte has also been demonstrated in the literature, but not using a solid-state PEM electrolyte.

Taking into account that the hydrogen storages of metal hydrides are only about 1 wt%, and they have a high cost, activated carbon has been studied in this thesis.

The activated carbons used in the present study were made by KOH activation. The precursors were ground and the carbonised under nitrogen gas at 900°C. The samples were then mixed with KOH with the mass ratio of 3 to 1 or 4 to 1 of KOH to carbon. The activation was carried out under nitrogen gas at 700°C and 800°C. Four activated carbon samples were also provided by Monash University.

From the total nine activated carbons, six activated carbons were selected to be mixed with nafion to fabricate composite materials. The composite materials were made by solution casting and were protonated with sulphuric acid. The protonation step was carried out to ensure proper proton conductivity in the nafion of the composite materials.

Five different relative humidities were used in this thesis. For 0% relative humidity, the samples were placed in a desiccator jar. For the 40% relative humidity the samples were placed in an air-conditioned room with constant relative humidity. For the 75% relative humidity, the standard of American society for testing and materials (E104-02) were used that uses saturated salt solutions to create a constant relative humidity. Sodium chloride salt was used to obtain 75% relative humidity. For 100% relative humidity, the samples were placed in an environment saturated with water vapour. For fully hydrated conditions, the samples were immersed in water.

The results of the physical characteristics in the different relative humidities showed that the water uptake of the composite materials increases with increasing relative humidity. The values of water uptake increase from 5-12 wt% at 35% relative humidity to 45-85 wt % at fully hydrated in water. The measurements of volumetric swelling of the composite materials show that it also increases with increasing relative humidity. The volumetric swelling ranges from 20 % AC4 to 60 % for ACN.
The proton conductivity at fully hydrated state is in the range of 0.04 S/cm (AC4) to 0.11 S/cm (ACK2.5). One explanation of the high values of proton conductivity might be due to the high water uptake of the composite materials. The electron conductivity of the composite materials decreases with increasing the relative humidity. This might be because of the volumetric expansion of the composite materials and increasing the distance between activated carbon particles in the composites. The electron conductivities of all the composites at fully hydrated condition were around 0.5 S/cm, except ACN with 2.3 S/cm.

The composite aC-nafion material designed and fabricated within this project itself constitutes a novel material with the very interesting property of being capable of conducting both electrons and protons at the same time. This form of material alone is a significant discovery. Such a dual proton and electron conductor has potential applications in devices such as battery electrodes, chemical sensors, gas separators, electrochromic windows, and photocatalytic systems that directly use sunlight to split water to hydrogen gas and oxygen gas.

The efforts to scale up the size of composite material revealed the fabrication limitations. To address the issue, a backing layer was used to reinforce the structural integrity of the composite electrodes. Aluminium foil was initially chosen, but further experiments revealed the corrosion in the PEM URFC environment. Carbon cloth was later selected as the backing layer for the composite electrodes. The composite electrodes were hot-pressed with Nafion 115 membrane and oxygen electrode that contained 2 mg/cm² of IrRuOₓ and 2 mg/cm² of PtB. In a previous PhD thesis (Doddathimmaiah 2008), this combination of catalysts was found to have the best performance for the oxygen electrode in a PEM URFC.

The experiments in the specially designed PEM URFC showed no observable signs of hydrogen storage in the tests conducted to date. The URFCs with composite electrodes were charged in constant current and constant voltage to study their performance. The highest discharge value was found to be 0.67 mAh per unit mass of activated carbon in the composite electrode, which is equal to 0.002 wt% of hydrogen storage. In brief, the most plausible explanations are:
• limited nafion penetration into the smaller pores of the activated carbons, in particular into ultramicro-pores, so that proton transfer to hydrogen storage sites would have to be though low-proton-conductive bulk water
• presence of oxygen groups on the activated carbon surfaces preventing access to hydrogen storage sites
• competitive reactions of hydrogen desorption and hydrogen gas formation that prevent hydrogen storage in the activated carbon
• irreversible storage of hydrogen in the activated carbon with a strong bond that needed a large activation energy for dissociation to take place in fuel cell mode.

From the findings in this thesis and the hypothesis that were developed from these results, the following recommendations are made for future works:
• Computer simulation on proton conductivity within the composite materials and rate of sorption and desorption reactions in various conditions
• Verifying The relationship between water uptake of composite materials and mesoporosity
• New aC-nafion composite materials with different carbon to nafion ratio
• Investigating irreversible hydrogen storage in the composite electrodes
• Doping activated carbon to encourage sorption reaction in the electrolyser mode

This thesis has reported on the first experimental tests of the proton flow battery concept with composite activated carbon – nafion storage electrodes. Although the results have showed no observable hydrogen storage in the activated carbons so far, several hypotheses have been developed that set a pathway for future work. In the course of the research within this project, a number of novel composite aC-nafion materials have been designed and fabricated with the very interesting property of being capable of conducting both electrons and protons at the same time. Such dual proton and electron conductors have potential applications in many fields.
1. INTRODUCTION

1.1 ROLE OF HYDROGEN IN A SUSTAINABLE ENERGY STRATEGY

The problems with an energy economy based on fossil fuels can be classified into two categories. Firstly, there is the rising cost of fossil fuels, particularly oil and natural gas, and alarming concerns for scarcity of fossil fuel sources (Meng and Bentley 2008). Secondly, there are the environmental issues of using fossil fuels, in particular emission of greenhouse gases, in unprecedented amount, leading irreversible global warming (Tomas et al. 2004; Lovins et al. 2004; IPCC Report 2012; Rogelj et al. 2012; Shakun et al. 2012). An alternative source to meet the global energy demand, and avoid the environmental problems is to use renewable energy, in particular solar and wind energy.

Electricity produced by photovoltaic panels and wind turbines has the potential to meet a major share of the total global demand (Jacobson and Delucchi 2011). However, an inherent characteristic of most renewable energy sources is their variability and intermittency (Yang et al. 2011). Hence, an effective and economic energy storage technology is needed to allow continuous energy supply from renewables (Beaudin et al. 2010). One solution is to use hydrogen as the storage medium (Andrews and Shabani 2012). The hydrogen economy has been described as a way to permit unrestricted economic growth with supplying an abundant source of energy in form of hydrogen while eliminating harmful environmental disadvantage of fossil fuels economy (Hultman and Nordlund 2013). In this ideal economy, all energy needs would be met from hydrogen, produced from renewables, fossil fuels or nuclear fission power.

One of main drivers towards a hydrogen economy was the introduction of the Californian zero emission vehicle (ZEV) law in early 1990s. This law required US automakers to produce and sell a limited number of ZEV cars starting from 1998. At the time of introducing the law, battery electric cars were considered to be the only feasible option to meet the requirements for a zero emission automobile (Hultman and Nordlund 2013). The separate collaborations between the Canadian firm Ballard Power Systems and two major car companies, Daimler-Benz and Chrysler in developing fuel cell cars led to switch the view of ‘car of the future’ from battery powered to fuel cell powered (Hultman and
Nordlund 2013). The number of fuel cell prototypes jumped from 1.5 prototype annually to 20.2 between 1996 and 1999 (Hultman and Nordlund 2013). USA and Iceland, that interestingly enough refused to sign Kyoto Protocol, were the main supporters for the new technology.

Interest in hydrogen economy and fuel cell intensified by President Bush’s State of the Union address in which he described commercialising fuel cell cars as a national commitment (Hultman and Nordlund 2013). The interest in hydrogen related research took off, as can be seen from the increased number of journal publications in the past decade. The International Journal of Hydrogen Energy was founded by T. Nejat Vaziroglu, professor of University of Miami, in 1974. It is one of most prestigious periodicals in the field of hydrogen-related science with an impact factor of 4.05 (Elsevier website 2013). In 2012, the journal published 24 issues and 19 426 pages, as compared to 12 issues and about 1 230 pages in 2000 (Bockris 2013).

Over 2006 – 2012 the US government to some extent lost its interest in Bush’s vision of hydrogen economy, and at the same time US car manufacturers concluded that, at least in short term, fuel cell technology is not a cost-effective alternative to the battery technology (Hultman and Nordlund 2013). An economic analysis examined the macroeconomic effects of fuel cell vehicles on California’s economy over the period of 2010-2030, taking into account the projected number of fuel cell cars, transportation energy consumption, and fossil fuel savings (Wang 2011). Wang (2011) concluded that even in the most optimistic scenario, hydrogen vehicles would only make up a minor fraction of the on-road fleet in the future of California. Moreover, both moderate and aggressive scenarios have a slightly negative effect on California’s economy (Wang 2011).

However, in recent years, a new wave of interest has appeared in hydrogen-related technologies around the globe. European countries are the new major supporters of hydrogen related technologies, with several R&D programmes have been launched and research-funding opportunities have been allocated to this field (Fernandez et al. 2013; Hultman and Nordlund 2013). The Chinese government also has made huge investments in hydrogen related technologies, in particular fuel cell powered cars (Lu et al. 2013). China’s ambition to become an innovation-oriented nation by 2020 requires heavy investment in
science and technology including developing hydrogen fuel cell technology. Shanghai Tongji University is leading the fuel cell car project while Tsinghua University is working on fuel cell powered bus (Zhang and Cooke 2010). Furthermore, the State Council of China has listed hydrogen fuel cell vehicles on the list of vehicle-types to be supported in a New-Energy Vehicle Industry Developing Plan for 2012-2020 (Cited in Andrews and Shabani 2013).

The Intergovernmental Panel on Climate Change included an important role for fuel cell vehicles in its global energy strategies relying greatly on renewable energy sources in order to meet 2050 greenhouse gas reduction targets (IPCC 2012). This report considered the technology of hydrogen fuel cell vehicles a true zero emission technology with hydrogen produced by electrolysis using wind (or solar) electricity, and electric vehicles charged from zero-carbon grid electricity (IPCC 2012).

Although, the time for exclusive hydrogen economy has passed, hydrogen fuel cell vehicles can still play a role where medium and long distance trips are required (Andrews and Shabani 2012). In this new vision, a hierarchy of spatially-distributed hydrogen production, storage and distribution centres would be created. These local centres rely on local renewable energy sources such as wind, solar and geothermal. The locally production, storage and consumption of hydrogen minimise the need for hydrogen pipelines. The required hydrogen pipeline system would be limited to link separate distribution networks for the main metropolitan areas and regions (Andrews and Shabani 2012).

1.2 HYDROGEN STORAGE TECHNOLOGIES

Progress towards a sustainable hydrogen economy has two main bottlenecks: hydrogen distribution and hydrogen storage. If 40 million hydrogen-powered cars are to be used in Europe by 2030, $8-33b is needed to build about 19 000 hydrogen fuel stations (Pollet et al. 2012). Even if the distribution challenge is solved, on-board hydrogen storage imposes a greater technical difficulty (Zuttel et al. 2008). Table 1 shows the US Department of Energy’s (DOE) original and revised targets for on-board hydrogen storage for light-duty vehicles (US DOE 2009; Dierci and Miele 2011). A comparison between the original targets and the revised target shows the difficulty in increasing hydrogen storage.
### Table 1: DOE targets for on-board hydrogen storage for light-duty vehicles

<table>
<thead>
<tr>
<th>Storage system parameter</th>
<th>Original targets (released in 2003)</th>
<th>Revised targets (released in 2009)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2010</td>
<td>2015</td>
</tr>
<tr>
<td>Gravimetric capacity (kg H₂/kg system)</td>
<td>6 %</td>
<td>9 %</td>
</tr>
<tr>
<td>Volumetric capacity (g H₂/L system)</td>
<td>45</td>
<td>81</td>
</tr>
</tbody>
</table>

The DOE’s targets are for the system of storage. A system includes a storage material, a storage tank, a heat exchanger, manifolds, regulators, valves and safety devices (Klebanoff and Keller 2013). The most mature technologies, like compressed hydrogen gas in vehicles, are still far below the targets. For example, Honda FCX has a volumetric capacity of 23.9 g H₂/L and Honda Clarity 2009 has a volumetric capacity of 22.9 g H₂/L (Datta and Johnson 2012).

There are three main methods for storing hydrogen (Sakintuna et al. 2007; Askri et al. 2009; Weidenthaler and Felderhoff 2011; Demirci and Miele 2011). Firstly, in physical storage, hydrogen is either stored as pressurised gas or cryogenic liquid. The second method is sorption that can store hydrogen either by physisorption or chemisorption in solid-state hosts. The third method is chemical storage by converting hydrogen to methanol or other chemicals. Compressed hydrogen and liquefied hydrogen are the most mature techniques in storing hydrogen and are discussed here in more details.

Many of the car manufacturers use 70 MPa as their technology of choice in on-board hydrogen storage (Eberle et al. 2012). Honda and Nissan use 35 MPa (Pollet et al. 2012). Hydrogen is a non-ideal gas and deviates from ideal gas behaviour at pressures higher than 35 MPa and shows volume higher than expected (Eberle et al. 2009). Round-trip efficiency for this method of hydrogen storage is about 87 % for 80 MPa (Jensen et al. 2011). In other words, 13% of the energy content of the stored hydrogen is used to compress the gas.

Liquefying of hydrogen occurs at 20 K, and so imposes the practical problems of preventing heat transfer from ambient environment, i.e. room temperature. The heat
exchange between an environment at 300 K and hydrogen tank at 20 K leads to partial evaporation of the liquid hydrogen and pressure-increase inside the tank. When the pressure reaches a maximum level (in order of 1 MPa), hydrogen gas needs to be vented. The vented hydrogen is called boil-off gas (Eberle et al. 2009). Moreover, an energy equivalent of about 30 % of the stored energy has been already used to liquefy the hydrogen gas (Weidenthaler and Felderhoff 2011). Round trip efficiency for this method of hydrogen storage is about 70 % (Jensen et al. 2011).

Adsorption is the borderline between physical and chemical storage. There has been considerable interest over many years in storing hydrogen in solid-state hydride form (Zhang 2012). This method of storage can be further divided into two groups: physisorption and chemisorption. Usually, the energy of adsorption is used to discriminate between chemisorption and physisorption (Zuttel et al. 2008; Íñiguez 2008)

The physical adsorption is caused by weak van der Waals forces between the gas and the surface of the host. The attraction between the gas and the surface is because of the fluctuations in the charge distribution of the gas molecules and of the atoms on the surface. The attraction between the gas molecules and the surface and the repulsion between the two that is resulted from their electron clouds, results a shallow minimum in the potential energy between 1 to 10 kJ mol$^{-1}$ (Zuttel et al. 2008).

Chemisorption is the creation of covalent bonds between the gas molecule and the surface atoms. The enthalpy of chemisorption (order of magnitude of 100 kJ mol$^{-1}$) is higher than physisorption, but lower than an average chemical bond. Without spectroscopic techniques, it is very difficult to distinguish between strong physisorption and chemisorption (Zuttel et al. 2008). Hydrogen uptake appears to be proportional to the surface area and porosity of the adsorbent (Eberle et al. 2009). When hydrogen atoms bond with another material, the hydrogen atoms can get even closer to each other than in compressed or liquid forms. That is the reason for potentially higher storage capacities in hydrides compared where chemical bonds are formed compared to physisorption, where only weak bonds are formed between hydrogen molecules and the surface of a material.
1.3 ELECTROCHEMICAL STORAGE OF HYDROGEN

In the electrochemical storage of hydrogen, hydrogen is directly stored in an electrode during electrolysis (Jurewics *et al.* 2002; Bleda-Martinez *et al.* 2008). This method has been used in nickel-metal hydride accumulators (Jurewics *et al.* 2002). By diffusing highly reactive protons directly into the solid storage material, it is possible that bonding reactions can be encouraged with materials with a high potential for storing hydrogen (Babel and Jurewicz 2008).

The key requirements of the storage medium for a successful wide application of hydrogen-related technologies are safety, low maintenance, stability and low cost. All the conventional storage methods, such as compression, liquefaction, or usage of metal hydrides fail to achieve at least one of the requirements (Jurewicz *et al.* 2001). Metal hydrides have been used in electrochemical storage of hydrogen, but they are heavy, expensive and not stable (Jurewicz *et al.* 2002). Moreover, their reversible capacity in hydrogen storage is only about 2 wt% (Vix-Guterl *et al.* 2005).

Carbon is a cheap and widely available material that is more environmentally friendly than metal hydrides (Babel and Jurewicz 2008). The initial claims of Dillon *et al.* (1997) sparked great interest in the usage of carbon nanotubes in storing hydrogen, although their result has never confirmed by others. It is suggested that it is highly unlikely that carbon nanotubes can store a significant amount of hydrogen with hydrogen ingress in the form of gas (Bleda-Martinez *et al.* 2008).

In reviewing the data on hydrogen storage in single wall carbon nanotubes, Jurewicz *et al.* (2001) noticed that there is no systematic relationship between the indicated purity and the maximum discharge capacity. They concluded that the hydrogen storage in these studies occurs in other forms of carbon other than SWCNT (Jurewicz *et al.* 2001). In any method of preparation, besides the nanotubes, the material always contain other forms of carbon, in particular disordered carbon (Jurewicz *et al.* 2001). Jurewicz *et al.* have focused their efforts on activated carbon. Activated carbon is a porous carbon with high surface area. Activated carbon has a good thermal and electrical conductivity. It is also chemically stable and present relatively low cost and easy processability (Bleda-Martinez *et al.* 2008; Jurewicz 2009).
In the electrochemical storage, hydrogen penetrates into the pores of the activated carbon where it can be adsorbed due to the driving force of the negative polarization (Vix-Guterl et al. 2005). The pores smaller than 0.7 nm have been identified as the hydrogen storage sites in the activated carbon (Beguin et al. 2006; Vix-Guterl et al. 2005; Bleda-Martinez et al. 2008; Babel and Jurewicz 2008). The state of the hydrogen in the activated carbon is in its atomic form (Tsao et al. 2011). The values of hydrogen storage in activated carbon have been reported from 0.95 wt% to 2.17 wt% (Bleda-Martinez 2008; Jurewicz 2009).

1.4 THE PROTON FLOW BATTERY CONCEPT

The conventional hydrogen system consists of an electrolyser, a storage device for hydrogen and a fuel cell. The electrolyser produces hydrogen gas usually by splitting water with DC current. When the electricity demand is higher than the electricity production, hydrogen and oxygen can recombine together in a fuel cell.

After hydrogen is produced by the electrolyser, it needs to be stored. In compressed hydrogen storage in a conventional hydrogen system, hydrogen is compressed to 35 or 70 MPa and stored in a high-pressure cylinder. A fuel cell is used to produce electricity from the hydrogen gas. Conversion efficiencies at the various stages in the process show that losses in producing and storing the hydrogen gas and then reconverting this gas back into electricity in a fuel cell reduce the roundtrip energy efficiency to be under 50% (Gray et al. 2011).

In the new concept that has been investigated in this project, a carbon-based hydrogen storage electrode has been integrated into a single proton exchange membrane (PEM) cell that could operate both as an electrolyser to split water and as a fuel cell to generate electricity. This single devise is capable of generating hydrogen, storing hydrogen and regenerate electricity by using the stored hydrogen. A/Prof John Andrews had the idea for such a device while working earlier on URFCs. Production of protons for storage can continue for as long as water is being supplied and of course, as long as the protons can be accommodated in the storage electrode, hence the concept has been named “proton flow battery”.
In charge mode, water splits on the left electrode (oxygen electrode). Oxygen gas escapes the electrode. Hydrogen ions (protons) go through the membrane to the other electrode due to the potential difference. On the right electrode (hydrogen electrode), protons react with electrons and atoms of the hydrogen-storage electrode to form a hydride. Determining whether this is a physisorption or chemisorption is beyond the scope of this research.

In discharge mode, the hydrogen ions are liberated from the hydrogen storage material by applying an electric load. The protons go through the membrane from the hydrogen electrode to the oxygen electrode. On the oxygen electrode, protons, electrons and oxygen atoms react together. The by-product of the reaction is water that is removed from the oxygen electrode.

The proton flow battery cuts out many steps in the conventional process that incur energy losses. Hence, there is the potential for an overall higher roundtrip energy efficiency. In the concept, the avoided steps include conversion of protons produced during electrolysis into hydrogen gas, the compression of this gas, and subsequently the splitting of gas molecules in the fuel cell to release protons once again and generate electricity.

The aim of the present project is to investigate the technical feasibility of the proton flow battery in directly storing protons produced by electrolysis in a carbon-based electrode and recover the protons in fuel cell mode. A more detailed description of the concept is provided in chapter 3.

1.5 SIGNIFICANCE OF THE RESEARCH

This proposed device inherits some of the advantages of batteries, like small size, safety, and a single unit with electricity in and electricity out, as well as retaining the advantages of a conventional hydrogen storage system, such as long-term energy storage time and high energy density. It also promises to be a cheaper device compared to common batteries by using carbon-based electrodes. Moreover, end-of-life recycling of this device produces less toxic materials compared to recycling batteries.
Potential advantages of the concept proposed in this thesis are the following:

- Less energy losses by allowing hydrogen to be taken directly from production (as H\(^+\) ions) in an electrolyser into a solid-state storage material, without having to form hydrogen gas, be stored and compressed, and then fed as a gas into the storage material, with dissociation into atomic form once again before forming bonds with the MH material.

- Higher mass and volumetric energy densities of the hydrogen stored in MH materials, since ions may more readily bond with the substrate than H\(_2\) molecules that first have to be split into atoms.

- A higher roundtrip energy efficiency than the conventional system that includes electrolyser, storage and fuel cell.

- Hence overall more economic and practical solid state hydrogen storages for vehicular and stationary applications.

The areas of potential application are on-board hydrogen storage in hydrogen fuel cell vehicles, energy storage for electronic devices, energy storage for remote power supply systems, and stationary applications such as central grid storage of intermittent solar, wind or wave energy. The actual applications depend on the performance of the concept. If this device is successfully commercialised, it will accelerate the integration of renewable energies into both stationary power plants and electric vehicles, and assist in reducing Australia’s carbon footprint.

### 1.6 OBJECTIVES OF THE PROJECT

The specific objectives of this study are:

1. To conduct a literature review on carbon-based hydrogen storage electrodes and direct proton absorbance in various forms of carbon
2. To prepare and characterise activated carbon samples with proper porosity for the present application
3. To manufacture and characterise a range of composite materials containing carbon material and a proton-conducting medium such as nafion in various levels of hydration
4. To fabricate a number of membrane-electrode-assembly (MEA) from the composite materials
5. To design and construct a PEM URFC cell to test the MEAs
6. To measure the reversible hydrogen storage performance of the electrodes in the URFC and demonstrate the feasibility of the concept of a URFC with an integrated carbon hydrogen storage electrode

1.7 RESEARCH QUESTIONS

The principal research questions are therefore:

1. What types of carbon materials have been used in reversible and direct hydrogen storage?
2. What is the proper procedure to fabricate activated carbon samples, the composite materials and the composite electrodes for this application?
3. What would be the performance of composite materials of carbon and proton conducting media in different levels of hydration?
4. How does the performance of the URFCs with composite electrodes compare with that of typical standard URFCs?
5. Is it feasible to corporate the fabricated composites for direct reversible hydrogen storage in URFCs?

1.8 SCOPE

The scope of the present project is limited to:

- PEM unitised regenerative fuel cells with hydrogen and oxygen electrodes constant
- Relatively small single-cell experimental URFCs, with an active area of ~5 cm²
- Water splitting and reformation reaction
- Carbon-based materials for the composite electrode
• Fabrication and testing composite electrodes by mixing carbon and nafion as the proton conducting media
• Operation at room temperature and atmospheric pressure.

1.9 OUTCOMES

The main expected outcomes of this research project were expected to include the following:
• Identifying appropriate carbon types and treatment technique for the application of direct hydrogen storage in an electrochemical reaction
• Development of a practical technique to manufacture composite electrodes of carbon and nafion
• Development of a test procedure and analysis technique for obtaining and interpreting proton conductivity of a composite electrode
• Proof of concept of direct and reversible hydrogen storage in a PEM-URFC with an integrated carbon-based composite electrode

1.10 NOVELTY OF THE PROJECT

This thesis aims to contribute to the body of knowledge by:
• Developing a method for fabricating composite electrode from activated carbon and nafion with a high carbon content. The available literature studies composite electrodes that have low carbon content (up to 20 wt.% that perform predominantly as membranes). This thesis describes composite electrodes that perform mainly as electrodes.
• Modifying the method of testing and interpreting results in proton conductivity measurement of carbon and nafion composite materials with high electron conductivity. The published results on EIS measurements have been on low electron-conductive composites. For a high electric-conductive composite, a new test set-up and analysis method of the results had to be developed.
• Investigating the effects of relative humidity on conductive properties of the AC-nafion composite material that possesses both electron and proton conduction. 
   Literature of proton conductivity on aC-nafion composite material has been in fully hydrated condition.

• Presenting the results of direct and reversible hydrogen storage in an integrated carbon-based composite electrode in a URFC with solid membrane. The previous work had been done by using a metal hydride-nafion composite electrode.

1.11 STRUCTURE OF THE THESIS

In chapter 2, the methodology of the present research project is discussed. Since the major part of this study has been creating a new material and investigating its properties and suitability for the new application, it seemed necessary to allocate one chapter to discuss the methods of investigation, selected experimental techniques and the methods of collecting and analysing data. The main activities conducted throughout this project have been outlines. The Gantt chart is provided to summarise the activities and relate them to the research questions and the objectives of the project.

In chapter 3, a comprehensive background on PEM-URFC systems is provided. The concept of the present research is described in details. Earlier works on this concept that has been done by other research groups, in particular General Electric and a Poland-France academic collaboration are introduced and the findings of these research groups are discussed in more details. The earlier work on this concept conducted at RMIT University is disclosed and its findings are presented. Finally, activated carbon is introduced and the reasons for selecting this material for the application of this research concept are explained. The current state of electrochemical hydrogen-storage in activated carbon is provided.

In chapter 4, a detailed documentation is provided of fabrication of activated carbon and carbon-nafion composite and determining their properties. This chapter starts with describing the procedure and method of characterisation of the composite materials outside the cell. Experimental steps in preparing activated carbon from raw materials are explained in details, followed by characterisation of the samples. Selection criteria for suitable types of activated carbons for making composite electrodes are discussed. Next, fabrication of
composite material is discussed. Physical properties that are water uptake and volume expansion and electrochemical properties that are proton and electron conductivity are also discussed. The correlation between physical and electrochemical properties and relative humidity is investigated. A discussion about the application of this composite material in other applications is done. This chapter ends with a discussion on technical difficulties in casting the full size composite electrodes.

In chapter 5, fabrication of MEAs from the composite electrodes is covered. Design modification and construction of the URFC test-cell is described. Design of a test-rig is presented and the testing procedure is discussed in details. Performance of each MEA in charge and discharge mode is reported.

In chapter 6, thorough analyses of the experimental results are carried out and a comparison between the performances of the MEAs is made. In addition to the data of MEAs’ performances, hydrogen-uptake capacity is calculated from the charge-discharge cycles. Possible explanations of MEAs’ performance and hydrogen-uptake capacity are proposed.

Finally, chapter 7 summarises the findings and addresses the research questions. A critically review about the contributions and limitations of this thesis is provided. The chapter concludes with a list of recommendations for the future research direction.
2. RESEARCH DESIGN AND METHOD

2.1 OVERVIEW

This research project is a contribution towards creating a new engineering device that could link together the fields of hydrogen storage technology, fuel-cell technology and battery technology. The project also aims to contribute to the current body of knowledge on the science of materials by fabricating and characterising a new composite material that is capable of conducting both protons and electrons simultaneously. This new low-cost composite material has been used together with a solid polymer electrolyte membrane (PEM) in a unitised regenerative fuel cell (URFC), and its capacity for electrochemically storing hydrogen has been investigated.

2.2 GENERAL METHODOLOGICAL APPROACH

The present research project has been predominantly an experimentally-based investigation, with most of the duration of the project allocated to fabrication and characterisation of the new carbon-based composite materials that may be suitable for electrochemical hydrogen storage. A special unitised regenerative fuel cell has also been designed that can incorporate solid-state hydrogen storage electrodes to study the capacity of these new materials to store and discharge hydrogen reversibly. The project has focused on selected forms of activated carbon and nafion polymer as the materials of choice in the composite electrodes fabricated and tested.

2.3 EXPERIMENTAL PROCEDURES

Carbon-based materials were selected as potentially suitable candidates for storing hydrogen electrochemically, since there was some initial indication from the literature that carbon might hinder hydrogen gas formation in the water electrolysis process (Zuttel et al. 2008), compared to the use of metals and formation of metal hydrides, as had been investigated in a previous study (Seif Mohammadi 2013). In the present study, coal and charcoal were used as the precursors because of their high carbon content, availability,
low-cost and the interest of mining industry. Physical, chemical and morphological properties of the precursors were obtained.

The precursors went through mechanical and chemical treatments, *i.e.* grounded and carbonised, to get the suitable state for activation process. KOH chemical activation was chosen to activate the precursors. Samples of activated carbon with different porosity were obtained by altering the parameters of KOH activation process such as the ratio of potassium hydroxide to carbon (KOH/C) and the final activation temperature. The porosity of these samples has been characterised by adsorption isotherm technique with CO$_2$ and N$_2$. Moreover, five samples of activated carbon were made available to the author by Professor Allen Chaffee and PhD candidate Lachlan Ciddor at Monash University, Australia. In the end, six activated carbon samples were selected from the total of nine samples to fabricate composite samples.

Composite material was synthesised using activated carbon and commercially available nafion solution. Carbon content of the composite material were set to be 50 wt%. The composite materials were then treated with concentrated H$_2$SO$_4$ for nafion to be protonated in the composite.

The composite samples were tested using physical measurement tests to obtain water-uptake and volume expansion at five different relative humidity environments, *i.e.* 0%, 40%, 75%, 100% and fully hydrated.

Proton and electron conductivity of the composites were also obtained in each of the different relative humidity environments using ASTM E104-02 standard and thermodynamics principles (ATSM 2012). Two samples were selected from the total six samples by taking into account the values of their proton and electron conductivity and porosity of their activated carbon components.

The two composite material samples were used for casting working electrodes for a PEM-URFC. Scaling-up the fabrication of the composite electrode to a larger size (2.5 × 2.5 cm$^2$) proved to impose some technical difficulties. The method of manufacturing the large composite electrodes has been described in details in chapter 4. After overcoming the
difficulties in fabrication of composite electrodes, four composite electrodes were made; 
two composite electrodes from each of the two selected composite materials.

Membrane-electrode-assemblies (MEAs) were made with the constructed composite 
electrodes. Each composite electrode was hot-pressed to a nafion 115 membrane and 
another electrode which had IrRuOₓ and Pt as catalysts.

A pair of experimental URFC end-plates with the same active membrane area as the MEAs 
was designed by the author. Flow channel configuration for hydrogen and oxygen sides 
had to be reviewed and modified to match the specific application of this research project. 
The end-plates were constructed by the RMIT University workshop.

The MEAs were placed between the two end-plates in a unitised regenerative fuel cell. The 
electrodes on the oxygen side were connected to water for at least 12 hours to fully hydrate 
the electrodes and nafion membranes. The performances of the MEAs were measured via 
charging and discharging cycles. The charging was done in constant voltage and constant 
current and discharge had been done in constant current and/or constant resistance. The 
changes of polarisation curves of each MEA were recorded for a series of consecutive 
cycles. Moreover, charging current and duration of charging were altered to examine their 
corresponding effects on hydrogen storage capacity of the composite electrodes.

### 2.4 INSTRUMENTATION AND COLLECTING DATA

The precursors were characterised by energy-dispersive X-ray spectroscopy (EDX) 
technique for elemental analysis and X-ray diffraction analysis (XRD) for determining 
crystalline structure. The particle size was measure using scanning electron microscope 
(SEM) imaging technique.

Carbon activation was carried out in a horizontal tube furnace under nitrogen gas flow. 
KOH, water and activated carbon were blended together using a magnetic-stirrer/hot-plate. 
The samples were dried in a conventional laboratory oven.

Characterising the activated carbon samples such as porosity, surface area, and average 
pore diameter were carried out using adsorption isotherm technique with nitrogen gas at 77
K and carbon dioxide gas at 273 K in a gas adsorption analyser. Brunauer-Emmett-Teller (BET) equation and Dubinin-Radushkerich (DR) equation were used to interpret the values of gas adsorption. Elemental composition of the activated carbon samples were acquired using EDX technique.

Nafion and activated carbon were mixed using a hot-plate and the mixture was stirred manually. Before mixing with nafion, activated carbon samples were put in a vacuum oven so that surface oxide group can be removed. A conventional laboratory oven was used to dry the samples.

A digital hygrometer/thermocouple was purchased to simultaneously measure temperature and relative humidity. A desiccant jar and constant humidity chambers were used to obtain the different relative humidity conditions. The humidity chambers were designed by the author according to the available standards and some principles of thermodynamics.

The proton conductivity of the composite material was measured using electrochemical impedance spectroscopy (EIS). The equivalent circuit for interpreting the results of the EIS was developed by A/Prof John Andrews. The electron conductivity was measured with a digital ohmmeter using the EIS set-up. Physical properties were measured using a digital scale and a digital vernier calliper.

Charging was carried out with a DC power supply with constant current output and constant voltage output. Current was drawn from the cell using an electric load for constant current discharge and a variable resistor for the constant resistance discharge. Voltage and current in the discharge mode were measured by digital multimeters. Produced hydrogen and oxygen gases were stored in graduated cylinders.

2.5 ACTIVITIES

The main activities conducted to achieve the objectives of the project were as set out in the Gantt chart in Table 2.
<table>
<thead>
<tr>
<th>Step No.</th>
<th>Activity title</th>
<th>Activity description</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
<th>Relation to the research questions</th>
<th>Relation to the objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Literature review</td>
<td>critical review on URFC technology, direct reversible storage of hydrogen in electrolysis, selecting candidate materials for precursors, electrochemically storing hydrogen in carbon-based materials, specifying objectives and scope of the project</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Preparation of the precursors</td>
<td>Grinding the precursors, grain size measurements by SEM, elemental analysis by EDX, crystalline structure by XRD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Activation of precursors</td>
<td>Selecting the proper activation method, obtaining materials and equipment, altering activation parameters to obtain different porosity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Characterisation of activated carbons</td>
<td>Porosity, surface area, and pore size measurements using adsorption isotherm technique with N₂ at 77 K and CO₂ at 273 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Fabrication of carbon and Nafion® composite</td>
<td>Purchasing nafion solution, Mixing nafion and carbon together, protonation of the composite in H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Characterisation of the composites</td>
<td>Design and constructing humidity chambers for five different relative humidity, obtaining volume increase, water uptake,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

18
<table>
<thead>
<tr>
<th>Task Description</th>
<th>Description</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>designing the EIS rig, proton and electron conductivity in each relative humidity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting composite electrodes</td>
<td>Casting the electrode in the proper size, protonation of nafion in the composite electrode by H₂SO₄</td>
<td>2</td>
</tr>
<tr>
<td>Fabricating MEAs</td>
<td>Hot-pressing the composite electrodes, nafion 115 membrane and oxygen-side electrode together</td>
<td>4</td>
</tr>
<tr>
<td>Designing and construction of URFC experimental cell</td>
<td>Modifying the flow channels configuration for the specific application of this project, identifying proper material for constructing the cell, visualisation of flow field, manufacturing the experimental cell</td>
<td>5</td>
</tr>
<tr>
<td>Tests on the electrodes</td>
<td>Testing the MEAs in the URFC experimental cell, investigating hydrogen storage capacity via charge-discharge cycles</td>
<td>4</td>
</tr>
<tr>
<td>Analysis of the experimental data</td>
<td>Presenting the polarisation curve for each MEA, investigate the hydrogen storage capacity, identifying the challenges in the experiments</td>
<td>5</td>
</tr>
<tr>
<td>Thesis writing and submission</td>
<td>Write the draft according to SAMME format, revision according to supervisors’ feedback, submitting the thesis</td>
<td></td>
</tr>
</tbody>
</table>

*Table 2: Activities conducted in this research project*
3. THE CONCEPT OF A REVERSIBLE URFC WITH AN INTEGRATED CARBON HYDROGEN STORAGE ELECTRODE

3.1 COMPONENTS OF A HYDROGEN SYSTEM

3.1.1 PEM electrolysers

The procedure of using electricity to decompose water into its constituent elements was first described by Anthony Carlisle and William Nicholson in 1800 (Nicholson, 1801). They connected two conducting wires to two poles of a Volta battery and immersed the wires in salt water. Gas formation was observed around the wires (Andujar and Segura, 2009). Some historians credit Troostwijk and Diemann for discovering the effect in 1789 (Trasatti 1999).

The proton exchange membrane (PEM) electrolyser is so-called because of using a polymer membrane as the electrolyte that is capable of conducting protons (Gallant 2008). PEM electrolysers can operate at current densities up to three times higher than their alkaline counterparts (Ito et al. 2011; Carmo et al. 2013). The higher current density may compensate for the higher cost of PEM electrolyser compared to alkaline electrolysers (Briguglio et al. 2013). The solid electrolyte can be much thinner than an alkaline electrolyte and so the PEM electrolyser can be smaller and lighter than alkaline electrolysers (Garcia-Valverde et al. 2012; Carmo et al. 2013). Further advantages of PEM electrolysers are the ability to cope with transient electrical power variations and the potential to compress hydrogen at a higher pressure within the unit and with higher safety level (Atlam and Kolhe 2011).

The water travels via channels in the oxygen side end-plate and gets distributed over the gas diffusion layer (GDL). Water diffuses into the GDL and reaches the catalyst layer where the water molecules are split into electrons, diatomic oxygen, and protons (H⁺). The oxygen gas has to flow back through the catalyst layer and GDL to the flow channels and
then out of the cell. The electrons travel from the catalytic layer, through the GDL, to the end-plate. The protons leave the oxygen side catalytic layer and are transferred through the solid membrane and reach the catalyst layer on the hydrogen side. There the protons combine with electrons and form hydrogen gas. The hydrogen gas then has to go through the GDL to the flow channels of the hydrogen side end-plate and leaves the cell. A schematic of a PEM electrolyser is presented in Figure 1.

![Schematic of a PEM electrolyser](image)

**Figure 1:** Schematic of a PEM electrolyser (modified from Garcia-Valverde *et al.* 2012)

The chemical reaction in the cell is (*Ito et al.* 2011):

\[
\text{H}_2\text{O} + \text{electricity} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2e^- \quad \text{Eq. 1}
\]

In the hydrogen side, the reaction is:

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad \text{Eq. 2}
\]

The overall reaction at the PEM electrolyser is

\[
\text{H}_2\text{O} + \text{electricity} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2. \quad \text{Eq. 3}
\]
Figure 2 shows the state-of-the-art performance of PEM electrolysers from 2010 to 2012 for a range of publications with Ir and Pt as catalysts (Carmo et al. 2013). It can be used as a benchmark to compare with other electrolysis methods.

![Figure 2: Polarisation curve for PEM electrolysers (Carmo et al. 2013)](image)

The reader is referred to a comprehensive review written by Carmo et al. (2013) for more details of the performance of over 80 PEM electrolysers.

### 3.1.2 Methods of hydrogen storage

#### 3.1.2.1 High-pressure hydrogen storage

Compressed hydrogen storage refers to storing hydrogen gas in a pressure vessel at elevated pressure (Hua et al. 2011). Three main pathways exist for compressing hydrogen (Bensmann et al. 2013). In the first method, hydrogen gas is produced under ambient pressure and then is compressed by a multi-stage compressor. The second method uses pressurised water in high-pressure electrolysis. In the third method, hydrogen is produced
under ambient pressure but does not leave the cell. The production of hydrogen is continued and accumulated hydrogen gas increases the pressure. Once the pressure is reached to a desired value, a valve opens and the compressed hydrogen gas escapes the cell and is stored in a high-pressure cylinder. The latter method is limited by the ability of a membrane to withstand the resulting mechanical stresses because of the pressure difference between oxygen side and hydrogen side (Bensmann et al. 2013).

In the present hydrogen fuel cell cars developed by the car manufacturing industry, typically pressure of 35 MPa and 70 MPa are being used (Eberle et al. 2012; Pollet et al. 2012). Storing 1 kg of hydrogen at atmospheric pressure and room temperature requires 12.3 m³. Storing 1 kg of hydrogen gas at 35 MPa reduces this volume by 99.6 % (Hosseini et al. 2012). Hydrogen can be compressed by a piston-type compressor, although modification should be applied to the compressor because of the higher diffusivity of hydrogen compared to air (Zuttel et al. 2008).

For two reasons, pressures higher than 70 MPa are not sought after. Firstly, the hydrogen gas diverts from ideal gas behaviour and more work has to be done to get to the higher pressure (Eberle et al. 2009). Secondly, higher pressure requires higher strength of the high-pressure cylinders. This usually means thicker walls and heavier cylinder. The combination of these two facts leads to ultimately lower gravimetric hydrogen density at very high pressures (Zutter et al. 2008).

High-pressure storage is currently the cheapest solution to store hydrogen and in particular attractive for fuelling stations (Walker 2008). Another advantage is the short refill time of the tanks. An empty tank can be filled with 5 kg of hydrogen within three minutes (Eberle et al. 2009).

The major limitation of high pressure storage of hydrogen is still the relatively low volumetric density (Walker 2008). The volumetric density only goes up to 39.5 for kg/m³ for 70 MPa (Petitpas and Aceves 2013). The volumetric density of petrol is 740 kg/m³ (Caltex MSDS 2009). The volumetric energy density of hydrogen gas is about one third of the volume energy density of natural gas at the same pressure (Zuttel et al. 2008). The other issue in on-board storage is the shape of the pressure vessel. A large amount of space
has to be allocated in the car to fit a cylindrical shape vessel (Walker 2008). Other shapes lead to lower gravimetric hydrogen density (Walker 2008). Another issue is concerns about safety in vehicles and populated areas (Zuttel et al. 2008).

3.1.2.2 Liquid hydrogen

Hydrogen becomes liquid at temperature below 21.2 K at atmospheric pressure (Zuttel et al. 2008). The simplest liquefaction cycle is the Joule–Thompson cycle. There are two major challenges in storing hydrogen in liquid form. The first issue is the large amount of energy that is required for cooling hydrogen gas to 21 K. The energy required for liquefying hydrogen is about 30% of the lower heating value of the stored hydrogen (Walker 2008). The second issue is the thermal insulation of the cryogenic vessel and heat transfer to the environment (Zhou 2005).

Thermal conduction into the vessel happens through its surface, cables and fixtures (Walker 2008). Thermal radiation also contributes to heat transfer to the vessel (Eberle et al. 2009). The transferred heat to the vessel causes evaporation of hydrogen. The evaporated hydrogen increases the pressure inside the vessel and before the pressure goes above allowed limit the gas should be vented. The part of hydrogen that is vented is called boil-off gas and happens after a period of time that is called dormancy (Hosseini et al. 2012). Boil-off volume is a function of size, shape and thermal insulation of the vessel (Zuttel et al. 2008). The boil off issue imposes a major safety issue for the vehicles left for few days in a closed space like a garage (Walker 2008, Brennan and Molkov 2013). The vessel within vessel construction may reduce the rate of boil off losses an increases safety even in sudden rapture of the inner vessel (Petitpas and Aceves 2013).

A problem with using liquid hydrogen in fuel stations is that the entire transfer line from the station’s hydrogen reservoir to the car tank needs to be cooled down to 21 K (Eberle et al. 2009). Pressure cryogenic tanks that can work at cryogenic temperatures and high pressures are the next generation of vehicular storage systems that have been developed in BMW (Aceves et al. 2010).
3.1.2.3 Hydrogen sorption in solid state

The two types of sorption of hydrogen in solid materials are chemisorption and physisorption. The physisorption depends on weak van der Waals attraction between the host material and molecular hydrogen. Chemisorption is the much stronger chemical bonding between the host material and atomic hydrogen (Yang et al. 2010a). Chemisorption is due to formation of covalent bonds between carbon and host material (Varin et al. 2009). Sorption is considered to be the borderline situation between weak bonds of physical storage and strong bonds of chemical storage (Eberle et al. 2009). Metal hydrides are examples of chemisorption and activated carbon is an example of both chemisorption and physisorption.

Typical metal hydrides are in the form of AB$_5$ and AB$_2$ where A is typically a rare earth metal that tends to form a stable hydride and B is often a transition metal that forms unstable hydrides (Zhuo 2005). There are two types of metal hydrides. The crystal structure of an interstitial hydride like LaNi$_5$ does not change upon insertion of hydrogen. The other type of metal hydrides, like MgH$_2$, forms a new structure upon insertion of hydrogen and is called a structural hydride (Yang et al. 2010a). Materials with high surface area like metal-organic frameworks, carbon nanotubes and activated carbon are also good candidates for hydrogen adsorption (Yang et al. 2010a).

The hydrogen storage capacity of metal hydride is limited to roughly 2 wt% (Eberle et al. 2009). The search to find new metal hydrides is ongoing (Hu 2013). Hydrogen storage in complex hydrides like the family of the borohydrides, e.g. Mg(BH$_4$)$_2$ or Na$_2$Zr(BH$_4$)$_6$, has ignited interest in research in this family (Klebanoff and Keller 2013). Although these materials have high hydrogen storage density, e.g. NaBH$_4$ (10.8 wt%), NH$_3$BH$_3$ (19.5 wt%), and N$_2$H$_4$ (12.5 wt%), the system-based storage density is much less than DOE targets (Demirci and Miele 2011, Klebanoff and Keller 2013; Stetson et al. 2013). Another key limitation of metal hydrides is the need for heat removal during charging (Stetson et al. 2013).

Carbon materials have received exceptional attention as possible hydrogen storage materials because of low cost, availability, environmentally-friendly recycling, low density,
and good chemical stability (Yurum et al. 2009). A range of carbon materials have been proposed like carbon nanotubes, carbon nanofibers, and activated carbon (Yurum et al. 2009). Hydrogen storage in activated carbon seems to be more promising than in carbon nanotubes (Zhuo 2005).

3.1.2.4 Chemically bonded hydrogen storage liquids

In chemical storage, hydrogen makes a strong covalent bond with the host material, like methanol (Zuttel et al. 2008). The energy of the bonds is at least an order of magnitude higher than physisorption (Zuttel et al. 2008). Some of the chemical storage materials are ammonia and methanol (Weidenthaler and Felderhoff 2011). Ammonia is 18 % hydrogen and is produced over an iron catalyst in the Haber-Bosch process (Kelly 2011). Although ammonia is a gas, it can be easily liquefied (Kelly 2011). Although liquid ammonia can be catalytically decomposed at 400°C, it is very corrosive (Walker 2008). The process of introducing hydrogen to the material and extracting hydrogen from it is called hydrogenation and dehydrogenation (Eberle et al. 2009). The hydrogenation is a complex process and needs to be done off-board (Yang et al. 2010a). Obtaining hydrogen from these components may also require some energy loses. Compared to the compressed, liquid and metal hydrides, this method of hydrogen is in its early stages of development (Aardahl and Rassat 2009). The hydrogen is produced by a chemical reaction. The reaction products should be removed and recycled off-board (Alfonso Alonso et al. 2012).

3.1.3 PEM fuel cell

A fuel cell is an electrochemical cell that directly converts the chemical energy of reactants to electricity (Zhang 2012). Sir William Grove is credited with using electrolyser principles to electrochemically compose water by reassociating hydrogen and oxygen atoms in a fuel cell or as he named it, a gaseous voltaic battery (Grove, 1839; Grove, 1842).
Thomas Grubb and Leonard Niedrach from General Electric made the first PEM fuel cell for the Gemini Program in the early 1960s (Spiegel 2007). In early 1990s, a renewed interest in this field expanded fuel cell application to PEM fuel cell-powered submarines (made by Perry Energy System 1989), buses (made by Ballard Power System), and passenger cars (made by Perry Energy System 1993).

The operating temperatures of PEM fuel cells are between 50 and 100°C and their efficiency lies between 40-60% (Zhang 2012). The advantages of PEM fuel cells are using a solid electrolyte, low operating temperature and quick start-up (Zhang 2012).

In a PEM fuel cell, hydrogen gas is supplied from the storage system to the anode electrode and oxygen (or air) is supplied to the cathode (Gallant 2008). At the hydrogen electrode (anode), hydrogen splits to hydrogen ions (protons) and electrons.

\[ H_2 \rightarrow 2H^+ + 2e^- \]  
Eq. 4

The protons go through the membrane to oxygen electrode (cathode) and electrons go through an external load and produce electric current. The protons, electrons and oxygen combine on the oxygen electrode and produce water.

\[ 2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O \]  
Eq. 5

Many car manufacturers are using PEM fuel cells as their technology of choice; Honda (FCX Clarity), General Motors (Chevrolet Equinox), Hyundai-Kia (Kia Borrego SUV), Volkswagen (Passat Lingyu), Toyota (FCHV-adv), and Nissan (Xterra FCV) (Wang et al. 2011). A more detailed review of PEM fuel cells in automobile is available in Andujar and Segura (2009).

3.1.4 Structure and principles of a PEM URFC

The unitised regenerative fuel cell is a single device that is capable of functioning in either electrolyser mode or fuel cell mode (Pettersson et al. 2006). In URFC the same cell is
capable to split water to hydrogen and oxygen by using electricity in the electrolyser mode and also recombine oxygen and hydrogen to produce DC electricity in fuel cell mode (Coalson 1998). The reaction of a PEM URFC is:

\[ \text{H}_2\text{O} + \text{electricity} \leftrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \quad \text{Eq. 6} \]

In electrolyser mode, the reaction moves in the forward direction and in fuel cell mode the reaction moves in the reverse direction. First, the URFC works as an electrolyser to produce hydrogen and oxygen which are stored in a separate storage unit. The hydrogen and oxygen are later supplied back to the same URFC that is now working as a fuel cell (Pettersson et al. 2006). The difference between a URFC and a secondary battery is that the URFC needs an external storage system.

The concept of a PEM URFC was introduced in early 1960s, mainly for space application (Millet et al. 2011). Early promising results of PEM URFC were obtained at General Electric in 1972 when reversible operation was shown to be feasible without significant degradation of the cell membrane (Grigoriev et al. 2011).

Today many companies like Lynntech Inc., Glenn Research Centre, Giner Inc., and Green Volt Power Corp are active in the field of PEM URFC technology (Grigoriev et al. 2011). NASA applications for PEM URFC include high altitude airships, lunar or Mars-based outposts and other applications instead of secondary battery where the discharge period is one to two hours long or longer (Burke 2003).

There are two types of PEM URFC (Doddathimmaiah 2008). In ‘hydrogen and oxygen electrodes constant’, the electrode that evolves hydrogen in electrolyser mode is the same electrode that uses hydrogen in fuel cell mode. This concept was also called ‘hydrogen and oxygen electrodes’ in the literature (Grigoriev et al. 2011). This electrode is called the hydrogen electrode. Similarly oxygen is evolved and used on a same electrode, which can be called the oxygen electrode. A schematic of this type of URFC is presented in Figure 3.
In this type of PEM URFC, the catalyst layers on both electrodes need to be bifunctional. On the oxygen electrode, the catalyst should assist water splitting in electrolyser mode and encourage water formation in fuel cell mode. The catalysts on hydrogen electrode should encourage hydrogen formation in electrolyser mode and assist hydrogen splitting in fuel cell mode.

The major advantage of this type of PEM URFC is that hydrogen gas and oxygen gas are completely separated from each other and cannot mix. Another major advantage of this type is that water is introduced to and extracted from the same side and water management can be limited to only that side of the cell.

The second type of PEM URFC is called ‘hydrogen and oxygen electrodes interchange’ or ‘reduction and oxidation electrodes’ (Doddathimmaiah 2008; Grigoriev et al. 2011). In this type, hydrogen (or oxygen) is produced on one electrode and consumed on the other electrode. The advantage of this type of URFC is that the need to use bifunctional catalysts is eliminated.
The first type of PEM URFC was selected for this project, since it has been used the same electrode for evolving and splitting hydrogen.

First attempts to build a PEM URFC were made in 1960s, but it was only in 1972 that General Electric made a PEM URFC with good performance and acceptable lifetime (Grigoriev et al. 2011). A commercial PEM URFC was manufactured in 1992 by Proton Energy Systems that was able to produce 5 kW in fuel cell mode and 15 kW in electrolyser mode (Grigoriev et al. 2011). Dirhab et al. (2009) suggest that titanium is a good choice for bipolar plates for a PEM URFC due to its high resistance to corrosion. Catalysts materials such as Ir, Ru and Pt have been found to produce the best results on the oxygen electrode in a PEM URFC (Doddathimmaiah, 2008; Dirhab et al. 2009). The method of preparation of the above catalysts has also been found to affect performance (Zhuo et al. 2013).

PEM URFCs still require more study to optimise their electrochemical performance (Millet et al. 2011). The performance of a PEM URFC may be very close to state of the art dedicated electrolysers and fuel cells; for example, the PEM URFC that was developed in the GenHyPEM project showed an efficiency of 80% in electrolyser mode and a cell voltage of 0.8 V in fuel cell mode (Millet et al. 2011). Even so, PEM URFCs suffer from short lifetime and their performance depreciated after only a few hundred cycles (Millet et al. 2011).

3.2 CONVENTIONAL HYDROGEN SYSTEMS

3.2.1 A hydrogen system employing an electrolyser, storage unit, and fuel cell

A conventional hydrogen system includes an electrolyser, a hydrogen storage system, and a fuel cell. A schematic of the conventional hydrogen system is presented in Figure 4.
The excess solar energy can be used to produce hydrogen via electrolysis of water. The hydrogen is stored and later used in a fuel cell to produce electricity when the electricity demand is higher than electricity supply (Paul and Andrews 2008). Power supply for remote areas can be a niche market for such systems (Doddathimmaiah, 2008; Paul and Andrews 2008). The electrolysis of water is one of the most developed methods of producing hydrogen in industries (Koumi Ngoh and Njomo 2012). Among the technologies in water electrolysis, PEM electrolyzers are very practical in producing high-quality hydrogen (Koumi Ngoh and Njomo 2012).

The main advantages are scalability and zero emission production (Koumi Ngoh and Njomo 2012). A study in Algeria, showed that a 50 W PEM electrolyser connected to a PV module is estimated to produce between 20-29 m$^3$ of hydrogen, annually (Ghribi et al. 2013).

Another advantage of the hydrogen system over batteries is that batteries have a self-discharge tendency and so can only store energy for short periods of time (Agbossou et al., 2001).
The main disadvantage of the system is the number of devices in the system. The roundtrip energy efficiency when going from electricity in to electricity out – typically 40-45% via electrolyser, gas storage unit, and fuel cell – compared to batteries at 70-80% (Gray et al. 2011). Another issue is the size of the system. A large volume needs to be allocated to the system and hence, diminish the prospect of using the system for mobile applications.

3.2.2 A hydrogen system employing a URFC and storage unit

It has been shown that a unitised regenerative fuel cell is a single device that can be used both as an electrolyser and fuel cell in different times. Since in the conventional hydrogen system, electrolyser and fuel cell never work simultaneously, these two devices can be replaced with a single URFC. In this hydrogen system, first the URFC works as an electrolyser and splits water into hydrogen and oxygen by using the excess electricity. The hydrogen is stored in a separate unit. When the electricity demand is higher than electricity production, the hydrogen is supplied from the storage unit to the URFC that now works as a fuel cell and combines hydrogen and oxygen and produce electricity (Wittstadt et al. 2005). The schematic of this hydrogen system is presented in Figure 5. This system has fewer devices compared to the conventional hydrogen system in the previous hydrogen system.
The URFC should be compatible in efficiency and lifetime to a dedicated electrolyser and fuel cell (Doddathimmaiah, 2008). From a financial viewpoint, by using a URFC, the purchase of a separate electrolyser and a separate fuel cell, both expensive items, can be avoided with purchase of a single cell at a lower cost (Doddathimmaiah and Andrews 2006). The efficiency of the URFC, both in electrolyser mode and fuel cell mode, has been an interest for many research activities (Pettersson et al. 2006; Doddathimmaiah 2008; Doddathimmaiah and Andrews 2009). The performance of PEM URFCs can be very close to the state-of-the-art electrolysers and fuel cells, but URFCs suffer from short lifetime and their performance degrades significantly after few hundred cycles (Millet et al. 2011).

One of the issues related to the hydrogen system with URFC is that it still needs an external hydrogen storage unit. The present project seeks to overcome this shortcoming by integrating a hydrogen storage electrode into a PEM URFC.
3.3 INTEGRATED HYDROGEN STORAGE IN A PEM URFC

3.3.1 The concept of the proton flow battery

In the proton flow battery concept to be investigated in the present project, a solid hydrogen storage electrode is integrated into a single proton exchange membrane (PEM) cell that can operate reversibly as an electrolyser to split water or as a fuel cell to generate electricity, that is, a unitised regenerative fuel cell (URFC) (Doddathimmaiah and Andrews, 2008, 2009). A schematic of the concept is shown in Figure 6.

![Schematic of Integrated hydrogen storage in PEM URFC](image)

**Figure 6:** Schematic of Integrated hydrogen storage in PEM URFC

In electrolyser mode, water is split into hydrogen ions (that is protons, H⁺), electrons and oxygen gas, as shown in equation 7. The oxygen gas goes through the oxygen electrode and channel flows of the oxygen-side end-plate and leaves the cell. The electrons also leave the cell through an external circuit. The hydrogen ions go through the membrane to the hydrogen electrode:

\[
\text{H}_2\text{O} + \text{electricity} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2e^-.
\]

Eq. 7
On the hydrogen electrode, that is, the hydrogen storage electrode, protons, emerging from the membrane enter the solid storage directly and then react with electrons and storage material atoms to form a hydride without producing hydrogen gas:

\[ H^+ + e^- + M \rightarrow M-H \]  \hspace{1cm} \text{Eq. 8}

where M is the material of the hydrogen storage electrode. Production of protons for storage can continue for as long as water is being supplied, and of course as long as the protons can be accommodated in the storage electrode, hence the proposed concept has been called proton flow battery. The hydrogen can be stored in the electrode of the PEM URFC for a period of time. Hence, the hydrogen electrode of the proton flow battery acts as a storage unit.

When there is a demand for electricity from the PEM URFC, the hydrogen ions would be liberated from the storage material like a secondary battery. The protons go through the membrane to the oxygen electrode and react with oxygen gas and electrons:

\[ M-H \rightarrow M + H^+ + e^- \]  \hspace{1cm} \text{Eq. 9}

\[ 2H^+ + \frac{1}{2} O_2 + 2e^- \rightarrow H_2O + \text{electricity.} \]  \hspace{1cm} \text{Eq. 10}

It can clearly be seen by comparing Figures 5 and 6 that the proton flow battery cuts out many steps in the conventional process that incur energy losses. Avoided steps include conversion of protons produced during electrolysis into hydrogen gas, the compression of this gas, and subsequently the splitting of gas molecules in the fuel cell to release protons once again and generate electricity.

### 3.3.2 Benefits and potential applications of a proton flow battery

The proton flow battery can avoid the need for using an external hydrogen storage system in URFC hydrogen systems. The concept also only has one device and hence it is more
compact compare to URFC hydrogen system and may be more suitable for mobile applications.

By diffusing highly-reactive protons directly into the solid storage material, it is possible that bonding reactions can be encouraged with materials with a high potential for storing hydrogen but which cannot be made to react with hydrogen gas unless the pressure (and sometimes temperature too) is prohibitively high (for example, graphitic carbon, aluminium, and magnesium). Thus there is the possibility of storing hydrogen in relatively light and abundant materials (for example, graphitic carbon and aluminium), and hence achieve higher gravimetric and volumetric energy densities, and lower costs per unit mass of hydrogen stored, than presently available metal hydrides, which tend to be the heavier elements and often contain very costly rare earth elements as well.

In the conventional process, protons must combine in pairs with electrons in the catalyst layer of a conventional PEM electrolyser to form hydrogen gas. This hydrogen must then be compressed, by continued production by the electrolyser so that the amount of hydrogen gas in a fixed volume container steadily increases, or by using an external compressor. In either case there is an energy penalty to accomplish the compression. Hence there is the potential for overall higher roundtrip energy efficiency (electricity to hydrogen to electricity) in the proton storage process.

### 3.4 PREVIOUS WORK ON THE CONCEPT OF INTEGRATING HYDROGEN STORAGE ELECTRODE IN URFC

#### 3.4.1 History of the concept

Associate Professor John Andrews from RMIT University had the idea for such a device while working earlier on URFCs (Doddathimmaiah and Andrews 2009). A subsequent literature search revealed that there have only been a handful of publications that dealt with a similar concept. Earlier research on hydrogen storage in solid electrodes has focused on alkaline membranes and metal hydride electrodes (Bronoel et al. 1976). Further research on the concept led to Ni-Metal hydride batteries in 1990s.
The researchers from Fiat Research Centre, Italy, used a solid electrolyte instead of liquid electrolyte for hydrogen storage in a metal hydrides electrode of a fuel cell (Folonari et al. 1980). They chose LaNi$_5$ over MmNi$_5$ and CaNi$_5$ and use solid electrolyte to eliminate the need to purify and circulate the electrolyte. Folonari and co-authors discarded the idea of using a proton conducting solid electrolyte (nafion) since “tests of LaNi$_5$ corrosion by acid membranes revealed no dissociation of lanthanum or nickel ions in the absence of an electric field” (Folonari et al. 1980). They selected an alkaline solid membrane of Permaplex (BDH), LaNi$_5$ hydride electrode and an air electrode in their study. Chartouni et al. (2002) notes that the acidic solid membrane was not selected because the hydride metal dissolved anodically in contact with acidic cationic membrane. The exploded view of one of the cell is presented in Figure 7. Folonari et al. (1980) used the data of a single cell to predict the performance of a 50-cell fuel-cell engine.

Figure 7: the exploded view of Folonari et al.’s cell (Folonari et al. 1980)
Folonari et al. (1980) noted some important innovations in their paper. Firstly, they seem to be the first researchers to incorporate solid membranes into the concept of hydrogen storage in the electrode of a solid electrolyte fuel cell, although they were unable to set proton conducting membranes working for the application. Secondly, they propose the idea of using a composite electrode in “which hydride powder is supported and bonded by a polymer resin”. Thirdly, they realised the future application of such system in automobile industry. And lastly, they noted that this system gives the owner the liberty to charge it by electrolysis of water or rapidly by a flow of hydrogen to the electrodes.

There are some unclear issues related to the work of Folonari et al. (1980). The first one is that the paper is silent on how the cell was charged in the experiment. The paper states that “the advantage of a hydride electrode is that the fuel is stored directly in the cell with a high energy density and without the need for an external gas-feeding system”. This statement does not say that the hydride electrode is charged via an electrolysis process. This sentence can be interpreted as, once the hydride electrode is physically charged by flow of hydrogen gas, there would be no need for an external feeding system. In addition, the paper does not disclose the charging performance and only presents discharge performance of the cell. The schematic of the cell that is reproduced in Figure 7, suggests that hydrogen gas goes to the hydride electrode to charge the electrode. The emphasis of the paper on the term hydride-air “fuel cell” might be a suggestion that the cell works as a fuel cell, not an electrolyser (or URFC).

The other major publication on this topic is the paper of Condon and Schober (1995). In their paper, they envision some future applications for high temperature ceramic proton conductors. One of the applications was “charging metals with hydrogen using water electrolysis”. A schematic of the system is presented in Figure 8.
Figure 8: Schematic of the hydrogen charging of metals using proton conducting ceramics proposed by Condon and Schober (1995)

Their paper indicates that since $\text{H}_2$ is not produced in the charging, some kinetic inhabitation can be avoided. Condon and Schober (1995) recognise the application of such system for vehicle use, and suggest that charging of a system like Figure 9 can be done by refuelling by hydrogen gas or slowly by reversing the voltaic cell, \textit{i.e.} using the cell in electrolyser mode. This suggestion is similar to Folorani \textit{et al.}'s (1980).

Figure 9: Schematic of the proposed system with proton conducting ceramic (Condon and Schober 1995)
Condon and Schober (1995) essentially presented a vision for a futuristic device. It should be bear in mind that they did not provide any theoretical or experimental work on this concept and the later works of these authors do not show any development toward realising this concept.

Another significant publication is Chartouni et al. (2002) from National Institute of Advanced Industrial Science and Technology, Japan. They follow the work of Folonari et al. (1980), but use liquid alkaline electrolyte (KOH) to increase ion conductivity and also penetration of electrolyte into the metal hydride electrode. Hydrogen gas was used to charge the metal hydride electrode and then the electrode was used in a three-electrode-cell to measure the storage capacity of the metal hydride.

One advantage mentioned in their work is that when the hydrogen supply is stopped, the cell can still supply electricity for a period of time (Chartouni et al. 2002). This might be an advantage for stationary and mobile application of the concept. For example, a car can have a tank of compressed hydrogen for ordinary work of the fuel cell engine and when the tank becomes empty, the car can still work for a short period of time using the stored hydrogen in the electrodes, until it reaches to a hydrogen fuel station. In stationary application, the hydrogen storage in the hydride electrodes can supply the electricity when suddenly the hydrogen supply system fails. By comparison a conventional fuel cell will stop working once hydrogen supply is stopped. The performance of Chartouni et al.’s cell (2002) is presented in Figure 10.

In their study, hydrogen gas was supplied with pressure of 50 mbar for 58 minutes and then the cell was discharged with no hydrogen supply at constant current of 16 mA/cm² (Chartouni et al. 2002). The discharge capacity was 233 mAh/g, that is equal to 0.85 wt% of hydrogen storage. Although this paper deals with the “H₂-chargebility of the metal hydride electrodes”, they note that the electrochemical charging has been done for this metal hydride researchable fuel cell (Chartouni et al. 2002). Even so, the problems associated with a liquid alkaline electrolyte, like circulation and purification of electrolyte and the sensitivity of the alkaline electrolyte to CO₂, still limit the application of this novel system.
Figure 10: Potential of the metal hydride electrode versus the reference electrode (Chartouni et al. 2002)

A patent by Sanders (2007) from Diffusing Science Inc., USA, is also a point of interest. The key feature for his invention is fabrication of hollow microspheres, also known as microbubbles. The material, like alkaline earth silicate, is permeable to hydrogen gas or oxygen gas and is covered with a catalyst layer. Two of his drawings are presented below. The figures have been simplified to get a clear understanding of the drawings. Figure 11 shows an electrode with microspheres connected to each other by the catalyst layer. According to Sanders each microsphere can include different catalyst coatings that yield different desirable reactions.
Figure 11: A schematic of an electrode from Sanders (2007)

Hydrogen and oxygen, produced by electrochemical dissociation of water, are stored within the hollows of microspheres in high pressure. Each microsphere acts as a small-volume high-pressure vessel. The gases can be extracted from the hollows by applying temperature control or controlled electrochemical reaction. The extracted hydrogen and oxygen then can react together and produce electrical energy as in a fuel cell. Figure 12 shows a complete cell with two electrodes, one for storing hydrogen and the other for storing oxygen and a liquid electrolyte. The electrolyte is circulated between the two electrodes using a pump.
In electrolyser mode, hydrogen can be stored in the microspheres of one electrode and oxygen in microspheres of the other electrode. An electrolyte circulation pump maintains a flow of fresh reactants to the surface of the microspheres.

The issues related to fabricating the so-called microspheres, coating the outer and inner surface of the microspheres, safety issues related to storing hydrogen in gaseous form in the microspheres. Furthermore, the patent seems to be more like a concept than an actual working prototype. All in all, the patent has some promising items. The system does not need a hydrogen and oxygen storage system which makes it suitable for space applications. The patent is like a secondary battery, but uses electrolyser/fuel cell principles.

**Figure 12:** A schematic of the complete cell suggested by Sanders (2007)
Another publication of Choi et al. (2010) from the University of Tokyo, Japan, investigates a similar concept as the one of Chartouni et al. (2002). They call it a fuel cell/battery (FCB) system in which a metal hydride electrode is charged by pressure hydrogen and discharge electrochemically in a KOH electrolyte. The schematic of the system is presented in Figure 13.

Figure 13: The schematic of the fuel cell/battery concept of Choi et al (2010)

The point of difference between this concept and the previous ones is that here the oxygen electrode is capable of storing oxygen and the performance of the fuel cell/battery in discharge is more like a battery. Unlike the patent of Sanders (2007), hydrogen and oxygen are stored by chemical bonds, not pressure gas inside microspheres. Choi et al. (2010) have used manganese dioxide for storing oxygen in the oxygen electrode. The paper showed that the concept works, although it suffers from low performance.

In the next section the works of two research groups that have worked for some years on this concept are presented; the first research group is from General Electrics; the second is
a French-Polish academic group who work on electrochemical storage of hydrogen in activated carbon.

### 3.4.2 General Electric Company and a rechargeable fuel cell

General Electric (GE) is the assignee for the following patents and Tao Wang and Chang Wei from GE Global Research Centre are the chief investigators. The first patent was filed in July 2004 and the latest published patent of this group was filed in September 2007. After that, they might have developed the concept further, but the results are not yet available to the public.

In July 2004, Wang and Wei (2007) of GE filed a patent that used the idea proposed by Sanders (2007). They improved his idea by replacing the method of gaseous storage with chemical storage, *i.e.* hydrogen (in atomic or molecular form) makes a weak chemical bond with the electrode’s material. The hydrogen storage electrode is suggested to be metal hydride, catalysed complex hydrides, carbon nanostructures, and conducting polymers. The Figure 14 is a simplified drawing from the patent that shows hydrogen storage electrode on the left.
Figure 14: Simplified schematic of the device proposed by Wang and Wei (2007)

They called their device a rechargeable fuel cell system. In the fuel cell mode, hydrogen is stored in the left electrode in Figure 15. In the fuel cell mode, the stored hydrogen is released from the electrode and reacts with the supplied oxidant, e.g. oxygen, to produce water and electricity. In this patent, the authors list many possible materials that may have been used as the hydrogen electrode, oxygen electrode, membrane, and also reactants other than water.

The fact that the idea was patented by General Electric Company which is a major global manufacturer of electrochemical equipment, makes this concept worth noting. Wang and Wei have provided a diagram of potential change during discharge mode, but they did not mention how the electrode was charged and what materials were used for the hydrogen storage electrode and the electrolyte. However, the use of metal hydride was singled out in the patent as a potential material.
The next patent from the GE researchers was filed in June 2005 by Huang et al. (2007a). The patent has two sections. The first section explains the two-step method for activating metal hydrides for hydrogen storage. The first step is to activate metal hydride particles in an alkaline solution before fabrication of an electrode. The second step is to activate the metal hydride electrode that was made from the activated metal hydride particles. In the second step the electrode is treated with an alkaline solution to remove the metal oxide formed on the surface of the electrode. The results of the paper show that a two-step activated electrode reached its maximum capacity after three cycles, whereas 15 cycles were needed for the electrode with only the first activation step. Also maximum capacity of the two-step activated electrode was 35% higher than its counterpart.

In the second section of this patent, the authors show a new configuration for the concept of ‘rechargeable fuel cell’. In the new configuration three electrodes are used for each cell. A schematic of the cell is presented in Figure 15.

Figure 15: Schematic of the new configuration for the concept of rechargeable fuel cell (Huang et al. 2007a)
During charging, the left electrode (coated with catalysts appropriate for associating oxygen gas) and the middle electrode (hydrogen storage electrode) operate, and in discharge mode, the second electrode and the right electrode (coated with catalysts appropriate for dissociating oxygen gas) operate. The reason behind this configuration is that the left electrode can be loaded with a catalyst specific for associating oxygen atoms and the right electrode loaded with a catalyst specific for dissociating oxygen molecules, thus improving the performance in both electrolyser and fuel cell modes.

The next patent from the GE researchers was filed in December 2005 by Huang et al. (2007b) and the patent was published July 2007. It explains the procedure to fabricate porous metal hydride electrodes that was to be used in the configuration of the previous patent. The porosity is intended for water and electrolyte to be able to defuse into the porous electrode and improve its performance by preventing water starvation and also reducing electrolyte transfer.

GE also filed another patent in December 2005 by Yang et al. (2011). This patent disclosed a method to reduce contact resistance between electrodes and the membrane by using an extra layer between electrodes and membrane. The hydrogen electrode is coated with gel polymer adhesive electrolyte and the oxygen electrode coated with a layer of tri-phase electrolyte. The patent explains the steps to fabricate a membrane-electrodes-assembly (MEA). The Figure 16 depicts the layers of such MEA. The purpose of the patent is to lower the contact resistance and hence increase the discharge ability of the hydrogen electrode, increase discharge voltage.
Figure 16: Schematic of the full cell of a rechargeable fuel cell (Yang et al. 2011)

The latest available patent from the GE research group became available in April 2012 (Huang et al. 2012). This application is almost identical to the patent filed in December 2005. The only difference is that this patent mentions that, in discharge mode, at potentials less than -0.09 V, hydrogen is evolves. This may mean that at potential lower than -0.09 Volts, the rate of the second chemical question exceeds the first one:

\[
\text{MH} + \text{OH}^{-} \rightarrow \text{M} + \text{H}_2\text{O} \quad \text{Eq. 11}
\]

\[
\text{MH} + \text{MH} \rightarrow \text{M} + \text{H}_2 \quad \text{Eq. 12}
\]

In this patent, the authors list many possible metal hydrides that can be used in the rechargeable fuel cell.
The latest publication of the GE research group was Huang et al. (2009). In this paper, the authors go into more details of electrochemically store hydrogen in a metal hydride electrode and also disclose the problems associated with their previous designs. Figure 17 is reproduction of a figure in their paper and is very similar to the concept of this project, although our concept was developed without knowledge of such work.

Although the system is called a rechargeable metal air battery in this paper, it is the same concept as the rechargeable fuel cell in their patents. The paper notes that each approach has its own downsides: corrosion of electrodes in the potassium hydroxide electrolyte and lower efficiency of thick electrodes due to lower mass diffusion and migration respectively. The metal hydride electrode that was fabricated by the General Electric Company had a 3 mm thickness and had 25 % lower metal hydride utilisation efficiency compared to commercial metal hydride electrodes with 1mm of thickness (Huang et al. 2009).

One noteworthy point is that the electrode used in this paper and other patents of GE are not composite electrodes. Mixing the metal hydride with an ion conducting material could improve the diffusion. It seems that the patents of the GE researchers on porous metal hydrides were an attempt to address this issue.

A review of the patents of General Electric Company shows that they are mainly concentrated on metal hydrides, although in their first patent, they suggest many materials
for the hydrogen storage electrode. Another observation is that, although they have proposed the concept of hydrogen storage electrode in a URFC-like system in their early patent (Wang and Wei 2007), they have moved to separate electrolyser and fuel cell for their later patents (Huang et al. 2007a and 2007b; Yang et al. 2011; Huang et al. 2012). Moreover the continuity of the outputs from this group, and their publishing of patents instead of papers, suggests that there is a sound basis for this concept, and a commercial potential for vehicle and mobile applications.

3.4.3 Electrochemical storage of hydrogen in activated carbon

Perhaps the most active research group on electrochemical sorption of hydrogen in carbon material has been the group led by Francois Beguin from CNRS-University, France and Krzysztof Jurewicz and Elzbieta Frackowiak from Poznan University of Technology, Poland.

The first publication of the group was in 2001 (Jurewicz et al. 2001). This early paper showed that activated carbon is capable of storing more hydrogen electrochemically than ingress of pressurised hydrogen gas. The authors mentioned that through analysing other researchers’ results on electrochemical storage of hydrogen in single-walled-carbon nanotubes, they found that there is no systematic relationship between storage and degree of purity of these nanotubes. They concluded that since there are other forms of carbon, especially disordered carbon, in any sample of single wall carbon nanotubes, the electro-decomposition of water is probably more efficient on other forms of carbon than it is on nanotubes (Jurewicz et al. 2001). They selected samples of activated carbon to test their hypothesis. The activated carbons were treated with nitric acid and NaOCl to modify the surface functionality. The activated carbon electrodes were charged with a constant current in a KOH electrolyte and their hydrogen uptakes were measured by discharge capacity at a lower constant current. They measured the reversible hydrogen storage to be 1.5 wt%, which was higher than reversible storage with high-pressure hydrogen gas.

Reversible storage of hydrogen in activated carbon was reported by Jurewicz et al. (2002), in a liquid acidic electrolyte (H$_2$SO$_4$) and a liquid alkaline electrolyte (KOH). The
electrolysis of water was carried out at a constant current with a great excess of charge (500 mA/g). The hydrogen capacity in the alkaline electrolyte (1.8 wt%) was four times the hydrogen adsorption capacity of the same activated carbon with hydrogen under 700 bar pressure. The value for hydrogen storage in acidic electrolyte was about half that of the alkaline electrolyte, and discharge in the acidic electrolyte did not possess a distinct discharge plateau like the alkaline electrolyte. Although the authors have shown that the acidic electrolyte is capable for electrochemically storing hydrogen in the activated carbon, they focused on alkaline electrolytes in their later works.

In the next paper the authors propose the mechanism for direct hydrogen storage in carbon (Jurewicz et al. 2004). The authors have quantified the surface groups on the sample using X-ray photoelectron spectroscopy (XPS) and intentionally use a sample with negligible surface functionality. In this paper for the first time in addition to N2 adsorption, the authors use CO2 adsorption to characterise the activated carbon. The chosen electrolytes for this paper were H2SO4 and KOH. The charging and discharging were exactly like previous papers. The importance of this paper is that it provides more explanation on why the acidic electrolyte had performed poorly.

Jurewicz et al. (2004) have suggested that the low overvoltage value of H2SO4 (\(\eta=0.32\) V) leads to lower kinetics of hydrogen diffusion and incorporation into the nanopores and consequently leading to molecular hydrogen evolution through Tafel and Heyrovsky reactions (see in section 3.5.2). In contrast, KOH has a high value of polarisation (\(\eta=0.55\) V) and adsorbs more hydrogen in the process. Another note from this paper is the efficiency of the process. The ratio between discharge and charge can be as high as 92%, but the discharge capacity or hydrogen storage was only 194 mAh/g (\(i.e. 0.71\) wt%) with a charge value of 211 mAh/g. Higher hydrogen capacity was achieved by using higher value for charging, but at the same time the discharge to charge ratio became less. For example, with the charge value of 14 000 mAh/g the discharge value reached to 475 mAh/g (1.74 wt%), \(i.e.\) the discharge/charge ratio was about 3 %. After this paper, their investigation concentrated on alkaline media.

Vix-Guterl et al. (2005) investigated the relationship between porosity and hydrogen storage capacity of activated carbon. The charging and discharging were similar to their
previous paper of the authors. Grand Canonical Monte-Carlo simulation had been used to predict the optimum pore size to be below 1 nm at room temperature. Vix-Guterl et al. (2005) found that there is a linear relationship between hydrogen capacity and the ultra-micro pores (smaller than 0.7 nm in diameter) volume. The amount of the ultra-micropore volume was determined by CO$_2$ adsorption. Another important point in this paper is the coexistence of hydrogen adsorption and electrical double layer in discharge mode. For a sample with the total discharge value of 432 mAh/g, voltammetry data was used to distinguish the value for electrical double layer that was 54 mAh/g. The rest of 388 mAh/g discharge value was due to hydrogen discharge from the activated carbon, i.e. 1.44 wt%.

Beguin et al. (2006a) investigate the role of pore size on hydrogen storage in more detail. They conclude that pores larger than 0.8 nm played no role in storing hydrogen in the activated carbon, whereas the suitable storage sites were pores between 0.6 nm and 0.7 nm. Another important conclusion of this paper was that a part of the ultra-micro pore estimated by CO$_2$ adsorption remained unavailable for reversible hydrogen storage. It might be because these pores are involved in irreversible hydrogen storage.

In the next paper, Beguin et al. (2006b) investigated the mechanism and characteristics of bonds between hydrogen and activated carbon. They found that in the electrolysis of water in KOH electrolyte, hydrogen forms a weak chemical bond with carbon that has an activation energy of 110 kJ/mol. They also show that the hydrogen capacity increases as the temperature of the carbon is increased from room temperature to 60°C. This observation has been attributed to increased thermal energy with rising temperature, assisting in overcoming the activation energy for bond formation of hydrogen with the carbon material.

Jurewicz et al. (2008) discussed the preparation of activated carbon from lignin based coal. The activated carbon was only used for fabricating electrode for a capacitor and not for electrochemical hydrogen storage. Even so, because they have used lignin as the precursor, this paper was of interest to the author of this thesis. The sample was activated by KOH chemical activation under argon gas. The porosity of the sample was determined by only N$_2$ adsorption isotherm at 77 K. The result show that by increasing the final activation temperature from 500 to 700°C, the average pore diameter decreases from 2.3 to 2.0 nm.
The authors did not provide an explanation for these data, but in Chapter 4 it is explained that some of activation processes only commence at temperature higher than 600°C. The authors conclude that the lignin is a suitable candidate for fabricating activated carbon.

Babel and Jurewicz (2008) investigated the use of KOH activated carbon in hydrogen electrosorption. They fabricated a highly porous carbon that has a BET surface area of almost 2000 m²/g with 31% of the micropore volume include pores between 0.5 nm to 0.64 nm. The activated carbon possessed a high hydrogen storage capacity of 1.89 wt%. They suggested that the large micropore volume and small mesopore volume enhanced the degree of electrochemical hydrogen sorption.

Jurewicz (2009) explored the effects of charge current density and the duration of charge on the hydrogen capacity of an activated carbon. The concept was briefly mentioned earlier in Jurewicz et al. (2004). In fact the precursor and procedure to activate carbon sample were similar to the previous study (Babel and Jurewicz 2008). The only difference was that the final activation temperature (700°C) was lower than the other paper (900°C). Jurewicz (2009) found that the maximum hydrogen capacity (2.17 wt%) could only be achieved by a large over charge and hence very low coulombic efficiency (about 2 %). Jurewicz does not distinguish the discharge value of electrochemical hydrogen storage and electrical double layer. He makes the point that the electrical double layer is an additional advantage and as useful as the charge due to hydrogen electro-oxidation. Jurewicz (2009) showed that the reversible hydrogen storage did not depend on the charge current density or the charging time, but only on the amount of supplied charge.

The next publication of this group included a schematic for a secondary battery that uses principle of electrolysis/fuel cell in a KOH electrolyte (Jurewicz et al. 2009). The schematic of the so-called rechargeable fuel cell in presented in Figure 18.
Figure 18: Schematic representation of the rechargeable fuel cell (Jurewicz et al. 2009)

During charging, the nanoporous carbon electrode was the positive pole, and the auxiliary electrode (nickel gauze) was the negative pole. The reactions in this mode were as follows:

Carbon electrode: \( C + xH_2O \rightarrow CH_x + xOH^- \)  Eq. 13

Auxiliary electrode: \( xOH^- \rightarrow (x/2)H_2O + xe^- + (x/4)O_2 \)  Eq. 14

In recharging carbon electrode was negative and air electrode (activated carbon layer with platinum black) was positive,

Air electrode: \( (x/2)H_2O + xe^- + (x/4)O_2 \rightarrow xOH^- \)  Eq. 15

Carbon electrode: \( CH_x + xOH^- \rightarrow C + xH_2O \)  Eq. 16

The reason for using an auxiliary electrode, in charging, is that, oxygen evolution on carbon can lead to oxidation of carbon. The carbon electrode was found to have a hydrogen storage capacity of 1.44-1.66 wt%. The cell showed a discharge capacity of 450 mAh/g (1.65 wt% hydrogen storage capacity) with a plateau voltage of 0.6 V.
Considering that in all the papers of this group (including this paper) the amount of charge was much higher than discharge capacity and also considering the point that the maximum hydrogen storage capacity can be only achieved by using a large over charge (Jurewicz et al. 2004; Jurewicz 2009), one can conclude that majority of charge was used in hydrogen gas formation (formation of hydrogen molecules). The proposed rechargeable fuel cell of these authors did not have any mechanism to vent the hydrogen gas. Even with such mechanism, the rechargeable fuel cell produces hydrogen gas and cannot be used as a stand-alone secondary battery. Even with this limitation, the fact that this fuel cell/battery has been proposed and also that activated carbon has been suggested for hydrogen storage, lend support for the concept of a proton flow battery.

Frackowiak (2010) investigates the bond between hydrogen as guest specie and carbon as host material. She confirms that the binding energy of H-C bond in electrochemical sorption is about 110 kJ/mol and so electrochemical storage of hydrogen in carbon can be categorised as chemisorption (Frackowiak 2010), as it was suggested in Beguin et al. (2006b).

Lota et al. (2011) studied the effect of charge parameters on hydrogen storage. They have used a method of charging the electrodes with an interval charging method. In this method, the electrode is charged for few seconds (pulse) and then is left to rest for few seconds without being charged (pause) and then charged again. These pulse-pause sequences are repeated for several times. By using an optimal parameters of 1 second pulses of 5 A/g and 0.5 second pauses for a total charging time of 9 minutes (6 min. charging + 3 min. pauses) the activated carbon was charged about to 60% of its total capacity (1.08 wt%). The authors concluded that the quick faradaic processes are the advantage for using in power devices. They investigate the effect of temperature on hydrogen storage capacity of activated carbon and show that a 10% improvement was achieved when temperature is elevated from 25°C to 60°C, confirming the result of Beguin et al. (2006b).

Babel et al. (2012) reported the fabrication of several activated carbons from different precursors. With one of the activated carbons that was made from blackthorn stone exhibiting 2.31 wt% hydrogen storage capacity. However, in this paper the authors
question the validity of the primarily proposed linear relationship between volume of ultra-micro pores and hydrogen storage capacity.

The lack of a straight-forward relationship between surface area (or even ultra-micro pore volume) and electrochemically stored hydrogen in activated carbon led Weselucha-Birczynska et al. (2012) to use Raman spectroscopy to get a better understanding of the structure of activated carbons. The data of the Raman spectroscopy from activated carbons of different precursors revealed that there were different phases and even different forms within a certain phase. The different phases of carbon can thus also be another important parameter in addition to surface area, pore distribution, and surface functionality in determining hydrogen storage capacity.

3.4.4 Recent work on the concept of a proton flow battery at RMIT University

Associate Professor John Andrews had the idea of the proton flow battery while working earlier on URFCs. A Master of Engineering (by research) project at RMIT University supervised by A/Prof Andrews and being conducted by Saeed Seif was initiated into this topic in early 2010 and was completed in 2013 (Seif Mohammadi 2013).

In Seif Mohammadi’s research, a preliminary design for a URFC cell capable of incorporating a solid hydrogen storage electrode has been developed, and the device has undergone its first tests. A number of metal hydride powder electrodes have been tested as the solid storage electrode in this cell, but all to date have shown a significant rate of direct hydrogen gas production, in addition to any direct ingress of protons into the metal to form the hydride. In many respects, this behaviour is not surprising since the metals employed (in particular Ni) are known to catalyse hydrogen production, and there are plentiful voids between the metal particles in which hydrogen gas can form. Moreover, the pressure in these voids has not been much above atmospheric pressure, so according to the usual pressure composition isotherm (PCI) graphs for the metal hydride employed it would be expected that most hydrogen atoms bonding to the metal would soon diffuse out of the body of the metal particles and form hydrogen gas molecules.
A further important finding from this initial research is that water is steadily drawn across the nafion membrane from the oxygen electrode in electrolysis mode and accumulates in the powered metal hydride electrode. This process is no doubt that of ‘electro-osmotic’ drag of water molecules (in the form of hydronium, Eigen and/or Zuntel cations). So even when this electrode starts dry, it soon becomes wetted and eventually flooded. Hence the electrochemical current varies over time from the start of applying the charging voltage, even when all other controllable parameters are held constant.

In the results that were obtained by Seif Mohammadi (2013), a hydrogen storage capacity was measured to be 0.6 wt% of hydrogen, although the amount of hydrogen recovered to run the device in fuel cell mode was much lower. His results provided the initial confirmatory evidence that the proton flow battery concept with metal hydride electrodes is technically feasible. However, additional research is still required to enhance both storage capacity and reversibility.

3.5 SOLID STATE HYDROGEN STORAGE IN ACTIVATED CARBON

3.5.1 Activated carbon as the medium for hydrogen storage

The initial results of Seif Mohammadi (2013) showed that in the proton flow battery with metal hydride electrode, most of the hydrogen is evolved in molecular form. The hydrogen gas evolution might be because the transition metal particles in the metal hydride electrode act as a catalyst. In fact, Chartouni et al. (2002) suggested that one of the advantages of metal hydride is that it can both store and catalyse hydrogen. Unlike transition metals, carbon does not have d-electrons to facilitate hydrogen association or dissociation (Zuttel et al. 2008).

Another reason for selecting carbon to test the feasibility of the concept of proton flow battery is the availability, low cost and light weight of carbon compared to metal hydrides. Also the promising results of Jurewicz, Frackowiak, and Beguin (see section 3.4.3) in demonstrating a relatively high capacity of hydrogen storage in activated carbon (about 2 wt%) indicates that carbon may be a suitable candidate for this research project.
3.5.2 Mechanism of electrochemical storage of hydrogen in activated carbon

It has been suggested that in highly disordered carbons, hydrogen has a better accessibility to the internal surface of the activated carbon (Jiménez et al. 2012). In fact, even in hydrogen storage with high pressure, the more disordered the (amorphous) carbon is, the more hydrogen is stored (Jiménez et al. 2012; Minoda et al. 2013).

In an alkaline environment, hydrogen is adsorbed through a reaction known as Volmer reaction (Jurewicz et al. 2004; Qu 2008):

\[
\text{C} + \text{e}^- + \text{H}_2\text{O} \rightarrow \text{CH}_{\text{ads}} + \text{OH}^-.
\]

Eq. 17

The adsorbed hydrogen then is inserted to the interlayer spaces and nanopores (Qu et al. 2012). At the same time, the adsorbed hydrogen atoms may follow a different path of reactions. The adsorbed hydrogen may be evolved to hydrogen molecule through the Tafel reaction (Jurewicz et al. 2004; Qu 2008):

\[
2\text{CH}_{\text{ads}} \rightarrow \text{H}_2 + \text{C}
\]

Eq. 18

and Heyrovsky reaction (Jurewicz et al. 2004; Qu 2008):

\[
\text{CH}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^- + \text{C}.
\]

Eq. 19

If the hydrogen adsorption energy is smaller than the energy of Tafel or Heyrovsky, and the activation barrier is low enough hydrogen gas is evolved (Jurewicz et al. 2004). The majority of the hydrogen is stored in the micro space of the imperfect structure of carbon (Qu 2008).

There has been some indicated that molecular hydrogen cannot be stored in activated carbon in ambient condition (Qu 2008). It has been suggested that stored hydrogen would be in atomic form. Tsao et al. (2011) experimentally proved the existence of atomic hydrogen in activated carbon. In their paper, they used the inelastic neutron scattering method to reveal the state of hydrogen in Pt-doped activated carbon (Tsao et al. 2011).
Furthermore, the studies of Beguin et al. (2006b) and Frackowiak (2010) showed that the C-H bond in electrochemically stored hydrogen in KOH environment is about 110 kJ/mol and the bond can be categorised as a weak chemical bond.

3.6 Conclusions

3.6.1 Limitations of previous studies and areas requiring R&D

The research of the General Electric Company has concentrated on metal hydride electrodes. These electrodes employ rare earth materials and therefore are expensive. In addition, recycling of metal hydride materials, gravimetric hydrogen density, and heat management related to metal hydrides are still need to have a solution before a widespread application of such materials. Carbon is a suitable candidate that is available, cheap, and easy to recycle. Carbon has a lower density compared to metal hydrides that may promise a higher gravimetric hydrogen capacity.

The works of Jurewicz, Frackowiak, and Beguin concentrate on electrochemical storage of hydrogen in alkaline liquid electrolyte. The need to purify and pump electrolyte, safety issues related to leakage of electrolyte, low current density of alkaline electrolyte, and sensitivity to CO₂ are the issues related to alkaline electrolytes. Proton exchange membranes are solid and have high current density, they work at low temperature and have quicker warm-up.

The research of Seif Mohammadi (2013) showed that the majority of electrochemically produced protons form molecular hydrogen gas and leave the electrode without making bond with metal the hydride electrode. Carbon does not have d-electrons and may prohibit the hydrogen gas formation in the electrolyser mode.
3.6.2 Towards realisation of the concept of a proton flow battery with activated carbon electrode

The present research differs from the work of General Electric researchers and Seif Mohammadi’s (2013) in using activated carbon electrode, instead of metal hydride. In this present research, activated carbon is selected to be used as the hydrogen storage electrode along with a solid acidic membrane, in hope to hinder the hydrogen gas formation. Moreover, carbon an abundant and light material is used in the PEM cell, thus reducing the weight of the cell and increasing the gravimetric hydrogen storage capacity of the cell. The activated carbon may also hinder the rate of gas formation, because carbon do not have d-electrons like transient metals in metal hydrides that may facilitate hydrogen gas formation in the electrolyser mode.

The present research differs from the work of Jurewicz, Frackowiak, and Beguin in using a proton exchange membrane instead of KOH liquid electrolyte. Proton exchange membranes promise higher charge density and elimination of the common problems associated with using a liquid electrolyte such as recycling and environmental issues. The solid proton exchange membrane may also increase the hydrogen storage capacity by transferring highly-reactive protons into the activated carbon electrode.

Based on the concept of integrated hydrogen storage electrode in PEM URFC (as known as proton flow battery), a composite electrode from activated carbon and a proton conducting polymer has been fabricated and tested in a specially designed PEM URFC within the present project.

The method to fabricate activated carbon from carbon precursors is described in the chapter 4. The method to fabricate the composite material of the activated carbons and nafion and the physical and electrochemical characteristics of the composite material are also described in the chapter 4. The method to fabricate full-size electrode from composite material, fabricating experimental cell, fabricating membrane-electrode-assembly and the experimental results from testing the electrodes in the experimental cell are presented in Chapter 5.
4. FABRICATION AND CHARACTERISATION OF ACTIVATED CARBON-NAFION COMPOSITE MATERIALS

4.1 FABRICATING ACTIVATED CARBON

4.1.1 Preparation and characterisation of precursors

4.1.1.1 Precursors

Many carbon-rich materials such as corn cob, banana peel, pistachio-nut shell, oil sands coke, wood sawdust and fruit stones have been used as precursors for activated carbon production (Chang et al. 2000; Lua and Yang 2004; Mopoung, 2008; Chen and Hashisho 2012; Foo and Hameed 2012; Venhryn et al. 2013). As a starting point in the present project, coal and charcoal were used as the precursors for carbon activation. Other carbon-rich materials will need to be tried out in the future to find the most suitable precursor for the proton flow battery application.

Charcoal is usually made by burning wood in absence of oxygen (Agirre et al. 2013). Millions of tonnes of charcoal are produced annually, virtually all around the globe (Zulu and Richardson 2013). Coal is formed by decomposition of vegetable matter that has been subjected to heat and pressure within bodies of water for over millions of years (Australia Institute of Energy 2013). One of the differences between charcoal and coal is their density. The density of charcoal is around 200 kg/m$^3$, while that of coal is above 1300 kg/m$^3$ (Walker 2011; Speight 2013).

Commercially available charcoal (Diggers) was purchased from the market for this project. The coal samples used were obtained from Queensland black coal (the Claremont mine, 2 km from Blair Athol) in Australia.

The coal lumps were broken down into pieces about 5-10 cm in diameter before grinding them to produce powder. The morphological differences between the outer and inner
surfaces of the coal are noticeable in Figure 19.

![Figure 19: The different morphologies of the outer and inner (fractured) surfaces of black coal pieces](image)

In this figure, the upper parts are the outer surface of the coal and the bottom parts are the inner surfaces of the coal after fracturing. The structure and porosity of the surface and inner parts of coal pieces are very different. Some of the pieces seem to have similar composition with different porosity (left in Figure 19). Others seem to have different elements in their surface (shown right in Figure 19). The presence of different elements was concluded based on the different colours of surface and the inner parts of the coal. The inner sections of the pieces that prior to fracture of the coal lumps were not exposed to air were used as the precursor material. These pristine parts were obtained by further fracturing the coal samples and removing surface area of the samples. Several coal pieces were used to have an average composition of the entire coal sample.

The bulk charcoal was also broken down to extract pristine parts. The charcoal was more brittle and much easier to break than the coal. The surface and the inner parts of the charcoal lumps did not show any noticeable difference in colour, porosity, or structure, as seen in Figure 20. Even so, several pieces of charcoal were used in preparing samples, to gain an average representation of the source charcoal.
It is interesting to note here that, in the process of activating solid-state precursors, the activated carbon retain the same structure within its bulk material as its precursor, but with less density. In technical terms the activated carbon is a pseudo-morph of its precursor (Marsh & Rodriguez-Reinoso 2006). The structure of the precursor may affect the properties of the final activated carbons. Hence, it is advisable to try out as many precursors as possible to find the most suitable candidate for the proton flow battery application. As mentioned before, the particular coal and charcoal samples used in the present project are just starting points within the much more comprehensive search that will over time be needed.

4.1.1.2 Morphology of precursors

The selected charcoal and coal samples were ground into a fine powder using a sand-paper no. 2 1/2. After that, an elemental analysis was carried out to ensure that elements of the sandpaper had not been mixed with carbon powder. Scanning electron microscopy (SEM) has been used to study the grain size of the powders. SEM can be also used to study the surface texture of samples, dimensional changes and structural changes before and after activation (Carrott et al. 2002; Kutchku et al. 2013). The sample is bombarded by electrons
that are emitted from an electron gun (usually tungsten filament). Image formation is based on detecting reflected electrons, *e.g.* backscattered electrons and secondary electrons, from the sample (Cazaux 2012). The initial tests showed that both carbon and coal samples are electrically conductive. Hence, coating the samples with an electrically-conducting material prior to SEM was avoided.

The two SEM machines that were used during this research project were Philips XL30 SEM and FEI Quanta 200 ESEM. The only reason for using two SEM machines was the availability of the machines. The images of the carbon powders were obtained at high vacuum and by using an accelerating voltage of 20 kV. The coal and charcoal samples were placed on SEM stubs by using double-sided conductive carbon tape. Figure 21 presents an SEM image of charcoal powder.

![SEM image of charcoal powder](image)

**Figure 21:** SEM picture of the charcoal powder before activation using Philips XL30 SEM
The particle sizes of the charcoal powder are in the range from a few µm to 70 µm with the majority at the lower end of this range. Since several charcoal lumps were ground to obtain the charcoal powder, the structure of the final powder is an average over these lumps. The diversity of the porous carbon structure within this charcoal can clearly be seen in Figure 22.

**Figure 22:** Different structures in the charcoal powder using Philips XL30 SEM
The grain size of the black coal powder is in the range of a few µm to 120 µm. Although the same sand paper was used for coal, the more brittle nature of the coal led to bigger grains in the coal powder. The SEM picture of coal powder is shown in Figure 23.

**Figure 23:** SEM picture of the black coal powder before activation using an FEI Quanta 200 ESEM

Coal particles have a rock-like appearance and all the grains have similar structure. A magnified SEM image of a coal grain is presented in Figure 24.
The grain sizes of the coal and charcoal powders obtained here are smaller compared to those reported in other literature, e.g. 600-1000 µm (Lozano-Castello et al. 2001) and 250 µm (Song et al. 2013). The reason for choosing a smaller grain size in the present work was to increase the surface area of the powder and hence increase the surface area for reaction between the activating agent and carbon. The author believed that smaller particles could result in an increase in the surface area of the final products. Recently published results by other researchers have supported this hypothesis (Karimi et al. 2013).

4.1.1.3 Elemental analysis of precursors

To investigate the elemental composition of the samples, energy-dispersive X-ray spectroscopy (EDX) was employed. EDX is a fast and accurate elemental analysis for determining the chemical characterisation of a sample. EDX can also be used to investigate the distribution of metals in a sample (Sun et al. 2011). Figure 25 shows a schematic of EDX system.
A beam of X-rays is focused on the sample excites electrons from atoms in the material to a higher energy levels. The excited electrons emit energy in the form of photons (in the X-ray region of the spectrum) as they go back to the ground level. The energy of the emitted photon is equal to the energy difference between ground level and excited level and is unique for each element. An X-ray adaptor is used to convert X-ray energy to voltage signals, which makes the horizontal axis of the spectrum. Leng (2008:178) provides a complete list of voltages by element. The counts of X-rays at each characteristic energy/voltage indicate the concentrations of the atoms that have this signature.

Many scanning electron microscopes have the EDX feature. The only difference between a stand-alone EDX and SEM-EDX is the source energy for excitation. In the latter, the electron beam is used for excitation instead of an X-ray beam (Leng 2008). SEM-EDX is commonly known as EDS. The elemental analyses throughout this thesis were carried out using a Philips XL30 SEM with Oxford Si (Li) detector at RMIT University Microscopy and Microanalysis Facility (RMMF).
In the EDS results, the vertical axis is the number of emitted X-rays from the sample, which are called counts. Counts show the relative intensities of the reflected electrons and are used to define the elemental composition of the samples. The sum of all the counts should be 100% of the sample's mass, so by comparing the relative height of the peaks, the mass percent of each element can be determined. Periods when no emission is counted are called Dead Times. The EDS result for the charcoal powder is presented in Figure 26.

![Figure 26: EDS result for the charcoal sample before activation using Philips XL30 SEM with Oxford Si (Li) detector](image)

For the charcoal sample, the results show that 66.6 wt% of the sample was carbon and 29.4 wt% is oxygen. From other elements in the sample 1.5 wt% is calcium. The EDS for the coal sample is presented in Figure 27.
In the coal sample, the carbon content was 68.4 wt% and oxygen 29.0 wt%. Silicon comprised about 1.3 wt% of the sample. The principal elements in the charcoal and coal sample are presented in Table 3.

<table>
<thead>
<tr>
<th>Element</th>
<th>Coal (wt%)</th>
<th>Charcoal (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>68.39</td>
<td>66.58</td>
</tr>
<tr>
<td>Oxygen</td>
<td>29.00</td>
<td>29.36</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1.34</td>
<td>-</td>
</tr>
<tr>
<td>Silicone</td>
<td>1.30</td>
<td>-</td>
</tr>
<tr>
<td>Calcium</td>
<td>-</td>
<td>1.54</td>
</tr>
<tr>
<td>Sulphur</td>
<td>-</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 3: The composition of the charcoal and coal

The oxygen to carbon ratios were in the expected range, *i.e.* 0.2-0.4, (Brodowski *et al.* 2005). The limitation of EDS (or EDX) method is that it cannot detect elements lighter than boron. So, if hydrogen exists in the sample, the EDS method is unable to detect it.
4.1.2 Activation techniques

4.1.2.1 Physical activation

Activation is the process of creating pores in the precursors to increase the porosity of the sample. Pores are categorised based on their diameter (Marsh and Rodriguez-Reinoso 2006; Achaw 2012):

- macropores > 50 nm,
- mesopores between 2 and 50 nm,
- micropores between 0.7 and 2 nm, and
- ultra-micropores < 0.7 nm

In physical or thermal activation, the carbon-rich precursor is first carbonised in the absence of air, usually in an inert gas. Activation is carried out with steam or CO₂ (activating agents) or a mixture of both at temperatures in the range of 800-1200°C (Vargas et al. 2010; Zhao et al. 2013; Sachin and Saka 2013). Some tests on coke and fibre samples indicate that steam activation creates more porosity compared to CO₂ (Zaini et al. 2010).

The reactions between carbon and the oxidising agent are (Marsh and Rodriguez-Reinoso, 2006):

\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad \Delta H = +159 \text{ kJ mol}^{-1} \quad \text{Eq. 20}
\]

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad \Delta H = +117 \text{ kJ mol}^{-1}. \quad \text{Eq. 21}
\]

Adding a controlled amount of oxygen will cause the following exothermic reactions, which act as a heat supply for the reactions and also reintroduce the activating agents to the system, \textit{i.e.} the products of equations 22 and 23 are the reactants for equations 20 and 21.

\[
\text{CO} + 0.5 \text{O}_2 \rightarrow \text{CO}_2 \quad \Delta H = -285 \text{ kJ mol}^{-1} \quad \text{Eq. 22}
\]

\[
\text{H}_2 + 0.5 \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \Delta H = -238 \text{ kJ mol}^{-1}. \quad \text{Eq. 23}
\]
By removing carbon from the precursor, according to equation 20 and 21, pores are created and the precursor becomes activated carbon. In this process the mass of the carbon sample will decrease. The difference between masses before and after activation - that is the absolute mass reduction - is called ‘burn-off’ and is a function of activation time (Chang et al. 2000). Some literature use yield instead of burn-off. Yield is defined as the weight of activated carbon divided by the weight of precursor (Foo and Hameed 2012b). In activation, carbon experiences two processes: first, creation of pores, which happens until 60% burn-off; then widening the existing pores and making mesopores (Marsh and Rodriguez-Reinoso 2006; Sahin and Saka 2013).

The factors affecting physical activation are (a) reacting temperature, (b) partial pressure of the reacting gas, and (c) structure of the carbon (Marsh and Rodriguez-Reinoso 2006). The volume and size of microspores are mainly dependent on: (a) activation equipment, (b) starting carbonaceous precursor, (d) the activation agent, and (e) the amount of oxygen surface complexes (Marsh and Rodriguez-Reinoso 2006).

4.1.2.2 Chemical activation

Another way to activate carbon is by chemical activation. The advantage of this way is the lower temperature required less activation time, and higher yields (Wang and Kaskel 2012). The material is treated with chemicals and then is activated in absence of oxygen. Zinc chloride, phosphoric acid, sodium hydroxide and potassium hydroxide are the most common chemicals used (Marsh and Rodriguez-Reinoso 2006; Linares-Solano et al. 2012). The mechanism of KOH activation is very complex and still not well understood (Lozano-Castello et al. 2001). Wang and Kaskel (2012) propose a nine-step mechanism for KOH activation.

Between 400ºC and 600ºC the following reactions happen:

\[2\text{KOH} \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O}\]  
Eq. 24

\[\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\]  
Eq. 25
CO + H₂O → CO₂ + H₂  
Eq. 26

CO₂ + K₂O → K₂CO₃  
Eq. 27

At temperatures higher than 700°C the following reactions occur:

K₂CO₃ → K₂O + CO₂  
Eq. 28

CO₂ + C → 2CO.  
Eq. 29

Also at above 700°C, metallic potassium is produced via these reactions:

K₂CO₃ + 2C → 2K + 3CO  
Eq. 30

C + K₂O → 2K + CO.  
Eq. 31

Lozano-Castello et al. (2001) observed decomposition of potassium on the cooler parts of the tube furnace at 700°C. It can be seen that KOH activation takes place in three stages; (a) pure chemical activation, as in equations 24-27, (b) physical activation, as in equations 28 and 29, and (c) expansion of carbon lattices via entering metallic K into the carbon matrix, in equations 30 and 31. The metallic K should be removed from the sample because the porosity that has been created in this activation method is blocked by the potassium components (Lozano-Castello et al. 2001). The removal of potassium was checked with an EDS elemental analysis of the activated carbons after being washed with water.

Chemical activation is especially suitable for controlling the pore size in activated carbon. The disadvantages of this method are using corrosive chemicals and the additional washing step to remove the activating agent. This method is explained in more detail in section 4.1.3.
4.1.2.3 Replica technique

The third and the lesser known technique for activating carbon is the replica technique using mesoporous silica as templates. This technique was first introduced by a group of researchers in Korea (Ryoo et al. 1999, Fang et al. 2006). A gas or liquid carbon is introduced to the silica template and fills the pores of the template. The material is placed in an oxygen-free furnace (Lee and Park 2011). Silica is then removed by an acid treatment. The product is called ordered porous carbon and is the negative replica of the silica template, i.e., walls of the silica template become pores of the ordered porous carbon and pores of the former become walls of the latter (Vix-Guterl et al. 2005). It is possible to tailor the pore size of the activated carbon by controlling the wall thickness of silica (Fang et al. 2006). The silica source and the ratio between silica and carbon can affect the characteristics of the activated carbon (Babic et al. 2013).

4.1.2.4 Selecting the activation technique

For the application in this research project, the techniques are graded from 3 to 1 in Table 4, with 3 being the best choice and 1 being the worst choice. Among these techniques, chemical activation method was selected for the present application because of the control it affords over pore size and temperature of each stage.

<table>
<thead>
<tr>
<th></th>
<th>Control over pore size</th>
<th>Level of convenience</th>
<th>Time required for activation</th>
<th>Equipment availability</th>
<th>Control over temperature</th>
<th>Total suitability value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Chemical</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Replica</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 4: Ranking the activating techniques for the application of this thesis

Further, KOH was chosen as the agent in this project because of its wide usage in activating of carbon for hydrogen storage application (e.g. Babel and Jurewics 2008; Bleda
Martinez et al. 2008; Jurewics 2009; Minoda et al. 2013). Song et al. (2013) compared the steam physical and KOH chemical activation for a same precursor and concluded that chemical activation is superior in porosity development and surface area.

### 4.1.3 Activating precursors with chemical activation technique

#### 4.1.3.1 Carbonisation

If the precursor is not pure carbon, the sample has to be placed in a furnace and heated in the absence of air to remove elements other than carbon. The macromolecular material decomposes as the heat-treatment temperature increases and gases and liquids of low molecular weight evolve. For instance, Chang et al. (2000) put 10 g of corn cob under a 200 cm$^3$/min stream of N$_2$ and heated it to 1173 K at a rate of 10 K/min. In the present research project, coal and charcoal powders were loaded into a ceramic boat and the boat was placed in a horizontal tube furnace as shown in Figure 28.

![Figure 28: Schematic of the horizontal tube furnace used in the present project (modified from Agirre et al. 2013)](image)

The furnace used for this project was a Lindberg/Blue made in USA (model number TF55035c-1) with maximum temperature of 1100°C. The activation test rig is shown in Figure 29.
Figure 29: The horizontal tube furnace at RMIT University used in KOH chemical activation

The furnace was started at room temperature and reached the final temperature after a period depending on the setting of the temperature increase rate. The sample stayed at the final temperature for a period of time, and then was turned off and left to cool down to the room temperature. Cooling down usually took about 12-15 hours. Nitrogen gas, supplied from a gas cylinder at room temperature, was connected to the tube furnace for the duration of the experiments. The nitrogen flow was selected high enough to remove the gasified elements from the sample and low enough to prevent a temperature gradient on the sample. At the time of the experiments, a flow meter was not available to quantify the flow rate of nitrogen gas.

4.1.3.2 Impregnation

KOH was selected as the most commonly used activating agent for carbon (Wang and Kaskel 2012). The mass ratio of KOH to carbon plays an important role in pore development of samples. Normally KOH/C mass ratios range from 2/1 to 5/1 (Wang and Kaskel 2012) and most often ratios of 3/1 and 4/1 have been used (Lozano-Castello et al. 2001; Babel and Jurewicz 2008; Jurewicz 2009). Lozano-Castello et al. (2001) studied the
effect of different ratio of KOH/anthracite, from 1/1 to 5/1, concluding that the micro-pore (pore with diameter smaller than 2 nm) volume reaches its maximum for ratio of 4/1. Above that ratio, the pores begin to widen and form meso-pores (pore with diameter between 2 and 50 nm). It should be noted that with a different precursor the optimum ratio of KOH/C would be different. High ratio of agent to carbon causes pore widening (Lozano-Castello et al. 2001). It has the same effect as the percentage of burn-off in physical activation.

For dissolving each gram of KOH, 2-3 ml of distilled water was used. The mixture of water-carbon-KOH was poured into a beaker and placed on a magnetic stirrer/hot plate and set at 70°C and medium rpm. The purpose of this step is to let KOH penetrate into the carbon particles. When the mixture lost most of its water content, the beaker was placed in an oven at 105°C overnight.

**4.1.3.3 Activation**

Activation was carried out under a flow of nitrogen at a temperature range of 700-800°C. The lower heating rate creates higher micropores. This may be because of a more controlled evaluation of gas products (Lozano-Castello et al. 2001). A higher flow of inert gas also enhances micropore creation. The inert gas removes the evaluated potassium from carbon, shifting the equilibrium of the reaction to produce more potassium and hence more micropores (Lozano-Castello et al. 2001). The heating rate (°C/minutes) affects the micropore volume of the final product. In general, a lower heating rate increases the micropore volume. A lower heating rate allows a more time for melted KOH to have contact with carbon (Lozano-Castello et al. 2001). Based on the mechanism of KOH activation, it can be seen that any temperature above 700°C is suitable. However, too high a temperature results in widening of the micropores to mesopores and burn-off of the sample (Lua and Yang 2004). The same horizontal tube furnace was used for this step.
4.1.3.4 Washing

As noted in equation 30, metallic K would be deposited between the carbon layers at temperatures higher than 700°C and would block the pores in an unwashed sample (Lozano-Castello et al. 2001). Fortunately, metallic K can be dissolved in water and removed from the sample. The sample should be washed by distilled water. Washing with an acid first and then distilled water does not remove more metallic potassium from the sample and does not improve the properties of the samples (Lozano-Castello et al. 2001); hence using acid first is unnecessary. The samples were placed on a filter paper in a funnel and a second funnel with filter paper was placed beneath it to trap any carbon that may go through the filter as shown in Figure 30. The first tests showed that passage through just one funnel with paper filter is enough. The funnels were placed beneath a distilled water tab and the samples were washed with an excessive amount of water.

![Figure 30: Washing apparatuses of activated carbon](image_url)

The washing was continued until the pH indicator papers showed that the pH of the water was the same before and after passing through the samples. This test showed that all the
potassium had been removed from the sample. Some samples were also tested with EDX, which confirmed that there was no sign of K in the elemental analysis of the samples, as in the EDS shown in Figure 31.

![Figure 31: EDS elemental analysis of an activated carbon sample after washing step](image)

There is no peak at the location of K on the graph, which would be around 3.5 keV on the spectrum.

### 4.1.3.5 Drying

Samples were placed in an oven at 110°C overnight to extract all the moisture in them and then kept in air-tight bottles. It is noteworthy that in some publications activated carbon has been treated with an acid like HNO₃ to introduce surface functional groups on the activated carbon and increase its activity in adsorbing elements (Shamsijazeyi and Kaghazchi 2010). In earlier researches on hydrogen storage in activated carbon, activated carbon was treated with nitric acid to modify the surface functionality (Jurewics et al. 2001, 2002). Later investigation showed higher proportions of surface oxygen groups decrease the amount of hydrogen uptake of the activated carbon (Bleda-Martinez et al.)
2008). Surface modification with nitric acid has not been used in more recent literature (e.g. Jurewicz 2009). Therefore in the present research project, samples of activated carbon were used without functionalising with HNO₃ or other acids.

4.1.3.6 Summary of the KOH activation procedures

In summary, the most important factors in chemical activation are the ratio of agent to precursor, the rate of heating step, and the final activation temperature (Lozano-Castello et al. 2001). The principal procedure is same in all papers, but parameters such as temperature and duration of activation depends on the type of precursor. A summary of the parameters in the KOH activation of the four activated carbon samples prepared by the author in the present study is presented in Table 5, along with their descriptors (e.g. AC1, AC2 etc.) that will be used to identify these henceforth.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>Carbonisation</th>
<th>Impregnation</th>
<th>Activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>precursor</td>
<td>Heating rate</td>
<td>KOH/C ratio</td>
<td>Heating rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[°C/min]</td>
<td>[°C]</td>
<td>[°C/min]</td>
</tr>
<tr>
<td>AC1</td>
<td>coal</td>
<td>4</td>
<td>N₂</td>
<td>3:1</td>
</tr>
<tr>
<td>AC2</td>
<td>charcoal</td>
<td>10</td>
<td>N₂</td>
<td>3:1</td>
</tr>
<tr>
<td>AC3</td>
<td>coal</td>
<td>10</td>
<td>N₂</td>
<td>4:1</td>
</tr>
<tr>
<td>AC4</td>
<td>coal</td>
<td>4</td>
<td>N₂</td>
<td>3:1</td>
</tr>
</tbody>
</table>

**Table 5:** Summary of the activation methods for the activated carbon samples prepared at RMIT in this project
4.1.4 Activated carbons from Monash University

Five samples of activated carbon were also provided by Professor Alan Chaffee and PhD candidate Lachlan Ciddor from Monash University for testing in this project. The samples were named: ACN, ACS, ACK2.5, ACK7.5, and ACK10. While the precursor and the activation process of these samples were not disclosed to the author, the porosities of the samples were disclosed and are presented in section 4.2.1.4.

4.2 CHARACTERISTICS OF ACTIVATED CARBONS AND SELECTING SAMPLES FOR COMPOSITE MATERIALS

4.2.1 Porosity measurement

4.2.1.1 Models of activated carbon and the concept of porosity

In a simplified model of the pore structure, activated carbon can be pictured as a bulk of crumbled segments of graphene layers with different degree of perfection. One can imagine cutting a graphene layer into many segments using an atomic scissor. These segments have different sizes and have different shapes and some of the segments are bent. When these segments randomly bond together and create three dimensional spaces, the empty spaces between the segments caused by imperfect packing are called pores (Marsh and Rodriguez-Reinoso 2006). It needs to be emphasised that in reality the segments do not exist in isolation. The segments form a body as a part of continuity (Marsh and Rodriguez-Reinoso 2006). Figure 32 represents this simplified structure of activated carbon. In reality, however, a particular structure of activated carbon depends on its precursor and the method of activation. That is the reason the activated carbons show a great variety of porosity and structure.
Acharya et al. (1999) used the chemically constrained model to create structure of activated carbon. More complicated atomistic simulation techniques like quench molecular dynamics method and hybrid reverse Monte Carlo method have also been used to model porous carbons (Palmer and Gubbins 2012). Recently, it has been suggested that porous carbon may have a fullerene-like structure (Harris 2013).

Porosity characteristics of a sample of activated carbon can be determined from adsorption isotherms of N\textsubscript{2} gas at 77 K (that is, at the boiling temperature of liquid nitrogen at atmospheric pressure) at relative pressure less than 0.1 (which fills micro and meso pores), and CO\textsubscript{2} gas at 273 K and relative pressure less than 0.03 (Vix-Gurtel et al. 2005). The relative pressure is the ratio of equilibrium pressure to saturation pressure of adsorbates at the temperature of adsorption.
4.2.1.2 Adsorption isotherm analysis method

The purpose of the adsorption isotherm is three fold: to measure the (1) adsorption capacity (mmol/g), (2) pore size distribution, and (3) accessible surface area of the sample.

In the adsorption process, CO₂ or N₂ gas (called the adsorptive) enters the pores of the activated carbon (the adsorbent) and gas molecules form chemical or physical bonds with the inner surfaces of the pores of the host material. The adsorbed gas (adsorbate) is retained in the pores because of the enhanced van der Waals forces between the adsorptive and adsorbent. It is important to highlight the importance and nature of the equilibrium condition of tests. An adsorbed molecule does not remain stationary in a pore; it moves in and out, at an average of more than a thousand times per second according to Marsh and Rodriguez-Reinoso (2006). The amplitude and frequency of this motion depends on the temperature. At equilibrium, the number of molecules entering the pores is equal to the number of molecules leaving the pores.

Gravimetric analysis is widely used to measure the amount of gas adsorption (Trexler et al. 2006). This method relies on precise monitoring of mass changes of the sample during the experiment, using, for example, a McBain balance (see schematic in Figure 33).

Figure 33: McBain balance for adsorption isotherm (adapted from Marsh and Rodriguez-Reinoso 2006)
In the McBain balance, the activated carbon sample is in a container connected to a silica spring. First the carbon sample needs to be degassed, by heating to a temperature of about 470 K and vacuumed close to 1.0 Pa. Next, the heater is replaced by a thermostat to maintain the temperature at 77 K or 273 K (depending on the adsorptive). The adsorptive gas is introduced into the system at a set pressure. The mass of the carbon sample increases as it adsorbs the gas. The difference between the new and initial position of the spring is correlated to the mass difference and hence is proportional to the amount of gas adsorbed at that relative pressure. More modern apparatus uses the volumetric method instead of the gravimetric method to measure the amount of gas adsorbed by continuously monitoring its pressure and volume (Busch and Gensterblum 2011). The volumetric method was proposed by Emmett and Brunauer in 1937 (Marsh and Rodriguez-Reinoso 2006).

The result of the adsorption isotherm test is a graph of the amounts of adsorbate in mmol/g of activated carbon versus relative pressure at the set temperature within the chamber, as shown in Figure 34. Point B represents the situation that a monolayer of adsorbate has formed on the sample (Marsh and Rodriguez-Reinoso 2006). The monolayer is the amount of adsorbate that is required to cover the surface with one layer of adsorbate (March and Rodriguez-Reinoso 2006).

![Figure 34: Typical adsorption isotherms for a porous sample (left adapted from Marsh and Rodriguez-Reinoso 2006 and right from the test results of AC2 activated carbon with N₂ adsorption isotherm)](image)
In the first section, PQB, the monolayer coverage takes place and point B is where it is assumed that the monolayer is complete. Point B is the point of inflection in the isotherm. Several empirical and mathematical models and equations have been developed to estimate the monolayer volume. Foo and Hameed (2010) have listed these models and equations. Here, the most common models, the Brunauer-Emmett-Teller (BET) equation and Dubinin-Radushkevich equation, are explained briefly.

The BET equation, proposed by Brunauer, Emmett and Teller in 1938 (Brunauer et al. 1938; Ladavos et al. 2012) and shown in Equation 32, is essentially an empirical curve-fitting equation (Marsh and Rodriguez-Reinoso 2006):

$$\frac{P}{V(P_0 - P)} = \frac{1}{v c} + \frac{(c - 1) P}{v c \ P_0} \quad \text{Eq. 32}$$

In this equation, $P_0$ is the saturation vapour pressure in Pa, $V$ is the amount of adsorbed gas at standard temperature and pressure (temperature = 273.15K and pressure = 101.3 kPa) in mol.g$^{-1}$, $P$ is the equilibrium vapour pressure in Pa, $v$ is the monolayer capacity at standard temperature and pressure (mol/g), and $c$ is a dimensionless constant representing the average adsorption energies. $v$ is the volume adsorbed in one complete unimolecular layer (Brunauer et al. 1938), also known as the limiting micropore volume (Jahandar Lashaki et al. 2012). In practice, a BET plot is generated by plotting $\frac{P}{V(P_0 - P)}$ against the relative pressure, $\frac{P}{P_0}$, as shown in Figure 35.
Values of $c$ and $v$ can be determined by using the values of the slope ($A$) and the intercept ($I$) from Equation 33 and 34. The calculated $v$ from Equation 33 is used to calculate surface area that is explained later in this section.

$$v = \frac{1}{A + I} \quad \text{Eq. 33}$$

$$c = 1 + \frac{A}{I} \quad \text{Eq. 34}$$

The Dubinin-Radushkevich (DR) equation is not a curve-fitting formula like the BET equation. By contrast, the DR equation is mathematically derived with its roots in the structure of porosity. It is thus more relevant to adsorption processes in pores than the BET equation. DR equation deals with the first segment of the profile in Figure 34 that is the low relative pressure (Marsh and Rodriguez-Reinoso 2006). The basic form of the DR equation is (Nguyen & Do 2001):

$$V = v \exp\left(-\frac{RT \ln \frac{P_0}{P}}{\beta E}\right)^2, \quad \text{Eq. 35}$$
where $R$ is the universal gas constant (8.314 J/mol K), $T$ is the temperature (K), $\beta$ is the affinity coefficient, and $E$ is the adsorption energy (J/mol) (Stoeckli et al. 2001; Nguyen and Do 2001). When the DR equation does not produce a linear plot, the more general Dubinin–Astakhov (DA) equation is used (Rand 1976; Marsh and Rodriguez-Reinoso 2006) with the exponent $n$ as an empirically-determined parameter:

$$V = \nu \exp\left[-\left(\frac{RT\ln P_0}{\beta E}\right)^n\right].$$  \hspace{1cm} \text{Eq. 36}

The value of $n$ employed is usually between 1 and 5 (Marsh and Rodriguez-Reinoso 2006). The value of $\nu$ is calculated from plotting $[\ln(P/P_0)]^n$ against $\ln V$. The slope of the straight line will be $-\left(\frac{RT}{\beta E}\right)^n$ and the intercept with vertical axis will be $\ln \nu$, as can be seen in Figure 36. In this figure, the point on nitrogen profiles shows the point that nitrogen adsorption deviates from monolayer surface covering to pore filling mechanism.

**Figure 36:** Comparison of CO$_2$ and N$_2$ adsorption isotherm data in DR plot (Marsh and Siemieniewska, 1967 cited in Marsh & Rodriguez-Reinoso 2006, p. 168)

In Figure 36, $\log n^a$ is similar to $\log V$ and shows the amount adsorbed gas in mmolg$^{-1}$ (Marsh & Rodriguez-Reinoso 2006).
When \( \nu \) is calculated from any of the above equations, the surface area of the sample can be calculated using:

\[
A = \frac{\nu \times \rho}{M} N a_m
\]

Eq. 37

where \( \rho \) and \( M \) are the density and molecular weight of the adsorbate respectively. The state of adsorbed nitrogen gas is suggested to be liquid and hence the density of 0.808 g/cm\(^3\) is used for calculations (Marsh and Rodriguez-Reinoso 2006). The quadrupole of nitrogen molecules interacts with carbon surface and this establishes the structure of nitrogen monolayer (Marsh and Rodriguez-Reinoso 2006). For CO\(_2\) a density of 1.023 g/cm\(^3\) is used (Bleda-Martinez 2008). \( N \) is the Avogadro constant, \( 6.022 \times 10^{23} \). \( a_m \) is the adsorbate cross-sectional molecular area. The value of \( a_m \) for N\(_2\) at 77 K is 0.163 nm\(^2\)/molecule and for CO\(_2\) at 273 K is 0.182 nm\(^2\)/molecule (Grillet et al. 1988). These values are the most common values used in the literature. Other values have also been used, e.g. 0.84 g/cm\(^3\) and 0.131 nm\(^2\)/molecule for nitrogen at 77 K (Ribeiro Carrott et al. 2001). The default values in the Micromeritics® ASAP 2000 for N\(_2\) isotherm adsorption and Micromeritics® ASAP 2010 for CO\(_2\) isotherm adsorption are used. These values are 0.17 nm\(^2\)/molecule for CO\(_2\) and 0.162 nm\(^2\)/molecule for N\(_2\).

The specific surface area is calculated using:

\[
A_s = \frac{A}{M_{sample}}
\]

Eq. 38

where, \( M_{sample} \) is the mass of the activated sample.

### 4.2.1.3 CO\(_2\) and N\(_2\) adsorption isotherms

Porosity analysis is commonly carried out using both N\(_2\) at 77 K and CO\(_2\) at 273 K (Lozano Castello et al. 2004). The reason for selecting the adsorptive gases is nothing other than their convenience (Marsh and Rodriguez-Reinoso 2006). Both CO\(_2\) and N\(_2\) molecules have almost the same critical size, 0.33 and 0.36 nm respectively (Beguin et al. 2006).
Adsorption of CO$_2$ and N$_2$ takes place by different processes. The two processes can be explained by using Figure 36. At lower relative pressures (right side of the plot, since $\log^2(P/P_0)$ increases as $P$ decreases, given that $P<P_0$) CO$_2$ is adsorbed to a larger extent than N$_2$. This is because of the higher quadrupole moment and higher kinetic energy of carbon dioxide molecules at 273 K. At higher relative pressures (left side of plot), a sudden increase in the amount of nitrogen adsorption is observed (see N$_2$ adsorption). This is nitrogen filling the mesopores. It seems that the quadrupole moment of the CO$_2$ molecules prevents them from filling the mesopore volumes even at higher relative pressure (Marsh and Rodriguez-Reinoso 2006).

But the tests with these two adsorptive gases may show different results. Like in any reactions, adsorption of N$_2$ or/and CO$_2$ requires a small but finite activation energy. For N$_2$ at 77 K, the rate of adsorption in narrow micropores becomes so slow that it becomes impossible to be detected within span of a day (Marsh and Rodriguez-Reinoso 2006). CO$_2$ is used at 273 K and the higher kinetic energy at this temperature results in a better diffusion of CO$_2$ within narrow micropores (Vix-Guterl et al. 2005). Based on the results of N$_2$ and CO$_2$ adsorption isotherms, the following points can be concluded (Garido et al. 1987; Marsh and Rodriguez-Reinoso 2006):

- CO$_2$ adsorption > N$_2$ adsorption: indicates high ultra-microporosity but low microporosity and mesoporosity
- CO$_2$ adsorption ~ N$_2$ adsorption: indicates a relatively homogeneous distribution of ultra-microporosity, microporosity and mesoporosity
- CO$_2$ adsorption < adsorption N$_2$: indicates mostly microporosity and mesoporosity.

In conclusion, the N$_2$ adsorption isotherm can be used to assess the microporosity and the CO$_2$ adsorption isotherm can be used to assess ultra-microporosity (Garido et al. 1987; Lozano Castello et al. 2004). In other words, the CO$_2$ adsorption isotherm provides information about ultra-microporosity that the N$_2$ adsorption isotherm is unable to provide, and vice versa. In applications like hydrogen storage in activated carbon where presence of ultra-micro-pores seems essential, the CO$_2$ adsorption isotherm at 273 K should be an additional measurement over and above N$_2$ adsorption at 77 K (Lozano-Castello et al. 2004; Vix-Guterl et al. 2005).
4.2.1.4 Summary of porosity tests on the activated carbons

The measurement of N₂ adsorption isotherms in the present project was conducted by using a Micromeritics® ASAP 2000 and the CO₂ adsorption isotherm was done by using a Micromeritics® ASAP 2010. Both apparatuses measure surface area by the static volumetric method. The porosity characterisation tests were done by Frank Antolasic, the Senior Technical Officer at the RMIT School of Applied Sciences. Tests were done at 77 K for N₂ and 273 K for CO₂. The results for the samples from Monash University were provided by PhD candidate Lachlan Ciddor (Lachlan Ciddor, PhD candidate, Monash University, 2012, personal communications).

The summary of the pore surface area and volume characteristics of the samples are presented in Table 6.
<table>
<thead>
<tr>
<th>Name of the samples</th>
<th>Limiting Micropore Volume from CO₂ adsorption isotherm [cm³/g]</th>
<th>Surface area according to limiting volume micropore volume [m²/g]</th>
<th>Surface area from CO₂ isotherm adsorption [m²/g]</th>
<th>BET surface area from N₂ isotherm adsorption [m²/g]</th>
<th>Adsorption average pore diameter N₂ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal powder</td>
<td>0.131</td>
<td>334</td>
<td>283&lt;sup&gt;a&lt;/sup&gt;</td>
<td>208.9</td>
<td>2.16</td>
</tr>
<tr>
<td>Coal powder</td>
<td>No result available</td>
<td>No result available</td>
<td>No result available</td>
<td>7.4</td>
<td>11.3</td>
</tr>
<tr>
<td>ACN</td>
<td>0.276</td>
<td>703</td>
<td>794.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>673.9</td>
<td>-</td>
</tr>
<tr>
<td>ACS</td>
<td>0.232</td>
<td>591</td>
<td>870.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>381.0</td>
<td>-</td>
</tr>
<tr>
<td>ACK2.5</td>
<td>0.197</td>
<td>502</td>
<td>463.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>No result</td>
<td>-</td>
</tr>
<tr>
<td>ACK7.5</td>
<td>0.204</td>
<td>520</td>
<td>589.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>No result</td>
<td>-</td>
</tr>
<tr>
<td>ACK10</td>
<td>0.229</td>
<td>584</td>
<td>602.9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>No result</td>
<td>-</td>
</tr>
<tr>
<td>AC1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>51</td>
<td>3.38</td>
</tr>
<tr>
<td>AC2</td>
<td>0.349</td>
<td>889</td>
<td>824&lt;sup&gt;b&lt;/sup&gt;</td>
<td>685</td>
<td>2.01</td>
</tr>
<tr>
<td>AC3</td>
<td>0.123</td>
<td>313</td>
<td>335&lt;sup&gt;b&lt;/sup&gt;</td>
<td>285</td>
<td>1.82</td>
</tr>
<tr>
<td>AC4</td>
<td>0.049</td>
<td>124</td>
<td>126&lt;sup&gt;b&lt;/sup&gt;</td>
<td>103</td>
<td>2.91</td>
</tr>
</tbody>
</table>

**Table 6**: Porosity of the activated carbon samples (DR equation (a), DA equation (b))

Although the same coal powder sample was used in both the N₂ and CO₂ isotherm adsorption test, the sample could not be degassed in the CO₂ test. It could have been because of a leak in the apparatus or the composition of the coal sample. Further investigation was terminated to prevent damaging the apparatus.
4.2.2 Selecting samples for fabricating composite material

4.2.2.1 Influential factors in selecting samples

A good candidate for the application of this research project should have both ultramicroporosity and mesoporosity. The literature reveals that pores smaller than 0.7 nm are the most suitable sites for hydrogen storage (Vix-Guterl et al. 2005; Beguin et al. 2006; Babel and Jurewicz 2008; Bleda-Martinez et al. 2008). The CO$_2$ adsorption isotherm at 273 K is a good indicator of such ultramicroporosity (Bleda-Martinez et al. 2008).

Activated carbon is used with nafion to make a composite electrode in this project. Protons, that is, hydrogen ions, move through the nafion in the form of H$_3$O$^+$ ions. Ideally macro pores are needed to let the nafion medium penetrate into the activated carbon, and then mesopores to allow hydronium ions probably within bulk water to diffuse into the and ultra-micro-pores. In other words, macro and mesoporosity are expected to be essential to allow the transport of hydronium ions into the activated carbon, and ultra-microporosity is needed to store the hydronium ions.

This critical issue of the pore size distribution that is best suited for electrochemical hydrogen storage will be returned to later in the thesis. Other factors such as type of precursor and the structure of the carbon in the precursor may also be of importance, but were beyond the scope of this project and have therefore not been investigated.

4.2.2.2 Selecting samples for fabrication of composite electrodes

Six activated carbon samples from the total nine samples of activated carbons, characterised in Table 6, were selected for fabrication of a composite activate carbon–nafion electrode for testing. ACN was selected since it has high adsorption values for both CO$_2$ and N$_2$ indicating that it has both a substantial ultramicropore and micropore surface areas. ACS was also selected since it had the highest ultramicropore volume (CO$_2$ adsorption) among the samples. ACK10 was also selected since it also had a high ultramicropore volume. ACK2.5 was selected since it had average ultra-microporosity
(obtained from CO₂ adsorption isotherm) and very low microporosity (obtained from N₂ adsorption isotherm). AC3 was selected since it had both an average level of microporosity and ultra-microporosity. AC4 was selected since it had very high mesoporosity based on the value of N₂ adsorption isotherm that could help nafion penetrate within the particles of activated carbon. The values for CO₂ and N₂ adsorption of both AC2 and ACN are high and close to each other. The ACN was selected because it was a commercially-available sample.

The values of ultra-micro-porosity of the activated carbons that have been used in fabrication of the composite electrodes in this thesis were 794 m²/g for ACN and 870 m²/g for ACS. These values were obtained from CO₂ adsorption isotherm at 273 K that has been used to identify ultra-microporosity (Jurewicz et al. 2004). To put these values in perspective, Babel and Jurewicz (2008) used an activated carbon sample with a surface area of 2064 m²/g and found that it is capable to electrochemically store 1.89 wt% of hydrogen in a KOH electrolyte. Jurewicz et al. (2004) used an activated carbon with 765 m²/g and found 1.3 wt% hydrogen storage again in KOH electrolyte.

### 4.3 FABRICATION OF COMPOSITE MATERIALS

#### 4.3.1 Ingredients for composite materials

##### 4.3.1.1 Nafion solution

Nafion was first discovered in DuPont by Dr Walter Grot in late 1960s (Grot 1994, cited in Heitner-Wirguin 1996).

The nafion solution (perfluorosulfonic acid-PTFE copolymer, 5% w/w solution) was obtained from Alfa Aesar for use in making the composite electrodes with the activated carbon samples. The nafion solution ingredients are listed in Table 7 (Alfa Aesar, 2013).
### Table 7: Composition of the nafion solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Content (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-propanol</td>
<td>45</td>
</tr>
<tr>
<td>nafion</td>
<td>5</td>
</tr>
<tr>
<td>ethanol</td>
<td>5</td>
</tr>
<tr>
<td>water</td>
<td>45</td>
</tr>
</tbody>
</table>

Nafion polymer is a perfluorosulfonated random copolymer with hydrophobic tetrafluoroethylene backbone and perfluoroalkyl ether side chains terminated by hydrophilic sulfonic acid groups (Zhao et al. 2011; Duan et al. 2012). The chemical structure of nafion is presented in Figure 37. The water and proton transport happens alongside the hydrophilic domains (Figure 37 right) (Fontananova et al. 2012).

![Structure of Nafion](image)

**Figure 37:** Structure of nafion. The chemical formula is on the left (Spiegel 2008), and semi-structural formula is on the right (Wu et al. 2011)

In reporting properties of nafion, the average equivalent weight per sulfonic group is a defining factor. The most common equivalent weight is 1100 g mol\(^{-1}\) SO\(_3\)H (Li et al. 2006), correspond to \(m\) equal to 6, \(n\) equal to 1, and \(z\) equal to 1 in figure 37 (Paul et al. 2006).
In this structure, the side-chain length (between CF and CF₂) is in the order of 0.8 nm, the backbone space (between CF₂ and CF₂) is in the order of 0.6-1.2 nm, and the length of a single extended molecule (Figure 37 left) is in order of 100 nm (Paul et al. 2013).

4.3.1.2 Activated carbons

Six samples of activated carbon were therefore selected to be mixed with nafion solution and fabricate composite aC-nafion electrodes for testing. The samples were selected to possess a range of porosity: high ultra-microporosity (ACN, ACS and ACK10), and medium ultra-miroporosity (ACK2.5), miroporosity (AC3), and mesoporosity (AC4). Activated carbons have not been functionalised as was done in some other studies (for example, Gharibi et al. 2011; Chien et al. 2012). One reason for not functionalising was that Bleda Martinez et al. (2008) found that presence of surface oxygen groups actually reduces the hydrogen storage capacity.

4.3.2 Mixing nafion and selected activated carbon samples

To obtain the composite material, a solution casting method was selected. This method has been widely used in making membranes from nafion (Li et al. 2006, Molla and Compan 2011). Nafion and activated carbon were mixed in a beaker at room temperature Figure 38. The mixture was stirred every 5-10 minutes until most of the solvent had evaporated and a uniformly dispersed ink remained in the beaker.
A good candidate for the present research application must have both high electron and proton conductivity. If the mixture was only nafion (0 wt% of aC) the product would be a pure membrane with high proton conductivity and no electron conductivity. At the other end of the spectrum, if the mixture had no nafion (100 wt% of aC), the product would be an electrode with high electron conductivity and no proton conductivity. There must be an optimum range within which both electron and proton conductivity are high enough for this application. A composite of 20 wt% of aC in the aC-nafion composite created a material with predominantly membrane behaviour (Chien et al. 2012). Accordingly, as a starting point 50 wt% was used as the activated carbon content of the composite materials and electrodes.

It will be important in future work of this topic to test a number of aC-nafion composites with a range of different carbon contents to find the optimal balance between proton conductivity and electron conductivity for the proton flow battery application.
4.3.3 Fabrication of the composite materials

4.3.3.1 Solution casting of the composite materials

The homogenous aC-nafion ink was poured and levelled in a mould by using a spatula as shown in Figure 39.

![Figure 39: Casting the composite materials in the mould. The mould is 70 mm by 70 mm and the size of the casting composite materials is 25 mm by 25 mm](image)

The mould was closed and loaded in an oven at 80°C overnight and post annealed at 120°C for 2 hours. A similar technique was proposed by Chien et al. (2012 and 2013). The composite materials were left in the oven to evaporate all the solvent from them. The post annealing step is for allowing reorientation of the polymer to disaggregate ionic clusters to form a glass-like structure (Zawodzinski et al. 1993). The glass transition temperature of nafion 117 membrane is about 110°C (Satterfield 2007; Yadav and Fedkiw 2012). The addition of another material to a polymer membrane generally increases its glass transition temperature (Satterfield et al. 2006), so that addition of activated carbon can be expected to
increase the glass transition temperature of nafion. Seif Mohammadi’s (2013) initial test of post annealing a metal hydride-nafion composite electrode at a temperature above 140°C led to changing the colour of nafion in the composite that can be possibly due to chemical alteration of the polymer. Hence the post-annealing temperature of 120°C was selected, as a middle temperature between the glass transition temperature of nafion (110°C) and the high temperature of 140°C. Finding the exact glass transition temperature of each composite was beyond the scope of this project.

4.3.3.2 Size and number of the composite samples

The proton conductivity of each sample is calculated from the measured resistance in electrochemical impedance spectroscopy (EIS). The resistance have a linear and inverse relationship with surface area of the sample, the larger the sample, the lower the resistance. For example by increasing the sample size from 1 to 5 mm in diameter, the ionic resistance drops from 100 to 1 ohm which is more difficult to measure (Yadav and Fedkiw 2012). To be able to clearly measure the resistance in EIS, sample needs to have a small size. The same consideration applies to measuring electron conductivity of the composite materials. To measure electric conductivity, the electric resistance of the sample is measured by a multimeter and then the conductivity is computed from the electric resistance. By increasing the size of the samples, the electric conductivity decreases and it is more difficult to measure the resistance accurately and with less error.

For each of the five composite materials made using the activated carbon materials, ACN, ACS, ACK10, AC3, and AC4, five samples for EIS tests were prepared. For composite materials made from ACK2.5, only three EIS samples were able to be prepared and the other two samples of ACK2.5 got broken during handling and protonation process because of their fragility. In total twenty eight prepared from the eight composite materials EIS samples were tested to measure the physical and electrochemical properties of the composites. The conditions under which each material were tested using EIS are described later (in section 4.6).
4.3.4 Protonation of composite materials

A common necessary step in preparing nafion membranes with high proton conductivity is to subject the membrane to a process called protonation (Zhao et al. 2013). This step is to ensure that all cations attracted to the $SO_3^-$ groups during preparation are completely exchanged with protons (Ufrano et al. 2004). This protonation step is widely used in preparing nafion membranes for fuel cells and other applications (Satterfield et al. 2006; Alvarez et al. 2012; Ghasemi et al., 2012) and composite nafion membranes (Chien et al. 2012; Chien et al. 2013; Ballengee and Pintauro 2013).

All the composite samples for EIS measurements were therefore protonated in sulphuric acid at 90°C for 30 minutes. The samples were then washed under a stream of distilled water until pH indicator paper displayed no change in pH with further washing. The treated samples were placed in distilled water at almost boiling temperature for 30 minutes to remove excess acid from the samples and placed in an oven at 80°C overnight. The mass and dimensions of the each sample when dry were measured by a digital balance with accuracy of 0.1 mg and a digital vernier calliper.

4.3.5 Investigation of proper dispersion of activated carbon in nafion

A uniform dispersion of nafion polymer between the activated carbon particles is desirable for this application. The proper dispersion of activated carbon ensures that the nafion has access to all carbon particles and the carbon particles are not clustered together in particular regions.

Minimising hollow spaces within the composite is desirable. Such hollows increase the volume of the composite electrode without contributing to hydrogen storage, and hence decrease the overall volumetric hydrogen capacity. Also it is highly likely that hollow spaces may encourage hydrogen gas formation and collection within these spaces, providing an escape route for this gas to outside the storage electrode. To investigate the uniformity of the distribution of the activated carbon particles dispersion within the nafion medium, and potential hollows within the composite material, scanning electron
microscope images of the facial surfaces and cross-section of each sample material were taken. The surface images of the EIS samples were all similar to each other. SEM images of the surfaces of the materials made from ACK10 and ACK2.5 are shown as examples in Figure 40.

![Figure 40: Surface of the EIS samples (left ACK10 and right ACK2.5)](image)

The Figure 40 shows that nafion polymer has covered the surface of the composite material. This may lead to a smooth proton transfer from nafion membrane to composite electrodes in the membrane-electrode-assembly of the composite electrodes.

The cross-sectional images of the composite materials have been obtained by scanning electron microscopy. The cross-section images of the samples provide two points. Firstly, nafion is seems to be uniformly dispersed in activated carbon as presented in Figure 41. The edges of activated carbon particles seem very smooth compared to the rough edges of carbon precursors in Figure 23. Moreover, the macro-scale structure seems to be similar in the entire composites. In other words, there is no observable clustering of carbon particles within the nafion medium. The cross-sectional SEM images also show that the carbon and nafion has not been separated, \textit{i.e.} carbon on top and nafion at the bottom of the mould,
during the solution casting. These points are more apparent in the higher magnifications in Figure 42.

**Figure 41:** Low magnified images of cross section of the composite materials (top: ACK2.5, bottom: ACK10)
Secondly the cross sectional SEM images do suggest that there are many hollow spaces within the composite materials. As can be seen from the top image in Figure 42, the hollow volumes are distributed in the entire composite material. However, the structure of the bottom image suggests that the nafion polymer is connecting the carbon particles. Presumably the hollow volumes were created during the solution casting of activated carbon and nafion. It might be due to the presence of solvents in the nafion solution.

For comparison the SEM images of AC4 are shown in Figure 43 at different magnifications. Again the widespread presence of voids within the structure of the composite materials can be clearly observed.
Figure 42: Higher magnified images of cross section of the composite material of AC3
Figure 43: The cross sectional of AC4 at different magnifications
4.4 SETTING UP DIFFERENT RELATIVE HUMIDITY ENVIRONMENTS

4.4.1 Design and manufacturing of a relative humidity chamber

An apparatus was designed and manufactured to obtain different values of relative humidity by using saturated salt solutions. In designing the set-up, the guidelines of American society for testing and materials (ASTM) E104-02 were used (ATSM 2012). This standard is applicable for temperatures from 0 to 50°C and relative humidity ranges from 2% to 98.5%. It has been used in food science (Beyer et al. 2005) and in electrochemical science (Yadav and Fedkiw 2012).

The principle behind this standard is that, at a constant temperature, a particular saturated salt solution generates a corresponding value of relative humidity, as illustrated for some examples in Table 8. A more detailed table is available in the ATSM (2012) standard.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Caesium fluoride</th>
<th>Potassium acetate</th>
<th>Sodium bromide</th>
<th>Sodium chloride</th>
<th>Potassium sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>3.8 ± 1.1</td>
<td>23.1 ± 0.3</td>
<td>59.1 ± 0.5</td>
<td>75.5 ± 0.2</td>
<td>97.6 ± 0.6</td>
</tr>
<tr>
<td>25°C</td>
<td>3.4 ± 1.1</td>
<td>22.5 ± 0.4</td>
<td>57.6 ± 0.4</td>
<td>75.3 ± 0.2</td>
<td>97.3 ± 0.5</td>
</tr>
<tr>
<td>30°C</td>
<td>3.0 ± 0.8</td>
<td>21.6 ± 0.6</td>
<td>56.0 ± 0.4</td>
<td>75.1 ± 0.2</td>
<td>97.0 ± 0.4</td>
</tr>
</tbody>
</table>

Table 8: Equilibrium relative humidities for selected saturated salt solutions at 20, 25, and 30°C (ATSM 2012)

After selecting the working temperature, the appropriate salt that generates the desired relative humidity is placed in a salt tray. Water is then added in about 2 ml increments and stirred until saturation. When the salt cannot absorb any more water, samples can be placed on a perforated tray which separates the samples from the salt solution. Finally, the container is sealed to allow the air inside the chamber to reach equilibrium. One hour should be allowed for temperature stabilization. Temperature instability of ± 0.1°C can cause instability of 0.5% of the value of relative humidity.

The apparatus includes an airtight container, a salt tray, a perforated tray to place the samples on, a hygrometer, a thermocouple, and a vent to prevent changes in pressure (see
Figure 44). It is recommended that the salt tray should have a depth of 4 cm for low relative humidity salts or 1.5 cm for high relative humidity salts. The maximum ratio of the headspace volume to the solution surface area is recommended to be below 25 cm³ volume/cm² (ATSM 2012).

Figure 44: The variable relative humidity chamber used to vary the level of hydration of the sample composite materials.

A 19 × 13 × 13 cm³ plastic container was selected with an airtight lid. A salt tray from aluminium with dimensions of 13 × 13 cm² was made to contain salts. The container volume to the surface area of the salt tray was 19 cm³/cm². To avoid any reaction between aluminium and salts, the tray was covered with a plastic sheet. The perforated tray was fabricated from a hollow plastic bottle with diameter of 7 cm. Perforation was done to expose the samples from all sides and facilitate a uniform condition in the chamber. A plastic tube was attached to the container, which can be open should there be any pressure change in the chamber. A digital hygrometer/thermocouple was purchased with the specifications stated in Table 9.
<table>
<thead>
<tr>
<th>Measuring humidity range</th>
<th>Humidity accuracy</th>
<th>Humidity display resolution</th>
<th>Measuring temperature range</th>
<th>Temperature accuracy</th>
<th>Temperature display resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ~ 90%</td>
<td>± 5%</td>
<td>1%</td>
<td>-50 ~ 70 °C</td>
<td>±1 °C</td>
<td>0.1 °C</td>
</tr>
</tbody>
</table>

**Table 9:** Specification of the hygrometer of the humidity chamber

The digital hygrometer-thermometer was tested by a manual hygrometer (G.H. Zeal LTD England). The hygrometer showed the room that the electrochemical experiments are conducted to be at to be 18.8°C and 44% relative humidity. The digital hygrometer-thermometer showed the room at 18°C and 40% relative humidity, which are within the error ranges of the device.

### 4.4.2 Test points in environments at various relative humidities

The various relative humidities (RH) used in this present research project were 0%, 40%, 75%, and 100%; in addition, tests were done on samples soaked in water. For 0% RH, the samples were placed in an oven at 80°C for 18 hours, then in a desiccator jar and kept at room temperature. The 40% RH was the room relative humidity and the samples were kept in an open jar in an air-conditioned room at constant temperature and constant relative humidity. For 75% RH, the RH chamber described in the previous subsections was used. The salt tray was filled to a depth of 3 cm with thick sodium chloride salt solution. For the 100% RH, the samples were placed in an open jar which was placed in an open jar with water in it. MiliQ water was used for keeping composite materials in wet conditions.

### 4.5 PHYSICAL BEHAVIOUR OF THE COMPOSITE MATERIALS IN DIFFERENT RELATIVE HUMIDITY ENVIRONMENTS

#### 4.5.1 Measurements of the composites in different relative humidity environments

The samples were kept at room temperature and at their respective RH for at least 42 hours. After removing the samples from their containers, they were quickly weighed and their dimensions measured using a similar digital balance and digital vernier calliper to those used in section 4.3.4. The results obtained are presented in Table 10.
<table>
<thead>
<tr>
<th>Relative humidity</th>
<th>Dry</th>
<th>Mass (mg)</th>
<th>Thickness (mm)</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>In the respective RH environment</th>
<th>Mass (mg)</th>
<th>Thickness (mm)</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ACN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>10.1</td>
<td>1.01</td>
<td>3.41</td>
<td>4.35</td>
<td>10.1</td>
<td>1.01</td>
<td>3.41</td>
<td>4.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>26.0</td>
<td>1.14</td>
<td>7.70</td>
<td>4.39</td>
<td>28.9</td>
<td>1.20</td>
<td>8.13</td>
<td>4.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td>5.4</td>
<td>1.14</td>
<td>2.09</td>
<td>3.37</td>
<td>6.9</td>
<td>1.25</td>
<td>2.20</td>
<td>3.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100%</td>
<td>9.0</td>
<td>1.14</td>
<td>3.38</td>
<td>3.50</td>
<td>12.5</td>
<td>1.31</td>
<td>3.80</td>
<td>3.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full hydration</td>
<td>14.7</td>
<td>1.14</td>
<td>4.04</td>
<td>4.74</td>
<td>27.1</td>
<td>1.55</td>
<td>4.25</td>
<td>5.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ACS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>3.2</td>
<td>1.01</td>
<td>2.27</td>
<td>2.60</td>
<td>3.2</td>
<td>1.01</td>
<td>2.27</td>
<td>2.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>3.3</td>
<td>0.99</td>
<td>2.70</td>
<td>1.95</td>
<td>3.6</td>
<td>1.01</td>
<td>2.75</td>
<td>1.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td>3.6</td>
<td>0.91</td>
<td>2.42</td>
<td>2.55</td>
<td>4.1</td>
<td>0.97</td>
<td>2.47</td>
<td>2.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100%</td>
<td>4.1</td>
<td>0.79</td>
<td>2.49</td>
<td>3.98</td>
<td>4.9</td>
<td>0.83</td>
<td>2.56</td>
<td>4.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full hydration</td>
<td>3.4</td>
<td>0.90</td>
<td>1.74</td>
<td>3.62</td>
<td>5.5</td>
<td>0.96</td>
<td>1.86</td>
<td>3.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ACK2.5</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td>5.3</td>
<td>1.09</td>
<td>2.40</td>
<td>2.20</td>
<td>6.1</td>
<td>1.14</td>
<td>2.41</td>
<td>2.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100%</td>
<td>3.2</td>
<td>1.09</td>
<td>1.92</td>
<td>1.93</td>
<td>4.1</td>
<td>1.12</td>
<td>2.07</td>
<td>2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full hydration</td>
<td>4.3</td>
<td>1.09</td>
<td>2.07</td>
<td>2.37</td>
<td>7.2</td>
<td>1.20</td>
<td>2.30</td>
<td>2.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ACK10</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>11.2</td>
<td>1.36</td>
<td>5.12</td>
<td>1.19</td>
<td>11.2</td>
<td>1.36</td>
<td>5.12</td>
<td>1.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>24.8</td>
<td>1.42</td>
<td>4.16</td>
<td>5.16</td>
<td>26.1</td>
<td>1.46</td>
<td>4.20</td>
<td>5.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td>12.4</td>
<td>1.40</td>
<td>2.19</td>
<td>5.75</td>
<td>13.1</td>
<td>1.44</td>
<td>2.39</td>
<td>5.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100%</td>
<td>19.9</td>
<td>1.38</td>
<td>4.25</td>
<td>4.10</td>
<td>27.2</td>
<td>1.42</td>
<td>4.75</td>
<td>4.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full hydration</td>
<td>21.8</td>
<td>1.48</td>
<td>4.10</td>
<td>4.75</td>
<td>31.6</td>
<td>1.50</td>
<td>4.45</td>
<td>5.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>AC3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>5.7</td>
<td>1.12</td>
<td>2.23</td>
<td>3.02</td>
<td>5.7</td>
<td>1.12</td>
<td>2.23</td>
<td>3.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>6.8</td>
<td>1.11</td>
<td>4.24</td>
<td>2.26</td>
<td>7.3</td>
<td>1.11</td>
<td>4.38</td>
<td>2.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td>3.6</td>
<td>1.09</td>
<td>2.12</td>
<td>2.40</td>
<td>4.0</td>
<td>1.10</td>
<td>2.15</td>
<td>2.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100%</td>
<td>4.8</td>
<td>1.12</td>
<td>2.28</td>
<td>2.85</td>
<td>5.6</td>
<td>1.14</td>
<td>2.35</td>
<td>3.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full hydration</td>
<td>4.9</td>
<td>1.08</td>
<td>2.12</td>
<td>2.74</td>
<td>7.7</td>
<td>1.14</td>
<td>2.33</td>
<td>3.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>AC4</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>7.8</td>
<td>1.15</td>
<td>3.30</td>
<td>3.10</td>
<td>7.8</td>
<td>1.15</td>
<td>3.30</td>
<td>3.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>5.4</td>
<td>1.12</td>
<td>2.88</td>
<td>3.02</td>
<td>5.7</td>
<td>1.12</td>
<td>2.94</td>
<td>3.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td>4.1</td>
<td>0.92</td>
<td>2.98</td>
<td>2.20</td>
<td>4.4</td>
<td>0.94</td>
<td>3.02</td>
<td>2.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100%</td>
<td>9.6</td>
<td>1.14</td>
<td>4.78</td>
<td>2.71</td>
<td>10.9</td>
<td>1.20</td>
<td>4.96</td>
<td>2.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full hydration</td>
<td>5.2</td>
<td>1.03</td>
<td>2.62</td>
<td>2.73</td>
<td>7.8</td>
<td>1.05</td>
<td>2.85</td>
<td>3.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10: Measurements of the samples before and after RH
Samples ACK2.5-a and ACK2.5-b were broken during the measurement process because of their fragility, so no results for these are presented in this table.

### 4.5.2 Water uptake of the composite materials

Nafion works as a good proton conductor only when it is fully hydrated, since other words water molecules within the nafion structure play a critical role in proton transfer (Choi et al. 2005). At low water content, water molecules mainly cluster near to the hydrophilic $\text{SO}_3^-$ groups, and is therefore called ‘surface water’. At high water content, water molecules also fill the central regions of the pores, and this is called bulk water (Beattie et al. 2001; Choi et al. 2005). Proton mobility is much higher in bulk water than in surface water, because of the strong electrostatic attraction of $\text{SO}_3^-$ groups near the latter, and in bulk water proton conduction is predominantly via the Grotthuss mechanism in which $\text{H}^+$ ions are successively exchanged between a hydronium ion ($\text{H}_3\text{O}^+$) and a neighbouring water molecule (Choi et al. 2005). Water path in nafion is between the hydrophilic sulphuric groups, as shown in Figure 45. This figure shows all three main proton transfer mechanism, namely surface hopping, Grotthuss diffusion, and *en masse* which is the ordinary mass diffusion of hydronium ions. The surface hopping occurs close to the walls (0.8 nm) or at low water contents of nafion. The Grotthuss mechanism occurs because proton jumps from one water molecule to the next water molecule. The *en masse* is the normal mass diffusion of hydronium in water.
To calculate the water uptake, the samples were weighed after being in their respected relative humidity environment at room temperature for at least 42 hours. Initial tests show that no mass increase occurred for durations longer than 42 hours. The time needed to reach equilibrium was found to be anywhere between 10 minutes to 24 hours depending on the temperature and RH (Zhao et al. 2011). Many tests that have been done at room temperature allowed the samples to rest in water for 24 hours (Chien et al. 2013; Anis et al. 2011; Satterfield et al. 2006). Yadav and Fedwik (2012) suggest a 24-hour-rest for water and 48-hour-rest for water vapour.

To calculate the water uptake by mass percentage, the following equation was used (Anis et al. 2011; Chien et al. 2013):

\[
\text{Water uptake (\%) = \frac{M_{\text{RH}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100}
\]

Eq. 39
where $M_{RH}$ and $M_{dry}$ are respectively the mass of the composite material under variable humidity conditions, and the mass of the dry composite material. The results obtained for water uptake are presented in Figure 46.

![Graph](image)

**Figure 46:** Water uptake of the aC-nafion composite materials in various relative humidity environments.

In the fully hydrated condition, excess water attached to the surface of the composite was removed by filter papers. The weight of the composite material was measured by a digital balance (precision ±0.1mg).

It should be pointed out that in this study the so-called “Schroeder’s paradox” was observed. Schroeder observed that a solid polymer, gelatine, had higher water uptake in liquid phase than in vapour phase at 100% RH at the same temperature (Schroeder 1903 cited in Vallieres et al. 2006). This phenomenon has been observed by many authors (Yadav and Fedkiw 2012, Bass and Freger 2008; Majsztrik et al. 2007). In thermodynamics, the chemical potentials of saturated water vapour and liquid water at the same temperature is equal. In other words, water uptake of solid polymer in liquid water should be the same as the water uptake in water vapour at 100% RH (Onishi et al. 2007). But the higher water uptake in water than saturated vapour is observed (for instance Yadav
and Fedkiw 2012). Common sense dictates that higher water uptake in water is logical since the concentration of water molecules in liquid water is over 10,000 times higher than the saturated vapour (Davankov and Pastukhov 2011). But in the framework of phase equilibrium thermodynamics dictates that the solvent uptake by cross-linked polymers like nafion is only linked to the chemical potential of the solvent in the fluid phase, irrespective of the state of the fluid phase (Davankov and Pastukhov 2011).

Water uptake can also be expressed as the number of water molecules per SO$_3^-$ site ($\lambda$), and can be calculated from the equation (Maldonado et al. 2012, Abuin et al. 2013):

$$\lambda = \frac{EW}{M_{H_2O}} \times \frac{M_{RH} - M_{dry}}{M_{dry,Nafion}}$$

where $EW$ is the equivalent weight of nafion, 1100 g/SO$_3^-$, $M_{H_2O} = 18$ g/mol for water, and $M_{dry,Nafion}$ is the mass of nafion in dry samples. First it is assumed that all the water is absorbed by the nafion in the composite. In this equation, an assumption is made that all water is absorbed in nafion within the composite. Figure 47 shows the results obtained for $\lambda$ for the nafion in the composite samples.

![Figure 47: Water uptake per SO$_3^-$ group ($\lambda$) of the aC-nafion composite materials in various relative humidity environments.](image)

114
The results obtained for $\lambda$ are far above the normal range for nafion, namely $1 < \lambda < 30$ (Pisani et al. 2008). The high value of $\lambda$ indicates that the majority of water has been stored in the activated carbon particles, and/or in spaces within the composite nafion-aC materials that have not been filled with the nafion medium, in addition to the water uptake in nafion itself.

### 4.5.3 Swelling of the composite materials

As water is absorbed by nafion, the water channels surrounded on their walls by sulphonic acid groups swell (Zhao et al. 2011), and create paths for proton conduction (Wu et al. 2011; Choi et al. 2005). The swelling properties of the composite materials were of interest in themselves. A concern in the present project was that swelling of the nafion medium within the composite material might lead to stress-related failures of the composite electrode and hence its fragmentation. In addition, when the composite electrode is located within the confined space of a reversible PEM cell, swelling could subject the MEA to unacceptably high pressure on the hydrogen side. Some of the undesirable effects of swelling of nafion membranes in the MEAs of PEM fuel cells have been investigated by Satterfield (2007). The pressure resulting from swelling in a PEM cell may to some extent be reduced by using a compressible gas diffusion layer in the URFC. But excess swelling-related pressure may result in intrusion into the GDL, as illustrated in Figure 48.

![Nafion intrusion into the gas diffusion layer](image)

**Figure 48**: Nafion intrusion into the gas diffusion layer (reproduced from Satterfield 2007)
The degree of swelling of the composite materials in the present study was calculated from the experimentally measured volumes under dry and hydrated conditions using the formula (Gebel et al. 1993):

\[ V_s = \frac{V_{\text{RH}} - V_{\text{DRY}}}{V_{\text{DRY}}} \times 100 \]  

Eq. 41

where \( V_s \) is the percentage volume increase or swelling of the composite material, \( V_{\text{RH}} \) is the volume of the composite material in the respected relative humidity, and \( V_{\text{DRY}} \) is the volume of the material in the dry condition. The swelling values for the sample composite materials obtained from the empirical measurements are presented in Figure 49.

**Figure 49:** Swelling of the aC-nafion composite materials in various relative humidity environments.

The volumetric swelling of the samples increases with increasing relative humidity and reaches it maximum at fully hydration state when the samples were immersed in water. Samples ACK10, ACK2.5, ACS, AC3, and AC4 show between 22 to 33 % volume increases in the fully hydrated condition. The ACN sample had the highest swelling in all relative humidities, with volumetric expansion of 58 % at fully hydrated condition.
4.6 MEASUREMENT OF ELECTRON AND PROTON CONDUCTIVITY OF THE COMPOSITE MATERIALS

4.6.1 Electrochemical impedance spectroscopy

Normally at the beginning of characterising an ionic conductor material, little is known about the chemical processes within that composite material. Electrochemical impedance spectroscopy (EIS) is a method of testing hypotheses of unknown electrochemical processes by fitting an equivalent circuit model to experimental data points, and it is widely used in battery and fuel cell technology (Buller et al. 2005; Yuan et al. 2007; Tliha et al. 2010). A small AC sinusoidal excitation signal (voltage) is applied to the system and the response (in terms of current) to this signal is recorded. The impedance is estimated using the measured amplitude and phase shift of the response and expressed in the usual way for AC circuit analysis as a complex number (Page et al. 2007). The EIS method can be used with a two-probe or four-probe method. The four-probe method is more accurate, but requires more sophisticated equipment (Yadav and Fedkiw 2012). The two-probe method is accurate enough to be used in conductivity measurement of composite and normal membranes (Soboleva et al. 2008; Yadav and Fedkiw 2012). In this thesis, two-probe method was used to measure through-plane proton and electron conductivity of the composite materials.

There is considerable variation in the published results for the proton conductivity of nafion. For example, for nafion 117 membranes at 20°C, proton conductivities has been reported in the range 0.063-0.09 S/cm in liquid water, and 0.051-0.096 S/cm in 100% relative humidity (Yadav and Fedkiw 2012). Some studies have reported that adding small quantities of activated carbon to a nafion membrane can increase its proton conductivity (Chien et al. 2012). Chien et al. (2013) found that the addition of 5 wt% activated carbon to nafion increased its proton conductivity by 10% in a saturated relative humidity environment.

Through-plane conductivity refers to conductivity parallel to the sample thickness and in-plane conductivity refers to conductivity perpendicular to thickness. Anisotropy of nafion can be expressed as in-plane conductivity ($\sigma_\parallel$) to through-plane conductivity ($\sigma_\perp$).
isotropic membrane $\frac{\sigma_{//}}{\sigma_{\perp}}$ is equal to one. Many of the commercially available nafion membranes are extruded and the value of $\frac{\sigma_{//}}{\sigma_{\perp}}$ is slightly above 1 (e.g. 1.3 for nafion 115 and 1.2 for nafion 117). Membranes fabricated by solution casting are expected to be isotropic (that is $\frac{\sigma_{//}}{\sigma_{\perp}}$ is equal to 1) where no preferred orientation for conductivity is expected in the membrane (Soboleva et al. 2008). In measuring in-plane conductivity, both EIS contact electrodes are placed on one side of the sample, and in through plane measurement, the EIS contact electrodes are placed on opposite sides of the sample, as in Figure 50.

**Figure 50:** EIS cell designs for (a) in-plane and (b) through plane arrangement (source: Soboleva et al 2008)

For the present research project, through-plane conductivity of nafion membranes and composite materials was measured by the two-probe EIS method at room temperature. Although conductivity of membrane depends on temperature, in many reports the value is reported at room temperature (Choi et al. 2005; Yadav and Fedkiw 2012), so the tests here were done at room temperature too. A two-probe test set-up was designed and manufactured by the author specially for testing the composite materials. All the EIS tests were done at RMIT University’s School of Applied Sciences by the author using a potentiostat-galvanostat from CH Instruments.
4.6.2 Design and manufacturing the test cell for EIS method

The EIS test cell included a G-clamp and two gold-coated ceramic plates as the outer electrodes and is shown in Figure 51. The EIS electrodes must not be involved in any chemical reaction with samples. Gold-coated ceramic plates were used for this purpose. The first design for the EIS cell tried (not presented in this thesis) did not have a clamp to control pressure, and it was found that the EIS results could not be reproduced with confidence, so that a different design was needed. Hence the clamp was used to provide some control over the pressure applied across the faces of the samples. Since no method for measuring pressure was available, a simple manual way was used to ensure that all samples were under a similar pressure. The samples were placed on the bottom flat edge of the clamp and the screw turned to lower the upper grip of the clamp down until it touched the sample; from there the screw was tightened three quarters of a turn.

![Figure 51: EIS test cell used to measure proton and electron conductivity of the ac-nafion composite materials](image)

Copper tape was applied on the edge of the electrodes to establish a good electrical contact between the EIS electrodes and crocodile clips of the EIS equipment. The EIS electrodes were replaced after each day’s usage. The clamp was covered with Teflon sheet for two
reasons; firstly to electrically isolate the EIS electrodes from the clamp; and secondly to act as a damper under the EIS electrodes. Because of the brittle nature of the gold-coated ceramic plates, care was taken not to break them on the uneven surface of the clamp. The EIS electrodes were fixed to the clamp by double-sided tape.

In theory, the area of EIS electrode should not affect the measurement of conductivity. If the area of EIS electrode is increased, the resistance would decrease so that the conductivity would stay the same. However, increasing the surface area of the EIS electrodes reduces the resistance to such a low value that it would be practically impossible to measure the resistance accurately. For example, increasing the diameter of a circular EIS electrode from 1 to 5mm, reduces resistance from, for example, 100 to 4 ohm.

The clamping force should be high enough to reduce the contact resistance between the EIS electrodes and the samples. However, too much pressure will compress the membrane and might change the EIS results (Yun et al. 2012). The cell assembly was tightened with screws. The upper EIS electrode was lowered until touching the sample, and from that point pressed onto the sample by tightening the clamp screw by a further three quarters of a turn. The same method was used in all the tests to ensure that all were conducted within a close range of pressure. It would be an improvement in future experiments to employ pressure sensors or other technique to measure accurately the clamping force between the EIS electrodes (Soboleva et al. 2008; Yun et al. 2012).

4.6.3 Equivalent circuit

4.6.3.1 Equivalent circuit of nafion membrane

Any electrochemical process could be modelled as an equivalent electrical circuit. The technique of electrical circuit analysis provides a useful insight into the interdependent reactions of electrochemical devices (Huggins 1999). An equivalent circuit is a useful representation of the chemical processes and mechanisms taking place in the material only if the observed experimental data exhibit the same response to excitation signals as the equivalent circuit (Yuan et al. 2010). In other words, a good equivalent circuit is developed
based on possible chemical and physical processes, should correspond to the experimental spectra with minimum deviations, and should have a minimum number of fitted model parameters (Buller et al. 2005).

The equivalent circuit for a nafion membrane and the EIS test method used in the present study are presented in Figure 52.

**Figure 52:** Equivalent circuit for nafion membrane and test configuration

In this figure, $R_{e1}$ and $R_{e2}$ are the electric resistance of EIS electrodes. The two sets of parallel capacitor (a constant phase element) and resistance represent double layer phenomena between the EIS electrodes and each side of the nafion membrane. $R_{\text{bulk}}$ is the resistance of nafion membrane to ion transfer. The equivalent circuits used for this set-up is similar to that those proposed by Yun et al. (2012). The total effective impedance of the circuit shown in Figure 52 to an applied alternative current voltage of angular frequency $\omega$ is given by:

\[
Z = R_{e1} + \frac{R1 \times \frac{1}{j\omega C1}}{R1 + \frac{1}{j\omega C1}} + R_{\text{bulk}} + \frac{R2 \times \frac{1}{j\omega C2}}{R2 + \frac{1}{j\omega C2}} + R_{e2}
\]

Eq. 42
R represents resistance and C represents capacitance. Z is a function of frequency (ω) and so as:

$$\omega \to 0, \quad Z \to R_{e1} + R_1 + R_{bulk} + R_2 + R_{e2}$$

and as:

$$\omega \to \infty, \quad Z \to R_{e1} + R_{bulk} + R_{e2}$$

It should be stressed that there is no unique equivalent circuit for an electrochemical system and many equivalent circuits may be fitted to an EIS spectra. Many equivalent circuits have been developed for nafion membrane that, although look different, produce similar spectra (Beattie et al. 2001; Yadav and Fedkiw 2012; Yun et al. 2012). The circuit used here, however, is found to give a good fit to the experimental data, as will be shown.

### 4.6.3.2 Equivalent circuit of composite material

Initially, an equivalent circuit was used to take into account mixed electron and proton conductivity of the aC-nafion composite material that have both proton and electron conductivity. The circuit was developed from the work of Jamnik (2003). As shown in Figure 53, the equivalent circuit of mixed conductive materials consists of an electric resistance in parallel with an ionic resistance and capacitor (Wang and Hong 2003; Tortello et al. 2012). This method was especially of interest since both electric and ionic conductivity would be measured with one experiment. Tortello et al. (2012) used the same method to measure ionic and electronic conductivity of a composite material of nafion and carbon nanotubes.
However, initial tests with EIS showed that, because of the high carbon content of the composite material, the electron resistance of the samples was very low (for the ACN sample, for example, between 0.01-0.3 ohm). With such low resistance, the intercepts at high and low frequencies were very close together, so that distinguishing the proton resistance was practically impossible.

A new equivalent circuit and method of conducting EIS experiments for a dual proton and electron conducting composite material was suggested by A/Prof John Andrews. In this method, the aC-nafion composite material was sandwiched between two layers of nafion membrane, which prevent any direct electron transport through the composite sample. Based on this idea, the equivalent circuit shown Figure 54 was developed.
The overall impedance of this equivalent circuit is:

$$Z = R_{e1} + \frac{R1 \times \frac{1}{j\omega C1}}{R1 + \frac{1}{j\omega C1}} + R_{bulk} + R_{composite} + R_{bulk} + \frac{R2 \times \frac{1}{j\omega C2}}{R2 + \frac{1}{j\omega C2}} + R_{e2}$$  \hspace{1cm} \text{Eq. 43}$$

At high frequencies, the impedance of the capacitive elements tends to zero so that the overall impedance $Z$ tends to:

$$Z = R_{e1} + R_{bulk} + R_{composite} + R_{bulk} + R_{e2}$$  \hspace{1cm} \text{Eq. 44}$$

In the majority of the literature, therefore, proton conductivity is measured by the high frequency intercept of $Z$ on the real axis of the Nyquist plot (Affoune et al. 2005; Soboleva et al. 2008; Ijeri et al. 2010; Anis et al. 2011).
4.6.4 Electrochemical characterisation of the test set-up

4.6.4.1 Identifying values of EIS test rig

To measure the proton conductivity of nafion membranes and aC-nafion composite materials, the electrical resistance of the EIS set-up should be measured, that is, in effect the $R_{e1} + R_{e2}$, in equation 44. The EIS set-up includes the EIS cell and EIS apparatus, so that the total electric resistance includes that of the gold-coated plates and the connecting wires to the EIS cell. The total DC resistance of the EIS set-up can be measured by a separate EIS test in which the EIS electrodes are simply connected together. The corresponding EIS result is presented in Figure 55.

![Figure 55: DC electrical resistance of the EIS set-up and the result of measuring DC electrical resistance of the EIS set-up](image)

This is a typical behaviour for a pure electrical conductor (Wang and Hong 2007). It shows that the set-up has a DC electric resistance of 0.8 ohm (that is, 0.4 ohm for each side or $R_{e1} + R_{e2} = 0.8$ ohm).
4.6.4.2 Proton conductivity of Nafion 115 membrane

To measure the proton conductivity of the nafion 115 membrane, it was successively boiled in H₂O₂ for one hour; rinsed under a stream of water; boiled in distilled water for one hour; rinsed under water; boiled in H₂SO₄ for one hour; rinsed under water; boiled in distilled water for one hour; and finally stored in MilliQ water for 48 hours (Yadav and Fedkiw 2012; Zhao et al. 2011; Satterfield et al. 2006). The time is allowed so that membrane can absorb water and be fully hydrated. After treatment and storing the membrane for 48 hours the membrane was cut to dimensions of 0.130 cm×0.130 cm to be tested in the EIS cell. The EIS result obtained is presented in Figure 56.

\[ R_{\text{EQ}} = R_{\text{bulk}} + R_{\varepsilon_1} + R_{\varepsilon_2} = 10.9 \text{ ohm} \]

By using the equivalent circuit of Figure 54, the intercept of the real axis at the high frequency, \( R_{\text{EQ}} \), is obtained to be 10.9 ohm. According to equation 42 at high frequency:

\[ R_{\text{bulk}} = 10.9 - 0.8 = 10.1 \text{ ohm} \]

**Figure 56**: Nyquist plot of nafion 115 soaked in water
The through-plane proton conductivity was calculated assuming a uniform current distribution from (Yadav and Fedkiw 2012, Chien et al. 2013):

$$\sigma_{\text{bulk}} = \frac{t}{R_{\text{bulk}}lw}$$  \hspace{1cm} \text{Eq. 45}

Where $\sigma_{\text{bulk}}$ is the proton conductivity in S/cm, $t$, $l$ and $w$ are respectively the thickness, length and width of the sample in cm, and $R_{\text{bulk}}$ is the DC resistance measured by a multimeter in ohm. The EIS electrodes have covered the whole sample face area. The thickness of the dry nafion 115 is 125 μm. After treatment and being store in MilliQ water for 48 hours, the thickness was measured to be close to 180 μm. The nafion membranes in the EIS tests were fully hydrated to ensure good proton conductivity.

The proton conductivity of fully hydrated nafion obtained from this experiment:

$$\sigma_{\text{bulk}} = \frac{t_{\text{bulk}}}{R_{\text{bulk}}lw} = \frac{0.018}{10.1 \times 0.13 \times 0.13} = 0.1 \text{ S/cm}$$

This value is close to the value of 0.095 S/cm reported by Lufrano et al. (2004).

4.6.5 Proton conductivity of the composite materials

The EIS tests were done in a CH Instruments at frequencies between 1 Hz and 1 MHz. The amplitude of the applied AC voltage was 5 mV and the quiet time was set to 10 seconds. The quiet time is the period that the sample rests in the EIS cell before each test.

To calculate the proton resistance of the composite, $R_{\text{composite}}$, the value of $R_{\text{bulk}}$ needs to be determined. The problem is that the resistance of nafion depends on the area of the membrane. There is an inverse relationship between resistance of the membrane and its area. In this thesis, an assumption was made that area of the membrane involve in test is similar to the area of the composite sample. It was assumed that there is a uniform current distribution in membrane that is parallel to the cross section of the membrane. So although,
the surface of the membrane is larger than composite materials, in the calculation it is considered the same size as the composite materials. The resistance of the nafion membranes with the same area as the composite material was determined from the proton conductivity of nafion, $\sigma_{\text{bulk}} = 0.1$ S/cm.

$$R_{\text{bulk}} = \frac{t_{\text{bulk}}}{\sigma_{\text{bulk}}lw}$$  \hspace{1cm} \text{Eq. 46}

Here $t_{\text{bulk}}$ is the thickness of nafion membrane (=0.18 mm), $l$ and $w$ are the length and width of composite material. The proton resistance of the composite material was then calculated from the equation:

$$R_{\text{comp}} = R_{E_Q} - R_{e1} - R_{e2} - 2R_{\text{bulk}}$$  \hspace{1cm} \text{Eq. 47}

where, $R_{E_Q}$ is the value of intercept at high frequency that was obtained from the Nyquist plot and equivalent circuit. The proton conductivity of the composite was hence calculated from:

$$\sigma_{\text{comp}} = \frac{t}{R_{\text{comp}}lw}$$  \hspace{1cm} \text{Eq. 48}

The experimentally-determined values for the proton conductivity of composite materials made from the range of aC samples as a function of relative humidity are presented in Figure 57.
Figure 57: Experimentally-measured proton conductivities of the aC-nafion composite materials in various relative humidity environments.

The results show that with increasing relative humidity, proton conductivity increased. ACS, AC3 and ACK2.5 showed higher proton conductivity compared to the other three composite materials. Except for ACK2.5, all the samples showed lower proton conductivity compared to nafion membrane in water, that is, 0.1 S/cm, as would be expected.

4.6.6 Electron conductivity of the composite materials

The electron conductivity of the composite materials was measured both in the EIS cell and by a multimeter. To measure the electron conductivity of the composite materials, the samples were placed between the same two EIS electrodes as used to measure proton conductivity. The EIS electrodes were connected to the multimeter by using leads with crocodile clips. The total resistance of the measurement system, including resistance of the
crocodile clips, was measured by attaching the two clips together and reading the resistance on the multimeter. This value was then subtracted from the total resistance for the whole assembly including the composite material sandwiched between the EIS electrodes. The clamping force on the composite material was sufficient to provide a good contact between the composite material and the EIS electrodes, but not too high to compress the composite material.

The electron conductivity was calculated using the standard formula:

$$\sigma_E = \frac{t}{R_E l w} \quad \text{Eq. 49}$$

where $\sigma_E$ is the electron conductivity in S/cm; $t$, $l$, and $w$ are respectively the thickness, length and width of the sample composite material in cm; and $R_E$ is the total resistance of the assembly measured by the multimeter in ohms.

To test the set-up, the electric resistance of a gas diffusion layer (ELAT LT1400), with known electron conductivity, was first measured. The electrical conductivity of the GDL was calculated from:

$$\sigma_E = \frac{0.032}{0.0005 \times 0.708 \times 0.608} = 148 \text{ S/cm}$$

All the composite samples were tested in the same way. The samples were kept in their respected relative humidity environments for at least 42 hours so that equilibrium levels of hydration were well established. They were then removed from their containers and their electric resistances were quickly measured, after placing the sample in the cell to allow time for stabilisation of the recorded values. If a longer time had elapsed before resistance measurement, there would have been a significant change in the hydration level of the samples. The electron conductivity was calculated using equation 49. The corresponding results for dry, 35%, 75% and 100% RH, and fully hydrated conditions for all the aC samples are presented in Figure 58.
Figure 58: Electron conductivity of the aC-nafion composite materials in various relative humidity environments.

The results show that electron conductivity of all the samples decreased with increase of relative humidity and hence level of hydration. The results also showed that AC3 and AC4 had the lowest electrical conductivity among the composite materials at all relative humidity environments. In the fully-hydrated condition, the electron conductivity all the composites are below 0.5 S/cm, except ACN that show higher electron conductivity close to 2.3 S/cm. For carbon black with packing fraction of 0.3, the electron conductivity has been reported 2.0 to 4.7 S/cm (Pantea et al. 2003). The packing fraction has been defined as the ratio between the volumes of carbon blacks excluding volumes between the particles to the volume of carbon blacks including the volume between the particles. It should be noted that the packing fractions of the composite materials have not been measured in this thesis and the Pantea et al. (2003) was used only to put the electron conductivities of the composites in perspective.
4.7 SELECTING THE COMPOSITE MATERIALS FOR FABRICATING FULL-SIZE COMPOSITE ELECTRODES

4.7.1 Overview of electron and proton conductivity of the composite materials

A summary of the electrochemical properties, i.e. electron and proton conductivity, of the aC-nafion composite materials, is presented in Table 11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative humidity, [%]</th>
<th></th>
<th></th>
<th></th>
<th>Full hydration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>35</td>
<td>75</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>ACN</td>
<td>$\sigma_E$ 27.84</td>
<td>18.95</td>
<td>15.28</td>
<td>10.94</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>$\sigma_p$ 0.007</td>
<td>0.007</td>
<td>0.012</td>
<td>0.020</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>$\sigma_E/\sigma_p$ 3925</td>
<td>2556</td>
<td>1184</td>
<td>545</td>
<td>49</td>
</tr>
<tr>
<td>ACK10</td>
<td>$\sigma_E$ 19.59</td>
<td>6.44</td>
<td>1.64</td>
<td>0.21</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>$\sigma_p$ 0.015</td>
<td>0.021</td>
<td>0.029</td>
<td>0.037</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>$\sigma_E/\sigma_p$ 1288</td>
<td>300</td>
<td>55</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>ACK2.5</td>
<td>$\sigma_E$ -</td>
<td>-</td>
<td>4.49</td>
<td>3.41</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>$\sigma_p$ -</td>
<td>-</td>
<td>0.032</td>
<td>0.052</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>$\sigma_E/\sigma_p$ -</td>
<td>-</td>
<td>139</td>
<td>90</td>
<td>3.9</td>
</tr>
<tr>
<td>ACS</td>
<td>$\sigma_E$ 11.40</td>
<td>9.60</td>
<td>2.93</td>
<td>1.18</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>$\sigma_p$ 0.031</td>
<td>0.051</td>
<td>0.057</td>
<td>0.065</td>
<td>0.089</td>
</tr>
<tr>
<td></td>
<td>$\sigma_E/\sigma_p$ 365</td>
<td>186</td>
<td>51</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td>AC3</td>
<td>$\sigma_E$ 0.63</td>
<td>0.40</td>
<td>0.38</td>
<td>0.31</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>$\sigma_p$ 0.007</td>
<td>0.019</td>
<td>0.033</td>
<td>0.071</td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td>$\sigma_E/\sigma_p$ 81</td>
<td>21</td>
<td>11</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>AC4</td>
<td>$\sigma_E$ 0.93</td>
<td>0.85</td>
<td>0.65</td>
<td>0.34</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>$\sigma_p$ 0.005</td>
<td>0.010</td>
<td>0.017</td>
<td>0.031</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>$\sigma_E/\sigma_p$ 180</td>
<td>84</td>
<td>36</td>
<td>10</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 11: Summary of proton and electron conductivities (S/cm) of the composite materials
As the results show, the electrical conductivity of the composite samples is much higher than its proton conductivity for all the samples, with the ratio of electron to proton conductivity varying between 49 to 3 at full hydration. The results also show that by increasing relative humidity, proton conductivity increases and electron conductivity decreases. This is clearly presented in decrease of ratio of electron to proton conductivity ($\frac{\sigma_E}{\sigma_p}$) with increase of relative humidity.

### 4.7.2 Selection of materials for test electrodes

An ideal candidate for the present research project should have three characteristics:

- high proton conductivity
- high electron conductivity
- high ultra-microporosity.

To determine which composite electrode has the lowest combined resistance to proton and electron transfer, it is instructive to add the proton resistance and the electron resistance across the electrode, as in equation 50. The idea behind this equation is that the resistance to proton transfer and resistance to electron transfer are in effect in series in the electrode of a proton flow battery.

$$R_P + R_E = \frac{t}{lw} \left( \frac{1}{\sigma_p} + \frac{1}{\sigma_E} \right)$$  \hspace{1cm} \text{Eq. 50}

where $R_P$ is the proton resistance; $R_E$ is the electron resistance; $t$, $l$ and $w$ are respectively the thickness, length and width of the composite electrode; and $\sigma_p$ and $\sigma_E$ are the proton and electron conductivity respectively. The results of the composite materials for a sample with unit dimensions are presented in Figure 59. Use of the unit dimensions is to be able to compare the total resistance of the different composite materials.
Figure 59: Electron and proton resistance of the composite materials in various relative humidity environments.

The aC-nafion materials selected for use in full-size electrodes and testing for hydrogen storage in a URFC were:

- ACS-nafion
- ACN-nafion.

It is evident from Figure 59 that the ACS-nafion composite had the lowest total resistance among all the composite electrodes across the full range of hydration levels. The ACN-nafion composite was also selected because it was a commercially-available activated carbon. Although ACN-nafion had a relatively high total resistance compared to the other samples, the differences between the total resistances of electrodes at higher relative humidity, and especially at 100 %RH and soaked in water, are very small. The hydrogen electrode would usually operate in these highly hydrated conditions.

Time and resource limitations in the current project have meant that only a limited number of composite electrodes could be tested in a reversible fuel cell. However, it is important in future work to test many of the other composite materials fabricated here in full to investigate their reversible hydrogen storage capacities.
4.8 ANALYSIS OF THE PHYSICAL AND ELECTROCHEMICAL CHARACTERISTICS OF THE COMPOSITE MATERIALS

4.8.1 Water uptake of the composite materials in different relative humidity environments

The water uptake in the composite materials increases with increasing relative humidity. The composite materials absorbed the highest amount of water when they were fully hydrated by being immersed in water. The amounts of water uptake of the composite materials are between 45 wt% to 85 wt% at fully hydrated state. At low relative humidity, i.e. 40 %, the water uptakes of the samples are close to each other, between 5 wt% to 11 wt%. These values are depicted in Figure 46.

The high water uptake could not be due only to the water absorption of the nafion polymer. The water uptake per $\text{SO}_3^-$ site of the nafion, depicted in Figure 47, shows much higher water uptakes compared to typically reported values that are between one and 30. The water uptake per sulphuric group in the composite are in the range of 55 to 105 $\text{H}_2\text{O}/\text{SO}_3$. These high values suggest that the water uptake of nafion is not the only water uptake mechanism in the composite materials. Two possible hypotheses are considered for this behaviour that both proved to be correct. The first hypothesis is that the activated carbon particles in the composite materials contribute to the high water uptake. Indeed, recent publications have studied that using low concentration of activated carbon in nafion membrane can lead to higher water uptake in the membrane (Chien et al. 2012; Chien et al. 2013). The second hypothesis is that there might be hollow macro volumes in the structure composite materials and these macro volumes are contributing to water uptake of the composite materials. A SEM image of the cross section of the composite materials in Figure 42 showed that there are indeed hollow macro volumes in the composite materials that can act as reservoirs of bulk water.

From the results of the fully hydrated composite materials in Figure 46, the following order is observed:

$\text{ACN} > \text{ACK2.5} > \text{ACS} > \text{AC3} > \text{AC4} > \text{ACK10}$. 

135
Since all the composite materials had the same amount of nafion (50 wt%) and the solution casting parameters were the same for all of them, one may conclude that the difference between water uptake of the composite materials is due to characteristics of the activated carbons and the macro volumes in the structure of the composite materials. From the available characteristics of the activated carbons in Table 6, the following order is observed between the surface areas obtained from the N\textsubscript{2} adsorption isotherm:

ACN > ACS > AC3 > AC4.

The order of mesoporosity in the first order (previous page) is similar to the order of water uptake in this order (this page). According to the researcher who fabricated and characterise the ACK2.5 and ACK10 samples, Lachlan Ciddor from Monash University, the data of N\textsubscript{2} adsorption isotherm for these two samples could not be obtained.

From the available data here, it is not possible to suggest a relationship between N\textsubscript{2} adsorption isotherm and water uptake in the composite electrodes, especially because the limited number of related experiments in this thesis and uncertainty of the contribution of the hollow macro volumes in the composite electrodes. However, a hypothesis can be developed that there might be a relationship between the water uptake in the composite materials and the mesoporosity and possibly the average pore diameter of the activated carbons. Further experiments are necessary to test the validity of this hypothesis.

### 4.8.2 Volumetric swelling of the composite materials in different relative humidity environments

The volumetric swelling of the composite materials that is the volumetric expansion of the composites, in the different relative humidities has been found to increase with increasing relative humidity. Except ACN composite, all other composite materials have close volumetric swelling. At full hydration, the values for swelling are between 22 wt% and 33 wt%. In the case of ACN composite, the value is close to 58 wt%. In fact, ACN composite has the highest volumetric swelling among the composite in all the relative humidities. This might be because the ACN composite had the highest amount of water uptake among
the composite materials as well. At lower relative humidities, the volumetric swellings of the composites are close to each other. At 40% relative humidity, the volumetric swelling of composites are between 2.8 wt% and 15 wt%. These values are depicted in Figure 49.

The volumetric swelling occurs because the water that had been absorbed by nafion in the water channels surrounded on their walls by sulphonic acid groups. This is shown in Figure 45. The thickness of bulk water that causes the swelling might be from 2.5 to 4.5 nm, according to this Figure. The swelling and the volume expansion of the composite might affect the performance of the composite electrode in the experimental cell. The composite electrode is in a confined space in the cell, under pressure by the end-plates. The pressure on the electrodes is required to reduce the electrical contact resistance between the electrodes and end-plates that are working as a current collector. The expansion of the composite electrode under working condition of the electrolyser mode and fuel cell mode would increase the stress on the composite electrode that can in turn, lead to mechanical failure of the electrode, i.e. breaking of the composite electrode.

### 4.8.3 Proton conductivity of the composite materials in different relative humidity environments

The proton conductivity of the composite materials increases with increasing relative humidity and reaches its maximum when the composite materials have been fully hydrated in water. The values of proton conductivity of the composite materials are between 0.044 and 0.11 S/cm at full hydration environment. The proton conductivity at dry condition is much lower, between 0.005 to 0.031 S/cm. Except the ACK2.5 composite, all the other composite materials had lower proton conductivity compared to nafion membrane. The proton conductivity for nafion 115 membrane has been reported to be 0.095 S/cm at full hydration (Lufrano et al. 2004). The value of the ACK2.5 composite material at full hydration condition needs to be checked again in the future, before any conclusion. ACS composite has one of the highest proton conductivity in all the relative humidities. The values of proton conductivity of the ACS composite are in the range of 0.031 S/cm at 0% relative humidity to 0.0889 S/cm at full hydration environment. These values are depicted in Figure 57.
There are two competitive factors in the composite materials that may influence the proton conductivity. The first factor is that by adding activated carbon to the nafion, the effective cross sectional will decrease and hence the proton conductivity would be reduced. In other words, proton conductivity would decrease by increasing the ratio of carbon to nafion in the composite material. The second competing factor is that the activated carbon, in the composite materials, increases the water uptake and enhances the proton conductivity of the nafion in the composite materials. In other words, proton conductivity would increase, up to a point, by increasing the ratio of carbon to nafion in the composite material is. It is obvious that if the composite materials were almost made entirely from activated carbon they would show no proton conductivity.

The future study of these two factors might be beneficial. Increasing the ratio of carbon to nafion in a composite material should decrease the proton conductivity because of the first factor and should increase it because of the second factor. A hypothesis may be formed that there should be an optimum carbon to nafion ratio that in that ratio, proton conductivity of the composite material will reach its maximum value.

4.8.4 Electron conductivity of the composite materials in different relative humidity environments

The electron conductivity of the composite materials decreases with increasing relative humidity. The values of the electron conductivity at 0% relative humidity are in the range of 0.93 S/cm for AC3 composite to 28 S/cm for ACN composite. The gap between the electron conductivity of the composites is significantly reduced at the full hydration environment. The values of the electron conductivity of the composites at the full hydration environment are between 0.17 S/cm for ACK10 composite and 2.32 for ACN composite. These values are depicted in Figure 58.

The possible explanation of this behaviour might be because of the volumetric expansion of the composite materials. The volumetric expansion of the composite materials means that the distance between the carbon particles increases and the contact between the carbon particles is reduced. Since the composite electrodes would work in an environment with
high relative humidity, it can be expected that the electron conductivity of the composite electrodes be a limiting factor in distribution electrons thorough the composite materials. By increasing the ratio of carbon to nafion in the composite, the electron conductivity would be improved, since there would be more carbon particles are in contact with each other in the structure of the composite. However, this suggestion may jeopardise the proton conductivity of the composite.

4.9 OTHER APPLICATIONS FOR THE FABRICATED COMPOSITE MATERIALS

The fabrication of a number of composite nafion-aC materials has been described in this chapter, and many of these materials have been shown to have both reasonably high proton and electron conductivity. It is important to note here that such materials with dual proton and electron conductivity have the potential to be used in a wide range of devices in addition to proton flow batteries, like sensors, electrochromic devices, and direct solar electrolysis of water (Qi and Lin 2000; Yang et al. 2010; Patel et al. 2012; Liu et al. 2012; Tortello et al. 2012). Research on mixed electron and proton conductors is getting more and more momentum in both solid state physics and chemistry (Riess 2003). Carbon is a cheap and abundant material, and fabricating activated carbon is a relatively simple procedure that requires relatively inexpensive equipment. Hence aC-nafion materials with dual proton–electron conducting capacity as designed, made and tested in this project have the potential to be a very cost-effective option in applications where this property is required.

In one system for direct solar electrolysis of water, in a photocatalytic system is employed that has a membrane that has to have both good proton and electron conductivity (Tortello et al. 2012). In such systems water splits on the anode to oxygen gas, a proton and an electron. Both electrons and protons are then transferred through the membrane by separate pathways to the cathode (Tortello et al. 2012). On the cathode protons and electrons recombine and produce hydrogen. A schematic of a photocatalytic system is shown in Figure 60.
Figure 60: Photocatalytic system using a dual proton and electron conductive material (source Tortello et al. 2012)

The photocatalytic system differs from a conventional PEM electrolyser, in which the nafion membrane transfers only protons, while and electrons are supplied to the cathode via the external circuit. The proton and electron conductivities of the best-performing composite nafion-aC materials fabricated in the present project are compared with those reported by Tortello et al. (2012) for composites of nafion and vertically-aligned carbon nanotubes (CNT) in Table 12.

<table>
<thead>
<tr>
<th>Composite name</th>
<th>Proton conductivity [S/cm]</th>
<th>Electron conductivity [S/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion and CNT</td>
<td>0.009</td>
<td>0.315 × 10^{-3}</td>
</tr>
<tr>
<td>ACN</td>
<td>0.047</td>
<td>2.32</td>
</tr>
<tr>
<td>ACS</td>
<td>0.089</td>
<td>0.58</td>
</tr>
<tr>
<td>ACK 2.5</td>
<td>0.11</td>
<td>0.43</td>
</tr>
<tr>
<td>ACK10</td>
<td>0.044</td>
<td>0.17</td>
</tr>
<tr>
<td>AC3</td>
<td>0.076</td>
<td>0.27</td>
</tr>
<tr>
<td>AC4</td>
<td>0.044</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 12: Dual proton and electron conduction at full hydration

Significantly, the electron conductivity of the best nafion-aC composite is over a thousand that of Tortello et al. (2012)’s nafion-CNT composite, and the proton conductivity is over ten times that of the latter. The low electron conductivity might be due to low CNT content of the nafion CNT composite in Tortello et al. (2012).
5. TESTS ON THE COMPOSITE ELECTRODES IN THE EXPERIMENTAL REVERSIBLE FUEL CELL

5.1 FABRICATION OF THE FULL-SIZE COMPOSITE ELECTRODES

5.1.1 Employing a backing layer in the composite electrodes

A backing layer was employed in the fabrication of the composite electrodes as shown in Figure 61. In this figure, the backing layer is beneath the composite materials and is integrated into the structure of the composite materials. In the composite material, nafion is depicted in blue and particles of activated carbon in black. The backing layer was in contact with the end plate when the electrode was incorporated into the URFC.

![Figure 61](image.png)

**Figure 61:** The backing layer beneath the composite material

The reasons for the backing layer were three-fold. First, a suitable backing layer has good electron conductivity and acts as a current collector in fuel cell mode and a current distributor in electrolyser mode. It should be noted that in the electrochemical measurements of the composite materials, all the samples have showed relatively low electron conductivity, compared to the corresponding aC powders. This might be because of relatively low contact
area between the carbon particles in the composite. Ideally, the composite material would diffuse into the backing layer, so that the interconnected carbon medium within this layer may act as highly-conductive pathways for electron transportation. Figure 62 shows a SEM image of a carbon cloth that is commonly used as gas diffusion layer (GDL) in fuel cells. The complex interconnected threads of carbon can clearly be seen.

![Figure 62: SEM image of carbon cloth by using Philips XL30 SEM](image)

The second reason to incorporate a backing layer into the composite electrodes is the necessity to ensure structural integrity. During the first tries to fabricate full-size composite electrodes (5 cm$^2$ in area) by the solution-casting method and without any backing layer, it became apparent that the final products always had multiple cracks in them. As an example one of the products is shown in Figure 63. Moreover, even the small pieces of the composite electrode were very brittle and could easily break with the smallest applied force.
The third reason is to act as a damper to absorb the pressure and protect the brittle composite electrode from uneven stresses caused by unevenness in the surface of the end-plate. Given that the composite electrode is very brittle, the composite electrode without such a protective damping layer might crack and lose its structural integrity when under compression stress in the cell.

The first material considered for the backing layer was aluminium foil. The reason for this choice was that an activated carbon electrode made by CSIRO for another project and given to our team for testing in the current project had used aluminium fold as the backing layer. However, early experiments by the author revealed that aluminium foil cannot be a good candidate for the present research project. Firstly the nafion in the composite material needs to be protonated by treating with sulphuric acid, explained in Chapter 4. Aluminium reacts with sulphuric acid and thus inhibits the activation process. Secondly, even if the composite electrode is used without protonation in sulphuric acid, the aluminium foil gets corroded in the electrolyser and fuel cell modes, since the environment within a PEM URFC is highly acidic, \(\text{i.e.} \quad \text{pH}\approx 2-4\) (Tan et al. 2011). Figure 64 shows the state of an aluminium foil before and after being used in the experimental PEM URFC for only three electrolyser-mode/fuel-cell mode cycles.
Furthermore, the aluminium foil did not protect the structural integrity of the activated carbon electrode. As can be seen in Figure 65, the activated carbon electrode was delaminated from the nafion membrane after the test in the experimental PEM URFC, with some of the activated carbon material attaching to the membrane and some to the aluminium foil.

**Figure 64:** The aluminium foil backing of an electrode before and after being tested in the experimental PEM URFC

**Figure 65:** Delamination of the activated carbon electrode from the membrane
As an alternative to aluminium foil, a porous backing like a gas diffusion layer can be integrated into the material of the electrode and strengthen its structure. Hence in the present project, carbon cloth (ELAT LT1400W) was used as the backing layer in the fabrication of the composite electrodes. It is commercially available and relatively cheap. The electrical conductivity of the carbon cloth was calculated in Chapter 4 and is 148 S/cm. It may be noted here that, while a carbon cloth backing layer was found to be necessary in the present experiments to maintain the structural integrity of the composite electrode, the addition of such a medium to the electrode adds to its mass and volume without contributing to the hydrogen storage capacity. In future designs it will therefore be desirable to seek ways to keep the electrode intact with minimal impact on its total mass and volume.

5.1.2 Casting the full-size composite electrodes

The area of the electrodes was 5 cm². The method of fabrication was the same as that used to fabricate composite nafion – activated carbon materials described in chapter 4. The carbon cloth was cut into pieces of area 5 cm² and the sections were weighed. The carbon cloth pieces were placed at the bottom of the mould. The activated carbon was mixed with nafion solution with mass ratio of aC/nafion= 50/50. When the majority of the liquid solvent in the mixture of activated carbon and nafion solution was evaporated, the slurry mixture was poured over the carbon cloth in the mould. The mould was then placed in an oven at 80°C overnight and later at 115°C for two hours. The initial result showed that some cracks still existed in the final electrode. However, the composite pieces were completely attached and infused into the carbon cloth. Figure 66 presents the electrode at this stage.
Another batch of composite activated carbon and nafion mixture was prepared and, after evaporation of the alcohol in the solution, the slurry mixture was poured over the already-made electrode of Figure 66. The slurry mixture filled the cracks and also increased the thickness of the electrode. After being in the oven at 80°C for another night and at 120°C for two hours, the electrode was again checked for cracks. A few cracks still existed in the electrode, but far less than the first try. The coating of the electrode was done for the second time. The final result showed a better structure. A very small number of cracks still existed, but they were surface cracks and did not penetrate significantly into the electrode. More interestingly, the cracks completely disappeared when the electrode was fully hydrated. This effect was expected due to the high water uptake and volume expansion of the composite materials that were calculated in Chapter 4. An image of the fully hydrated double-coated composite electrode is shown in Figure 67.
Figure 67: A fully hydrated composite aC-nafion electrode twice coated with aC-nafion slurry

After the last coating, the electrodes were placed in an oven at 80°C overnight, followed by 2 hours at 120°C.

5.1.3 Protonation of the casted composite electrodes

The electrodes were then boiled in distilled water for 1 hour, immersed in H$_2$SO$_4$ at 80°C for 1 hour, rinsed with distilled water, and finally boiled in distilled water for 1 hour. The water and sulphuric acid, were poured in two separate beakers and the beakers were placed on a magnetic hot plate/stirrer. The temperature was monitored by a thermocouple, as shown in Figure 68. The rotation of a magnetic bar in the beaker created a circular movement of the liquid and ensured better diffusion of the liquids into the electrodes.
Figure 68: The protonation of composite electrodes, left: the magnetic hot plate, right: washing the electrodes

The electrodes were immersed in the liquids when they reached the appropriate temperature. A 250-ml beaker filled with about 150 ml acid was used for sulphuric. A 1000-ml beaker was used for water, to ensure that all the sulphuric acid had been removed from the composite electrode in the last step. To ensure that the electrodes did not have any sulphuric acid left in them, they were rinsed with distilled water for 10 minutes, as shown in Figure 68. The acidity of water after contacting the electrode was determined by a pH paper indicator.

The electrodes were then left at room temperature for 2 hours and dried in an oven over night at 80°C. The samples were weighed and their dimensions measured.

5.1.4 The specifications of the composite electrodes

As mentioned before, two forms of composite electrodes were made: ACN-nafion and ACS-nafion, both with a mass ratio of 50/50 of activated carbon to nafion. Two electrodes were fabricated from each composite material using exactly the same fabrication process. ACN1
and ACN2 were made form ACN activated carbon. ACS1 and ACS2 were made from ACS activated carbon. The mass and dimensions of the electrode are presented in Table 13. All the electrodes had an area of $2.3 \times 2.3 \text{ cm}^2$.

<table>
<thead>
<tr>
<th>Name of the electrode</th>
<th>Total mass of electrode (composite and GDL) (mg)</th>
<th>Mass of GDL (mg)</th>
<th>Thickness of the composite electrode (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN1</td>
<td>707.1 ± 0.1</td>
<td>82.4 ± 0.1</td>
<td>2.24 ± 0.01</td>
</tr>
<tr>
<td>ACN2</td>
<td>1171.1 ± 0.1</td>
<td>77.2 ± 0.1</td>
<td>3.02 ± 0.01</td>
</tr>
<tr>
<td>ACS1</td>
<td>752.8 ± 0.1</td>
<td>75.8 ± 0.1</td>
<td>2.43 ± 0.01</td>
</tr>
<tr>
<td>ACS2</td>
<td>772.1 ± 0.1</td>
<td>92.3 ± 0.1</td>
<td>2.05 ± 0.01</td>
</tr>
</tbody>
</table>

Table 13: The mass and the dimensions of the composite electrodes

5.2 FABRICATION OF THE MEMBRANE ELECTRODE ASSEMBLIES

5.2.1 The catalysts for the oxygen electrode

Selecting of catalysts for the oxygen side of a URFC is challenging. There is no catalyst known to both exhibit good performance in associating and dissociating oxygen. Therefore when selecting a catalyst for a URFC, a compromise between its performance in fuel cell mode and electrolyser mode should be considered (Dihrab et al. 2009). Development of a bifunctional electrocatalyst for the oxygen electrodes is the key technical challenge in PEM URFC technology (Pettersson et al. 2006). Such catalysts must further be able to resist the corrosive acidic environment ($\text{pH} \approx 2$) of the electrolyser (Carmo et al. 2013).

RuO$_2$ exhibits less oxygen overpotential compared to other catalysts, but it is very vulnerable to corrosion (Carmo et al. 2013). Small amounts of iridium can significantly improve the stability of Ru (Carmo et al. 2013). Iridium is one of the rarest elements in the Earth’s crust with an average mass fraction of 0.001 ppm in crustal rock (Carmo et al. 2013). To put this in perspective, gold is 40 times more abundant than iridium (Carmo et al. 2013).
In the present study, the catalysts employed on the oxygen side were 2 mg/cm² of IrRuOₓ and 2 mg/cm² of PtB, with NuVant ELAT-LT1400W as the gas diffusion layer. The electrodes were purchased from Fuel Cells Etc, USA.

5.2.2 Nafion membrane protonation

Nafion comes in a number of different grades (for example, nafion 112, 115 and 117) varying according to thickness (0.051, 0.127 and 0.178 mm respectively), and hydration and permeation properties (Sportsman et al., 2002). The nafion 115 was used in this study. The nafion membrane was cut to 7.5 × 7.5 cm², 0.5 cm larger than the size of the experimental cell (7.0 × 7.0 cm²). Nafion membrane is a good electrical insulator and can prevent short circuit between the two end-plates of the experimental cell. The membranes were boiled in H₂O₂ for 1 hour, rinsed with distilled water, boiled in H₂SO₄ for 1 hour, again rinsed with distilled water until pH reached 7, and finally boiled in distilled water for 1 hour. They were then stored in MilliQ water. The difference between an untreated and a treated nafion membrane is shown in Figure 69. The nafion membrane, that has been treated, is transparent. It is because the treatment with hydrogen peroxide has removed organic impurities (Satterfield et al. 2006). Organic material and nafion residuals have been suggested to be the cause in brown coloration in not-treated-membranes (Bautista-Rodríguez et al. 2009). The treatment with sulphuric acid is suggested to remove any ionic impurities (Satterfield et al. 2006).
5.2.3 Hot pressing the electrodes and membranes

There are two hot-pressing techniques to bond electrodes to the membrane. The most common one is called the separate electrode method or gas diffusion electrode (GDE). In this technique, the electrode is printed onto the gas diffusion layer (GDL) and left to be dried. Later, the two electrodes attached to their GDLs and are hot pressed onto the membrane in between them to fabricate a membrane-electrode-assembly. The other technique to fabricate an MEA is referred to as decal method or catalyst coating membrane, in which the electrode is printed onto membrane directly. Next, the two GDL are placed over the areas of the membrane coated with catalysts and then the assembly is hot-pressed together (Sohn 2006, Liu and Sung 2012). Figure 70 depicts the difference between the two methods.
**Figure 70**: MEA fabrication techniques (Liu and Sung 2012)

For the hot press in this study an IDM Laboratory 15T press (model number: L0003) was used, as seen in Figure 71. The press has one heating element for each upper and lower metal block that can be digitally set to a desired temperature. In hot-pressing, temperature, pressure and the pressing duration are the three influential factors. Many different values are reported as being used in the literature, sometimes differing by an order of magnitude (Hasran et al. 2013).
The nafion membrane of the MEA was dried by a filter paper to remove excess water from it. The MEA was then placed between two Teflon sheets to prevent sticking to the metal plates of the hot press, as shown in Figure 72. The metal plates protect the metal blocks and ensure an even pressure distribution on the sample. Unbalanced forces might damage the MEA and lower its performance (Peng et al. 2011). The metal plates were kept at the same temperature as the blocks. The MEA was then placed in the press at 10 MPa pressure for 90 seconds at a temperature of 120°C. Before each test, sufficient time was allowed for the metal blocks to reach the 120°C. The MEA was then taken out and left to cool down to the room temperature.
5.3 DESIGN AND CONSTRUCTION OF THE EXPERIMENTAL PEM URFC CELL

5.3.1 Material of the end-plates

Metal alloys and graphite are among the most common materials used in bipolar plates and end-plates (Hamilton and Pollet 2010). The specifications of a good material are low cost, high electrical conductivity, high manufacturability, high mechanical strength, low weight, low volume, high chemical resistance, high thermal conductivity, and low permeability for gases, in particular hydrogen (Yuan et al. 2005). Many researchers are using metallic plates, like stainless steel, because they have high electrical and thermal conductivity, low cost, easy manufacturability and good mechanical property in thin form (Kumar and Reddy 2003). Graphite plates, on the other hand, are lightweight, provide an excellent corrosion resistance, good electrical and thermal conductivity, and necessary mechanical property like rigidness,
although graphite is more expensive and brittle (Turan et al. 2011). In the present research, metallic plates were omitted from consideration because they may increase the chance of hydrogen gas formation. Moreover, since the test cell was a single cell, the cost of manufacturing a graphite plate was not significant. The graphite plates used, 100×150×5 mm, were purchased from Selaby Australia Pty Ltd.

### 5.3.2 Design of the flow channels

Flow channels have a crucial effect in the performance of the cell. The main functions of the flow fields are proper distribution of oxygen or hydrogen on electrode, providing pathways for removing produced water from electrodes, and minimising the pumping force to circulate the reactant gases (Turan et al. 2011). Most commonly, channels are made with a rectangular cross section, although other cross sections have also been proposed (Hamilton and Pollet 2010). The most common flow-field patterns are presented in Figure 73.

![Flow field patterns](image)

**Figure 73:** Flow field patterns; 1 - Serpentine, 2 - Parallel, 3 - Parallel serpentine, and 4 - Pin-type (Tang et al. 2010)

In the serpentine flow field, there is one path for reactant gas, so that gas flow will blow out the water blockages and prevent blocking of channels. Xu and Zhao (2007) conducted a computational simulation of the effect of flow-field design and water flooding in the gas diffusion layer above the ribs. They showed that the pressure drop between adjacent channels is greater than the pressure drop along the channel, which may cause flow leaks from channels and strong convection in the GDL. The strong convection does facilitate mass transport and removal of water from the GDL. However, this pattern imposes a high pressure drop and may require using a pump to circulate reactants in large cell applications (Larminie
and Dicks 2003). However, this flow field is still the most common type of flow field that has been used because of advantages with regards to water management and gas utilization in fuel cell technologies (Kwon et al. 2011).

With the parallel flow field, when water is produced, droplets tend to cling to the channels and block them. These droplets are removed when the pressure of the reactant gases is sufficient to overcome the surface tension between water droplets and the sides of the channel (Larminie and Dicks 2003). However, since the size and numbers of droplets in channels are different, reactant gases flow through the channels that are least resistive to the flow. Hence, an uneven distribution of reactant gas may eventuate.

The parallel serpentine flow field consists of a number of separate serpentine channels connected to the same inlet and the same outlet manifold. Although this new pattern is reported to reduce total pressure drop and increase fuel cell performance, still each individual serpentine channel possesses a high pressure loss (Larminie and Dicks 2003).

The pin-type or grid flow field can be formed using a variety of cross-hatched channels with different spacing, shapes and sizes. This type of flow pattern has a low pressure drop since the gases can swirl in parallel and series flow paths. However, this pattern suffers from uneven flow distribution, poor water removal, which usually leads to poor performance (Larminie and Dicks 2003).

In this research project, a parallel pattern was selected for the oxygen side, since the serpentine pattern has been reported as having a poor performance in oxygen distribution, due to lower infusibility of oxygen (Ramos-Alvarado et al. 2012). The parallel pattern has better performance in oxygen distribution, although the performance depends on design of channels (Ferng and Su 2007). Another important parameter in the performance of parallel flow channels, which Ferng and Su (2007) did not consider, is the location of the inlet and outlet ports. In Ferng and Su’s (2007) design the inlet was in the upper-right and the outlet was in the bottom-left, which left a major part of the channels short of oxygen. In the design of the experimental cell in the present project, a proper distribution of oxygen is achieved by designing gas reservoirs and step-wise depth change along the flow distribution field. Also in
the current design the inlet and outlet are located at the centreline of the channels, promising a uniform oxygen supply in all the channels.

For the hydrogen side in the URFC designed in this study, no flow channels were incorporated. Exposure of the storage electrode to these channels may provide an escape route for hydrogen atoms to combine together as hydrogen gas and leave the electrode. Since there was still a chance of hydrogen gas formation, as a safety measure, a channel was designed around the electrode area and filled with GDL to provide an indirect route between flow channels and the electrode. If hydrogen gas is produced inside the electrode, it can escape from the edges of electrode to the GDL and from there it can leave the cell and hence be detected. The designs of the oxygen end-plate and hydrogen end-plate are shown in Figure 74. The details are presented in Table 14.

Figure 74: The designed URFC cell in this thesis (right: oxygen electrode, left: hydrogen electrode)
<table>
<thead>
<tr>
<th></th>
<th>Oxygen end-plate</th>
<th>Hydrogen end-plate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dimensions (mm)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell area</td>
<td>70 ×70</td>
<td>70 ×70</td>
</tr>
<tr>
<td>Active area</td>
<td>23 ×23</td>
<td>23 ×23</td>
</tr>
<tr>
<td>Ribs width</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Channel depth in zone 1</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>Channel depth in zone 2</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>Channel depth in zone 3</td>
<td>1.8</td>
<td>1.8\textsubscript{a}</td>
</tr>
<tr>
<td>Channel width</td>
<td>2.0</td>
<td>4.0\textsubscript{a}</td>
</tr>
</tbody>
</table>

**Table 14:** Dimensions of the experimental cell (a: The channel in hydrogen cell is located around the active area of the cell and so is not a part of floe field)

### 5.4 THE CONSTRUCTION OF THE EXPERIMENTAL PROTON FLOW BATTERIES

#### 5.4.1 The structure of the proton flow battery

The main components of the experimental proton flow battery are shown in Figure 75. At the centre of the cell is the membrane-electrode-assembly (MEA), which is in contact with the two end plates. To prevent leakage from the cell and from hydrogen side to oxygen side, seals have been used. The seals are placed around the electrode and are in contact with nafion membrane and endplates.
5.4.2 The components of the cell

5.4.2.1 Membrane electrode assembly

In Figure 75, at the centre of the structure is the nafion membrane that transfers protons from the oxygen electrode to the hydrogen electrode in electrolyser mode, and in reverse in fuel cell mode. The oxygen electrode consists of a gas diffusion layer (carbon cloth) and a catalyst layer (with loading of 2 mg/cm² of IrRuO₅ and 2 mg/cm² of PtB). The hydrogen electrode consists of a gas diffusion layer (carbon cloth) and composite material (activated carbon and nafion with ratio of 50 wt%). The gas diffusion layer of each electrode is in contact with an end-plate.

Figure 75: Components of a proton flow battery (modified from Doddathimmaiah 2008)
5.4.2.2 The end-plates and the flow channel

The end-plate of the oxygen electrode has flow channels that allow inflow and outflow of oxygen and water. The end plate of the hydrogen side does not have any flow channels since, if the concept of this project works in an ideal manner, hydrogen gas is not expected to form. However, if hydrogen is formed in the electrolyser form, for safety reasons there should be an escape route for hydrogen. The channel around the active area of the hydrogen electrode provides that escape route.

5.4.2.3 The sealing of the cell

Silicone rubber has been used as the sealing material in fuel cells because it is easy to fabricate and has a low production cost (Tan et al. 2007). In this project, a silicone rubber gasket was used to seal the edges around the gas flow field plates. The gasket should be slightly thicker that the electrode. The silicone rubber had a thickness of 0.38 mm ± 0.02 mm. Silicone rubber adhesive sealant was used to seal the surfaces of MEA to silicone rubber and also at the edges of the cell to avoid leakage of gases. After allowing time for the sealant to dry, the cell was immersed in water and checked for leakages. First the outlet of the oxygen side was blocked and air was blown into the outlet. The immersed cell was monitored to see if any bubbles formed in the water. Next, the outlet of the hydrogen side was closed and air was blown in the inlet and the immersed cell was again monitored for bubbles. The location of the seals in a PEM URFC is shown in Figure 76. Figure 77 shows the silicone rubber on the end-plates.
Figure 76: The position of the seal in a PEM URFC (Adachi and Kaneko 2003)

Figure 77: The silicone rubber seals on the end-plates of the experimental URFC
5.5 THE EXPERIMENTAL SETUP

5.5.1 Components of the experimental setup

5.5.1.1 Gas storage tanks

Hydrogen and oxygen storage cylinders manufactured by H-tec, Germany, were used to store the gases produced in E-mode and reuse them later in FC-mode. The cylinder used is shown in Figure 78.

![The storage tank used for hydrogen and oxygen gases in the experimental URFC system](image)

Figure 78: The storage tank used for hydrogen and oxygen gases in the experimental URFC system

The specifications of the cylinder were:

- Volume: 80 cm³
- H×W×D: 265 mm ×100 mm ×100 mm
- Accuracy of volumetric measurements: ±5 ml.
5.5.1.2 Power supply

The DC power supply that was used in the electrolyser mode was from Instek-GW (model: GPC-1850D). The apparatus has two outputs 0-18V/0-5A and the outputs can be used in series and parallel configuration. The instrument error for current is ± 0.005A and for voltage is ±0.005V. The DC power supply is shown in Figure 79.

![DC power supply](image)

**Figure 79:** The DC power supply used in the electrolyser mode

5.5.1.3 Hydrogen extraction cabinet

The experiments were done inside a cabinet designed specifically for hydrogen related experiments (Figure 80), as described by Paul (2008). Wallner et al. (2009)’s comprehensive review on safety consideration for testing on hydrogen was also used in planning the experiments conducted.
5.5.2 The experimental setup

The experimental setup that was used to evaluate the performance of the PEM URFC with integrated hydrogen storage electrode is shown in Figure 81. The experiment was conducted in the hydrogen cabinet in the Renewable Energy Laboratory at RMIT University Bundoora East campus.
Figure 81: The schematic of the experimental set up (modified from Doddathimmaiah 2008)

The experimental setup consisted of a single-cell PEM URFC with an activated carbon electrode, two hydrogen and oxygen storage tanks, a water supply tank, a variable resistor, and several multimeters to measure voltages and currents. In the electrolyser mode (Figure 82), the DC power supply supplied DC electricity and the water supply tanks provided distilled water to the cell. The produced hydrogen and oxygen were then stored in the gas storage tanks. In the fuel cell mode (Figure 83), only oxygen was supplied to the cell from the oxygen that was already produced in electrolyser mode. The hydrogen and water tubes were closed in the fuel cell mode. The cell was connected to a variable resistor. The cell voltage and current were recorded as a function of time.
Figure 82: The experimental setup in electrolyser mode

Figure 83: The experimental setup in fuel cell mode
5.6 EXPERIMENTAL PROCEDURE

5.6.1 Electrolyser mode

In electrolyser mode, distilled water was supplied to the oxygen electrode and the cell was allowed to equilibrate at room temperature for 18 hours prior to the tests. The cell was polarised by increasing voltage from 1.0 V in 0.1 V steps. The cell was held at each voltage for three minutes to stabilise the corresponding current. In all the tests, the current became stable in the first minute, but to follow the same procedure in all the tests, three minutes was allowed for each voltage before reading the corresponding current. The volumes of hydrogen and oxygen gases that were produced during the electrolyser mode were also recorded. The electric circuit of the electrolyser mode is shown in Figure 84.

![Figure 84: The electric circuit in the electrolyser mode](image)

5.6.2 Fuel cell mode

After the electrolyser mode, the PEM URFC with integrated activated carbon electrode was operated in fuel cell mode. Before the fuel cell mode, the connecting tubes were closed and
the cell was allowed to rest for 15 minutes to change the setup for fuel cell mode. The electric circuit of the fuel cell mode is shown in Figure 85.

In the fuel cell mode, only the oxygen that had been already produced in the electrolyser mode was fed back to the oxygen electrode. The hydrogen gas was removed and the channel on the hydrogen cell was filled with water to remove any produced hydrogen gas that had been trapped in the channel or in the GDL. The hydrogen electrode was filled with water to remove the remaining hydrogen gas from the gas diffusion layer of the hydrogen electrode and also increase water content of the hydrogen electrode to facilitate the possible proton conductivity from the composite electrode. The PEM URFC was connected to a variable resistor and the change in current and voltage of the PEM URFC were recorded. The level of oxygen in the oxygen storage tank was also checked before and after the fuel cell mode to see if any oxygen has been consumed.

![Figure 85](image)

**Figure 85:** The electric circuit in the fuel cell mode

In retrospect, the variable resistor should have had a much higher max value in this case, as explained later.
5.7 EXPERIMENTAL RESULTS

5.7.1 Voltage-current characteristics

The voltage – current characteristics of the composite electrodes in the experimental cell are presented in the Figures 86 to 89. The cells were allowed to equilibrate for 18 hours at room temperature prior to the tests. From the tests it can be seen that the over-potential increases after each cycle in electrolyser mode. In other words, after each test, a higher voltage is needed to produce the current that had been achieved in the previous test. The performance of electrolysers and fuel cells are normally reported in current density (A/cm$^2$) instead of current. Hence, the results of the cells are presented in current density so that the reader can directly compare these results with the performance of normal PEM URFCs and stand-alone PEM electrolysers and PEM fuel cells. The sudden jumps in Figure 86 are due to sudden changes of resistance. In the other experiments the change of resistance was done more smoothly.
Figure 86: The measured polarisation curves for the ACN1 (bottom: the results in the discharge mode in larger scale)
**Figure 87:** The measured polarisation curves for the ACN2 (bottom: the results in the discharge mode in larger scale)
Figure 88: The measured polarisation curves for the ACS1 (bottom: the results in the discharge mode in larger scale)
Figure 89: The measured polarisation curves for the ACS2 (bottom: the results in the discharge mode in larger scale)

In all the tests the hydrogen gas and oxygen gas evolved were collected in the gas storage tanks. For all the tests the ratio of collected oxygen gas to hydrogen gas was 1:2. The method of measuring of produced hydrogen gas and oxygen gas was by counting the number of gas
bubbles that had been produced in the gas storage tanks. Since the gas storage tanks are transparent and the connecting gas tubes have been connected to the lower gas inlet of the tanks, the produced gases would go through the water inside the tank before being stored on the top of the gas storage tanks. The current density in the electrolyser mode was very low, even at high voltages (above 2.5 V) and so the amounts of produced bubbles were low and countable. To obtain the ratio of oxygen gas and hydrogen gas, the number of bubbles in each of the hydrogen storage tank and oxygen storage tank was counted. It was always found that the number of hydrogen bubbles was very close to twice that of the oxygen bubbles. In all the tests, the performance of the cells in electrolyser mode depreciated after each cycle.

In hindsight, a higher resistance should have been used to prevent the sudden change from the open voltage to the 100 ohm resistance that can be seen in all the tests. An interesting founding is that as the load was reduced the current also reduced. In a normal fuel cell as the load reduces the current increases. This may suggest that the current obtained from this test is because of a potential difference between the electrodes, not an electrochemical reaction (proton transfer).

The measured performances of several normal PEM URFCs with various catalysts have been presented in Figure 90. The results were obtained by Doddathimmaiah (2008). The results showed that these PEM URFCs drew more than 0.2 A/cm² of current at an applied voltage of 1.8 – 1.9 V. The results also showed that in the fuel cell mode the voltage smoothly decreased by increasing current density. Current densities of above 0.1 A/cm² were measured for the normal MEAs.
To compare the results in the electrolyser mode, the performance of the normal URFC with an MEA containing 2 mg/cm^2 Pt black on the hydrogen electrode and 2 mg/cm^2 of Pt and 2 mg/cm^2 of IrRuOx as catalysts on oxygen electrode (blue line in Figure 90) is compared with the average values of the URFCs with composite MEAs in Figure 91. It should be noted that the composite MEAs did not have any catalysts on their hydrogen electrodes, but had similar catalysts and loadings on the oxygen electrodes. Although, the trends of the performance of the URFCs with composite MEAs are similar to that of the normal MEA, the former needed a larger voltage to withdraw a given current. For example, at 1.8 V, the URFC with normal MEA drew 0.09 A/cm^2, while the URFC with ACN1 electrode drew 0.003 A/cm^2, ACN2 0.011 A/cm^2, and ACS1 and ACS2 had not started to withdraw any current.
Figure 91: The performance of the fabricated composite MEAs compared to a normal MEA with same catalyst types and loading on oxygen electrode in the electrolyser mode.

To compare the results in the fuel cell mode, the performance of the URFC with normal MEA with 2 mg/cm² PtB on the hydrogen electrode and 2 mg/cm² of Pt and 2 mg/cm² of IrRuOx as catalysts on oxygen electrode (blue line in Figure 90) is compared with the values of the last cycle of the composite MEAs in Figure 92. In the fuel cell mode, the cells with the composite electrodes behaved completely differently to the normal PEM fuel cell; i.e. the highest current density was achieved at the highest voltage, rather than at the lowest voltage as is the case with a normal fuel cell. This abnormal behaviour was probably because first value of the load resistance was too low, so that a current beyond the capability of the cell to sustain was drawn right at the start. All the composite MEAs have lower open-circuit voltages than the normal URFC: the normal URFC’s open circuit voltage was 0.75 V, but the URFCs with composite electrodes had open circuit voltages less than 0.63 V.
5.7.2 Charging with constant current

The cells were charged at 0.01 A for 18 hours, that is, equal to 18 to 33 mA/g of activated carbon in composite, depending on the mass of activated carbons in the composites. The sensitivity of the DC power supply was 0.01 A, so the lowest value that could be used was 0.01 A. Selecting this value meant that the cells would be charged at a voltage of around 2 V, but at the same time, because of the sensitivity of the DC power supply, the relative error of the instrument became very high, *i.e.* 50% (0.01 A ± 0.005A). Selecting higher currents would decrease the instrumental error in the experiment but meant charging the cells at higher voltages that increases the chance of damaging membrane. For instance, in order to charge the cell at the current of 500mA/g that has been typically used by the research group of Jurewizs, Frackowiak, and Beguin (*e.g.* Jurewicz et al. 2001; Jurewicz et al. 2002; Beguin et al. 2006a; Lota et al. 2011), a voltage of about 3 V would have been necessary, which would have adversely affected the membrane in a long experiment. It should be noted that in the constant-voltage tests, the voltage in the electrolyser mode had been raised to 3 V, but it
was only for a short period of time. Each voltage in the constant-voltage tests had only been applied for three minutes. The constant-current tests were set to be done for much longer period of time, i.e. 18 hours. The discharge values of the composite electrodes are shown in Figure 93 to Figure 96. These values are reported in discharge current per mass of activated carbon that has been used in its composite electrode.

**Figure 93:** The discharge mode of the ACN1 electrode after charging at a constant current of 32 mA/g of activated carbon
Figure 94: The discharge mode of the ACN2 electrode after charging at a constant current of 18 mA/g of activated carbon
Figure 95: The discharge mode of the ACS1 electrode after charging at a constant current of 30 mA/g of activated carbon
Figure 96: The discharge mode of the ACS2 electrode after charging at a constant current of 29 mA/g of activated carbon

The cell with the ACN1 electrode was discharged at two different values of resistance that explains the sudden jump in the current. In the other tests the resistances were reduced gradually that led to the smooth curves. All the curves show similar trends to each other. The discharge values of each cell are shown in Table 15. The discharge value is calculated from
the surface below the current density-time curves. In the graphs, the currents densities are calculated from dividing the discharge current to the mass of activated carbon in the composite electrodes. It is should be noted that, based on the Faraday’s law, the equivalent charge of 1wt% hydrogen storage is about 274 mAh/g (Beguin et al. 2006a). Further a much higher charge current per unit mass of activated carbon (500 mA/g) was typically used in measuring the electrochemical hydrogen storage in KOH electrolytes (for example, Beguin et al. 2006a). But in this thesis, using such a high charge current could only have been achieved by applying a high potential (above 3 V), which could have damaged the nafion membrane in the duration of the constant current charge.

In Table 15, the hydrogen gas and oxygen gas productions in the electrolyser mode are reported. The produced hydrogen gas and oxygen gas were stored in the gas storage tanks during electrolyser mode operation. Considering the large instrument sensitivity (± 5ml), the values of hydrogen gas and oxygen gas have been round up to the closest value shown on the storage tanks. The volume ratios of hydrogen to oxygen were in the range 1.8 to 2.3, but all these ratios had an error of around ±0.5.

As can been seen in the Table 15, there is a difference between the values of hydrogen gas production among the composite MEAs (or consequently, difference between values of oxygen gas production). However, the duration of constant-current charge (18 hours) was the same for all the composites and the charge current (0.01 A) was also the same for all the composite MEAs. This means that the charge capacity (Ah) and consequently gas production should be the same for all the composite MEAs. The reason for the difference between the values of oxygen (or hydrogen) gas productions is probably therefore simply because of the accuracy of the constant current setting on the DC power supply. The accuracy of the DC power supply is 0.01 A ± 0.005A. This means that no smaller values can be seen between 0 and 0.01 A or between 0.01 A and 0.02 A. In other words the value of 0.01 A that has been used in the constant-current charges could be between 0.005 A and 0.015 A. The values of actual currents are calculated from the values of produced oxygen gas and are shown in Table 15.
### Table 15: The summary of the performance of the composite electrodes with constant-current charge at 0.01 A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of the composite electrode, [g]</th>
<th>Mass of GDL, [g]</th>
<th>Mass of the composite material in the composite electrode, [g]</th>
<th>Charge density per mass of activated carbon in the composite electrode, [mA/g]</th>
<th>Charge capacity, [mAh/g]</th>
<th>Discharge capacity, [mAh/g]</th>
<th>Produced hydrogen gas in the electrolyser mode, [ml]</th>
<th>Produced oxygen gas in the electrolyser mode, [ml]</th>
<th>Ratio of hydrogen to oxygen gas in the electrolyser mode</th>
<th>Accrual charge current, calculated from the produced oxygen gas [A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN1</td>
<td>0.707</td>
<td>0.082</td>
<td>0.624</td>
<td>0.312</td>
<td>33</td>
<td>594</td>
<td>0.68</td>
<td>70 ± 5</td>
<td>30 ± 5</td>
<td>2.3 ± 0.5</td>
</tr>
<tr>
<td>ACN2</td>
<td>1.171</td>
<td>0.077</td>
<td>1.094</td>
<td>0.547</td>
<td>18</td>
<td>324</td>
<td>0.44</td>
<td>55 ± 5</td>
<td>30 ± 5</td>
<td>1.8 ± 0.5</td>
</tr>
<tr>
<td>ACS1</td>
<td>0.753</td>
<td>0.076</td>
<td>0.677</td>
<td>0.338</td>
<td>30</td>
<td>540</td>
<td>0.48</td>
<td>80 ± 5</td>
<td>40 ± 5</td>
<td>2.0 ± 0.4</td>
</tr>
<tr>
<td>ACS2</td>
<td>0.772</td>
<td>0.092</td>
<td>0.680</td>
<td>0.340</td>
<td>29</td>
<td>522</td>
<td>0.49</td>
<td>60 ± 5</td>
<td>30 ± 5</td>
<td>2.0 ± 0.5</td>
</tr>
</tbody>
</table>
5.8 DISCUSSIONS

This chapter provides information on the processes and the challenges of fabricating the full-size composite electrodes. From each of the two selected activated carbon that were selected in Chapter 4, two full-size composite electrodes were fabricated. The four composite electrodes were hot pressed to nafion 115 membrane and oxygen electrode to fabricate membrane-electrode-assembly. The MEAs were tested in an experimental PEM URFC cell that was specially designed and modified for this project.

In the electrolyser mode the composite MEAs were first tested in constant-voltage to obtain the polarisation curve in the electrolyser mode. The cells were at each voltage for three minutes, so that current would become stable. The results are shown in Figures 86 to 89. A comparison is made between the performance of a normal MEA and the composite MEAs in Figure 91. The composite MEAs had similar catalysts and catalyst loading on the oxygen electrode, but had no catalyst on the hydrogen electrode. As can be seen in this figure, the composite MEAs needed a much higher voltage to reach the same current density as the normal MEA. The voltage of ACN1 was increased to 3.5 V, but in the later tests on the other composites, the maximum voltage was set to be 3 V. This was to prevent damaging nafion membrane in a high voltage. The current densities that were obtained at the 3 V were 0.015 A/cm² for ACS1 and ACS2, 0.036 A/cm² for ACN1 and 0.099 A/cm² for ACN2. The current is drawn in the electrolyser mode at 1.6 V for ACN1, 1.5 V for ACN2, 1.9 V for ACS1 and 1.8 V for ACS2.

The discharge performance of the composite MEAs that had been charged at a constant-current charge are also shown in Figures 86 to 89. The open voltages of the ACN1 were between 0.55 and 0.65 V. The open voltage of the ACN2 was 0.55 V. The discharge performance of the ACN2 was measured only in the first cycle, because the DC power supply was not available for further tests. The open voltages of the ACS1 were close to 0.33 V. The open voltages of the ACS2 were between 0.33 and 0.35 V. All the samples show similar behaviour in the discharge mode, i.e. the current decreases with decreasing voltage. A comparison is made between the performance of a normal URFC and the URFCs with composite MEAs in Figure 92. The composite MEAs had similar catalysts
and catalyst loading on the oxygen electrode, but had no catalyst on the hydrogen electrode. The normal MEA show a larger current density and higher open voltage.

The composite MEAs were also tested by charging the MEAs with constant-current for a long period of time and the discharge performance is shown in Figure 93-96. The charge capacities of composite electrodes were between 324 mAh/g and 594 mAh/g per unit mass of activated carbon. Although these charge capacity is similar to the values of Jurewicz et al. (2004) and Jurewicz (2009), the charge current per unit mass of aC in electrode used in this thesis was much lower. In the above references, a charge current per unit mass of aC in electrode of 500 mA/g was applied, but in this thesis the charges current per unit mass of aC in electrode were very much lower, at between 18 and 33 mA/g. The reason for choosing lower charge current per unit mass of aC in electrode that with these charge current per unit mass of aC in electrode, the composite MEAs were charged at voltages close to 2 V. Increasing charge current per unit mass of aC in electrode meant increasing the voltage to above 3 V that would have increased the chance of damaging the nafion membrane. The discharge capacities of the MEAs were measured by measuring current and the duration of the discharge. The discharge capacity that is shown in Table 15 is calculated in mAh per unit mass of activated carbon in the composite electrodes. The discharge capacities were less than one mAh/g.

In the experiments conducted to date for this thesis, the integrated composite electrodes of activated carbon and nafion have shown no detectable signs of reversible hydrogen storage. There are some key factors that led to this conclusion.

- The behaviour of the cells in fuel cell mode in Figure 86 to 89 showed no resemblance to a normal PEM URFC in fuel cell mode. If hydrogen was reversibly stored in the hydrogen electrodes of the cells, the cell would work like a fuel cell for at least a short time.
- The cells in Figure 86 to 89 show a very low open circuit voltage. If hydrogen was reversibly stored in the electrodes, the voltage in fuel cell mode would be higher than those values. The maximum open voltages of the URFCs with composite MEAs were between 0.33 V and 0.63 V, with the highest value being for ACN1.
- The value of discharge is very low. The discharge values are less than 0.68 mAh per unit mass \(i.e.\) per g) of activated carbon in the composite electrodes. The
The main limitation of the experiments is the significant measurement errors in certain parameters when testing URFCs with composite MEAs. The readings from the gas storage tanks have an uncertainty of ± 5 ml. This volume of hydrogen is equal to more than 0.12 wt% hydrogen in the activated carbon in the composite electrodes.

The DC power supply also had a significant error. The accuracy of the DC power supply was ±-0.01 A and it was used at 0.01 A constant current for charging the composite electrodes, that means the actual current was 0.01 A ± 0.005 A. This error affects the actual value of current that was used in the charging modes. The actual current of the DC power supply was calculated from the amount of oxygen gas that had been produced in the charging mode. Although, the data taken from the DC power supply was 0.01 A, the calculation based on oxygen gas formation showed that the actual values are between 7 to 9 mA.

Another limitation of the tests was the relatively low charging currents used per unit mass of activated carbon in the composite electrodes (that is, mA/g) per gram of. The charging currents per unit mass used in this thesis were 18 to 33 mA/g, which were far less than those used to store hydrogen electrochemically in KOH electrolytes (that is, ~500 mA/g).
The reason for using the low charging currents density was to protect nafion membrane in the long duration of constant-current charge. Charging the composite MEAs with a current density close to 500 mA/g would have meant applying a voltage to the URFC above 2.5 V, which could have damaged the nafion membrane in the cell.

In summary, the results of the testing of the URFCs with composite aC-nafion electrodes obtained in the present thesis have not indicated any sign of reversible hydrogen storage. The possible reasons for the unsuccessful results are discussed in Chapter 6.
6. DISCUSSIONS OF THE RESULTS

6.1 POSSIBLE EXPLANATIONS FOR THE EXPERIMENTAL RESULTS

6.1.1 Summary of the key findings

The characterisation of the composite materials showed good proton and electron conductivity. However, the tests on the composite electrodes in the experimental cell did not show any noticeable reversible hydrogen storage. The composite electrodes were tested under constant voltage to measure their performance in electrolyser mode. The maximum voltage was kept below 3V in order to protect the nafion membrane. The results showed that the URFCs with composite electrodes generally needed a much higher voltage to draw a given current compared to a normal URFC with an MEA with the same catalysts on oxygen electrode and Pt on hydrogen electrode. The current densities that were obtained at 3 V were 0.015 A/cm² for ACS1 and ACS2, 0.036 A/cm² for ACN1 and 0.099 A/cm² for ACN2.

In order to measure the discharge performance of the URFCs with composite aC-nafion electrodes, the storage electrodes were charged under constant current for 18 hours. The charge capacities were between 324 mAh/g and 594 mAh/g per unit mass of activated carbon. The steady-state voltage required to achieve the intended constant current (0.01A) was about 2V.

The discharge profiles of the storage electrodes did not indicate a significant amount of hydrogen storage. The discharge capacities of the composite MEAs were between 0.44 and 0.68 mAh/g of activated carbon, which corresponded to between 0.001 and 0.002 wt% of hydrogen. In this chapter, some hypotheses are developed in an attempt to explain these results.
6.1.2 Limited nafion penetration into activated carbons

The values of ultra-micro-porosity of the activated carbons that have been used in fabrication of the composite electrodes in this thesis were 794 m²/g for ACN and 870 m²/g for ACS. These values were obtained from CO₂ adsorption isotherm at 273 K, which has commonly been used in previous works to identify ultra-micro-porosity (Jurewicz et al. 2004). To put these values in perspective, Babel and Jurewicz (2008) used an activated carbon sample with a surface area of 2064 m²/g based on nitrogen adsorption measurement and found that it was capable of electrochemically storing 1.89 wt% hydrogen with a KOH electrolyte. Jurewicz et al. (2004) used an activated carbon with 765 m²/g and found 1.3 wt% hydrogen storage, again using a KOH electrolyte.

An earlier test of electrochemical hydrogen storage using a liquid acidic electrolyte showed that an activated carbon with BET surface area of 1500 m²/g could reversibly store hydrogen close to 1 wt% (Jurewicz et al. 2002). It should be noted that the CO₂ adsorption isotherm measurement of the value of ultra-micro-pores was not done in that paper. But the electrochemical hydrogen storage with a KOH electrolyte of the same activated carbon showed close to 2 wt% reversible hydrogen storage, which may indicate that the ultra-micropore surface area of the activated sample was close to 2200 m²/g on the basis of Babel and Jurewicz’s (2008) findings.

Since the values of the CO₂ adsorption isotherms of ACN and ACS are between the values used by Babel and Jurewicz (2008) and Jurewicz et al. (2004), the ACN and ACS were expected to at least store hydrogen in the range of up to 1.3 to 1.9 wt%. However, in chapter 5, the discharge values of the composite electrodes were found to be less than 0.7 mAh/g, that is, less 0.002 wt%.

One possible explanation of this very low reversible hydrogen storage in the composite electrodes is that in electrolyser mode protons may have failed to enter the ultra-micropores. As discussed in chapter 3, the ultra-micro-pores, i.e. pores with diameter smaller than 0.7 nm, have been identified as the primary hydrogen storage sites in activated carbons (Vix-Guterl et al. 2005). In the composite material, nafion is mixed with the activated carbon particles to provide a proton conducting medium to facilitate proton
transfer from the nafion membrane of the URFC into the storage sites of the activated carbon. However, the length of a single extended nafion molecule at ~100 nm is around double the diameter of the lower end of the range for the diameter of macro pores (macro pores > 50 nm). So it is most unlikely that the nafion would have penetrated to any significant extent into even the macro pores of the activated carbon, let alone into meso, micro and ultra-micro-pores.

In the aC-nafion composite electrodes fabricated in this study, the proton conductivity in the composite materials should not have been an obstacle for proton transfer in the composite electrodes, since the measured proton conductivity of the composite materials showed values close to that of the nafion membrane itself. The experimental value found here for the proton conductivity of the nafion membrane was 0.10 S/cm, while those for the ACN and ACS composite aC-nafion materials were measured to be 0.05 S/cm, and 0.09 S/cm respectively. Hence it can reasonably be expected that the protons in the experimental proton flow batteries were transferred from the nafion membrane of the URFC within the composite electrode to the surfaces of activated carbon particles, and possibly to a more limited extent into some of the macro-pores. However, if nafion failed to penetrate into ultra-micropores, as appears highly probable, protons would need to rely on another medium to reach the ultra-micropores.

Some bulk water may have entered the macro, meso, micro and ultra-micropores of the composite electrode, since protons emanating from the nafion membrane would be hydrated and hence in the form of hydronium (H₃O⁺) or higher order solvated ions, the ion, H₂O₂⁺ or the H₈O₄⁺ (Choi et al. 2005). Hence the protons may have dragged through the electrode water molecules that accumulate in the pores of the aC. It should be stated at this point though that the extent of such water penetration into the aC was not able to be measured within the present study, and thus remains uncertain. The diameter of a hydronium ion, H₃O⁺, is about 0.28 nm (Choi et al. 2005) and so it can probably penetrate into some of the ultramicro pores, which have diameters up to 0.7 nm. However, the higher-order solvated ions, H₅O₂⁺ or H₉O₄⁺ may have been inhibited from entry into the ultra-micropores.
A tentative hypothetical picture of the situation with respect to proton transfer within an aC-nafion composite electrode is thus advanced in Figure 97. The main features in this schematic picture are the following. Firstly, the limited penetration of nafion into the porous structure the activated carbon particles is represented by showing the nafion covering only the surface of activated carbon particles, and penetrating into macro-pores to only a limited extent. Secondly it is assumed in this figure that bulk water does fill pores of all sizes, including ultra-micropores within the aC particles. Hence the only route for protons to travel from the extremities of the nafion medium to the surfaces within ultra micropores is via conduction in bulk water through macro, meso, micro and then finally the ultra-micropore spaces.

Figure 97: The schematic of role of bulk water in defusing protons into a activated carbon particle.
In Figure 97, the upper-left image shows that nafion is coating the outer surface and some of the surface macro pores, but is unable to penetrate into pores smaller than macro-pores. The upper-right picture is the magnified image of the activated carbon particle and shows mesopores and micropores that have been filled with water. Nafion is shown to be connected to the water in the meso-pore channel. The bottom-right picture is the magnified image of the activated carbon particle showing micropores and ultra-micropores that are filled with water.

The only way protons can transfer from the surfaces and/or macropores of the activated carbon to the ultra-micropores is by the bulk water. However, the proton conductivity of water is a several orders of magnitude lower than nafion (Zenyuk and Litster 2012). Hence this low proton conductivity of water may inhibit proton transfer to the ultramicropores and might explain the unsuccessful hydrogen storage in the composite electrodes investigated in this thesis.

It will therefore be useful in future research to conduct computer modelling to investigate movement of protons in the pore structure of activated carbons and to check to what extend $\text{H}_3\text{O}^+$, $\text{H}_5\text{O}_2^+$, and $\text{H}_9\text{O}_4^+$ ions enter ultra-micropores. Moreover, Molecular Dynamic modelling may be appropriate in discovering their movements (see, for example, Hofmann et al. 2007).

### 6.1.3 Existence of oxygen groups on the activated carbon surfaces

The EDS results of the activated carbons in Chapter 4 show that the oxygen content of the activated carbons is 24.6 wt% for ACN and 24.4 wt% for ACS. This substantial oxygen concentration might also hinder hydrogen storage in the materials. In fact, Bleda-Martinez et al. (2008) state that the higher the amount of oxygen groups, the lower the electrochemical storage of hydrogen on activated carbon in KOH alkaline. However, Bleda-Martinez et al. (2008) have not quantified the amount of oxygen groups in the activated carbon samples. It seems that when oxygen groups saturate the storage sites in an activated carbon, these ultramicropore sites cannot contribute to the hydrogen storage.
The high oxygen content in the activated carbon samples in the present study may be due to washing process employed in the KOH chemical activation method. This washing step cannot be omitted since it is necessary to remove potassium from the samples. It is therefore suggested that in future work additional effort is made to remove oxygen groups from the samples. Such removal could be accomplished as follows. After washing and before being mixed with nafion, the samples should be dried at a high temperature under an inert gas and in absence of oxygen. In this way, the activated carbon would not be exposed to air and can be directly taken from the furnace and mixed with nafion. Horizontal furnaces are capable of cooling the sample down to room temperature under an inert gas, so at no point during heating or cooling are the samples exposed to air, that is, oxygen and humidity.

The problem associated with this suggestion is that porosity of the activated carbon can be altered after this heat treatment. From the literature of carbon activation, it is likely that the pores of an activated carbon widen from micropores to mesopores when the material exposed to high temperature for a long period of time (Marsh & Rodriguez-Reinoso 2006; Wang and Kaskel 2012). The heat treatment after washing samples of activated carbon may have similar effects.

To test the effect of the second heat treatment on porosity, a sample of activated carbon could be tested with and without the heat treatment after washing step. If the second heat treatment is found to widen the micropores to mesopores and decrease the contribution of ultra-micropores, proper consideration should be paid in setting parameters like final temperature and carbon to KOH ratio in the activation process.

In addition, oxygen groups can be formed on the activated carbons during mixing with nafion solution, and during the protonation step in making the composite electrodes. The nafion solution contains 45 wt% 1-propanol, 5 wt% ethanol, and 45 wt% water. The water and alcohol that constitutes 95 wt% of the nafion solution might lead to formation of oxygen groups on the surface of activated carbons. During the protonation step, the composite electrode is chemically treated by being boiled at sulphuric acid to ensure proper nafion proton conductivity in the composite electrodes. After that, the composite electrodes
are boiled in distilled water to remove the remaining sulphuric acid from the composite electrodes.

It thus needs in future to be checked whether oxygen groups are formed on the activated carbons when they are chemically treated with 1-propanol, ethanol, water, and sulphuric acid. To test this, one sample of activated carbon that has been through the heat treatment after washing and has not been exposed to air (so is oxygen group free), can be mixed with the above chemicals and the sample tested with X-ray photoelectron spectroscopy (XPS). The X-ray photoelectron spectroscopy can give information about existence and the characteristics of the oxygen bonds. The EDS method can also be used to detect the amount of oxygen content in the activated carbons. However, the EDS method cannot provide any information about the oxygen groups. In fact, oxygen may form bonds with other elements in an activated carbon such as Na, Al, and Si, and not just carbon. XPS is the method that can distinguish bonds between oxygen and other elements.

It should be noted that in the literature on nafion and carbon composites, the carbon has been used for three main purposes: to transfer electrons in mix transfer of proton and electrons (Tortello et al. 2012); to improve the mechanical properties of nafion membrane (Wang et al. 2008), and to increase proton conductivity of nafion membrane by increasing water uptake (Chien et al. 2013). In none of the above applications, the surface chemistry and the existence of oxygen group on the activated carbon have been investigated. The lack of investigation in this matter may suggest that the oxygen groups on carbon do not have a significant effect on these applications. But in the application of direct hydrogen storage in a composite electrode of activated carbon and nafion, the existence of oxygen group would have a significant effect on the results.

If indeed oxygen groups are formed during mixing and protonation of nafion, an alternative proton conducting medium may need to be used instead of nafion. Ideally the new proton conducting medium should not have oxidation chemicals in its solution and should eliminate the need for protonation with sulphuric acid or any other oxidising agent.
6.1.4 Competitive reactions that prevent hydrogen storage

Three reactions are likely to occur simultaneously in the electrolyser mode in this research project. The first two reactions are hydrogen storage reactions and the other reaction (Tafel) is the hydrogen desorption reactions:

Hydrogen adsorption reaction

\[ C + e^- + H^+ \rightarrow CH_{adsorbed} \]

Hydrogen storage reaction

\[ CH_{adsorbed} \rightarrow CH_{absorbed} \]

Tafel:

\[ 2 CH_{adsorbed} \rightarrow H_2 + C. \]

The first reaction encourages adsorption of hydrogen on the surface of activated carbon. These adsorbed hydrogen atoms can later be absorbed and stored in the composite electrodes via the second reaction. The absorbed hydrogen can later be released again from the composite electrode during fuel cell mode (discharge). The Tafel reaction encourages the dissociation of adsorbed hydrogen from the surface of activated carbon and forming hydrogen gas.

Another explanation for the apparent lack of hydrogen storage in the composite electrodes might be the simultaneous competition between the adsorption reaction and absorption reaction on the one hand, and the Tafel reaction on the other. The Tafel reaction produces hydrogen gas from the weakly adsorbed hydrogen and so is needed to be prevented in the concept of this research project. Because the PEM URFC is tested at the room temperature, i.e. \( \sim 300 \) K, the adsorbed hydrogen atoms may have enough energy to escape the adsorption state and go through desorption reactions. Although the experiments of electrochemical hydrogen storage have been done at room temperature, in those studies an alkaline electrolyte was used. The results of those papers suggest that existence of Volmer reaction together with Tafel and Heyrovsky reactions.
In the ideal case the rate of the adsorption of hydrogen should be a few orders of magnitude higher than the desorption reactions. The conditions that may reduce the rate of desorption reactions and at the same time increase the rate of adsorption of hydrogen on activated carbon are yet to be investigated. Such investigation has been carried out by other authors on alkaline electrolytes and the possible effects on the rates of absorption and desorption have been identified. For example, the research of Jurewicz et al. (2004) suggests that the rate of adsorption (and consequently absorption) reaction depends on value of charge per the munit mass of activated carbon in the KOH electrolyte. It should be emphasise that there is a difference between the ratio of discharge to charge on one hand and the amount of charge that the sample of activated carbon can retain. The ratio of discharge to charge decreases with increasing the amount of charge (amount of charge is in mAh per unit mass of activated carbon). The capacity of the activated carbon sample to retain its maximum hydrogen uptake increases with increasing with increasing the amount of charge.

Jurewicz et al. (2004) results showed that 92% of the charge was electrochemically stored in an activated carbon electrode when the charge value of 211 mAh/ per unit mass of activated carbon was used. But only 3% of the charge was electrochemically stored in the activated carbon electrode when the charge value of 14 333 mAh/ per unit mass of activated carbon was used. The majority of the discharge capacity is due to hydrogen storage rather than in the electrical double layer. Vix-Guterl et al. (2005) found that more than 85% of the discharge capacity in electrochemical hydrogen storage on activated carbons in KOH electrolyte is due to hydrogen storage and less than 15 % due to electric double layer capacitance.

A theoretical computer simulation needs to be done to investigate the probable reactions and the properties of bonds between hydrogen and carbon in composite electrodes of nafion and activated carbon. After identifying the possible resections, the simulation might also reveal the rate of the adsorption reaction against the desorption reaction in the various conditions (e.g. temperature, pressure, and voltage) of a working PEM URFC with composite electrodes of activated carbon and nafion.
6.1.5 Possible irreversible hydrogen storage

Another possible explanation for the unsuccessful results of these experiments might be that some hydrogen is actually stored in the composite electrode, but requires external activation energy, like thermal energy, to be released in the fuel cell (discharge) mode. In contrast to section 6.1.3 where the assumption was that the stored hydrogen forms a weak bond with carbon and could easily be dissociated from the carbon in charge mode at room temperature, it may instead be that the bond between hydrogen and carbon is so strong that in fact, it prevents hydrogen release in the discharge mode.

It should be noted that due to the significant instrumental error in electrolyser mode, in particular the low accuracy of gas storage tanks (± 5 ml), it was not possible to accurately detect possible irreversible hydrogen storage by comparing the levels of hydrogen gas and oxygen gas productions. The mass of ± 5 ml of hydrogen gas at the experiment condition (atmospheric pressure and 25°C), is equal to 0.4 mg. If this amount of hydrogen was stored in a composite electrode (for example ACN1), it would have been equal to 0.12 wt% hydrogen storage per unit mass of activated carbon in the electrode. The 0.12 wt% hydrogen storage capacity is equal to 32 mAh/g of discharge capacity. Considering that the discharge capacity was found to be less than 0.68 mAh/g, it is still possible that a lot more hydrogen may have been irreversibly stored in the activated carbon. The experiments in this research project cannot be conclusive about whether any hydrogen has been irreversibly stored in activated carbon or not.

If irreversible hydrogen has occurred in these experiments, two possible hypotheses can be developed. The first hypothesis is that the bond between hydrogen and carbon is strong and cannot be broken at the room temperature. The second hypothesis is about the low proton conductivity of bulk water in the fuel cell (discharge) mode. Considering the point in section 6.1.2 that states that some protons may have reached the ultra-micropores of the activated carbon in despite the low proton conductivity of bulk water in the composite electrode, another hypothesis can be developed. In this hypothesis, it is assumed that the condition in electrolyser mode, i.e. high potential deference between the two electrodes (about 2V), allows enough proton conductivity in the bulk water to transfer some protons from nafion to the ultra-micropores and the protons are stored in these sites. The condition
in fuel cell mode, that is low potential deference (about 0.3 V), may not have provided enough proton conductivity in the bulk water within the composite electrodes that allow proton transfer from ultra-micropores to the nafion polymer of the composite electrodes. In this case the hydrogen atoms are irreversibly stored in the activated carbon.

If hydrogen is irreversibly stored in a composite electrode, the performance of the composite electrode in the electrolyser mode would be degraded because the storage sites become saturated with this stored hydrogen. Although the results in chapter 5 show such degradation with increasing number of electrolyser-fuel cell cycle, the number of cycles is far too small to get a plausible confirmation. Moreover, there might be other explanations for the degradation of composite electrodes in electrolyser modes, like chemical corrosion. More investigation is necessary before any conclusion is made about this hypothesis.

6.2 FINDINGS

This chapter provides possible explanations for the results of detecting reversible hydrogen storage in the composite electrodes of nafion and activated carbon that were integrated in a PEM URFC experimental cell in chapter 5. These possible explanations are:

- Limited penetration of nafion into activated carbon and the low proton conductivity of bulk water
- Existence of oxygen groups on the surface of activated carbon pores that might inhibit access to hydrogen storage sites
- Higher rate of desorption reactions to sorption reactions in the electrolyser mode
- Possible irreversible hydrogen storage in the composite electrodes

Several hypotheses have been developed according to the above explanations. Further investigations to test the validity of these explanations are suggested in Chapter 7.
7. CONCLUSIONS AND RECOMMENDATIONS

7.1 RESPONSES TO THE RESEARCH QUESTIONS

7.1.1 What types of carbon material have been used in reversible and direct hydrogen storage?

Jurewicz et al. (2001) suggested that, even in studies of hydrogen storage in carbon nanotubes, it is disordered carbon that is contributing most to the hydrogen storage, as discussed in chapter 3. They concluded that the electro-decomposition of water is probably more efficient on other forms of carbon than it is on nanotubes, which tend to have relatively few defects. Jurewicz et al. (2002) showed that the same form of activated carbon can store four times more hydrogen by the electrochemical decomposition of water in electrolyser mode than when subjected to hydrogen gas at a pressure of 70 MPa. Jurewicz (2009) demonstrated hydrogen storage of 2.17 wt% in activated carbon in an alkaline electrolyte. Values as high as 1.8 to 1.9 wt% were also reported for electrochemical hydrogen storage in activated carbon (Jurewicz et al. 2002; Li et al. 2005; Fang et al. 2006).

Because of the successful results of electrochemical hydrogen storage in the literature, in this thesis various forms of activated carbon had been used to test for reversible and direct hydrogen storage. A comprehensive review of electrochemical storage of hydrogen in activated carbon revealed that the ultramicro-pores smaller than 0.7 nm are the main storage sites. So the ideal activated carbon for this thesis should have had a high surface area of ultramicro-porosity. According to the literature, a measurement of ultramicro-pores is usually obtained in from CO₂ adsorption isotherm at 273 K. At the same time, because the activated carbon needed to be mixed with a proton conducting solution in this thesis to make a composite, the activated carbon should also have had large values of meso and macro porosity to allow the proton conducting polymer penetrate the activated carbon particles.
Lignin-like precursors have been found to be good candidates for electrochemical hydrogen storage (Babel and Jurewicz 2008). Chemical activation with KOH is found to be the method of choice in activating precursors. The ratio of KOH to precursor is found to be optimised between 3:1 and 4:1 for high microporosity (Lozanno-Castello et al. 2001, Babel and Jurewicz 2008). Higher ratio of KOH to precursor leads to increasing mesoporosity (Lozano-Castello et al. 2001). The activation temperature should be between 700 and 800°C. At temperatures above 800°C, micropores widens to mesopores (Lua and Yang 2004). The heating rate of 5°C per minute is found to cause better microporosity development compared to higher heating rates (Lozano-Castello et al. 2001). Ideally, the activated carbon should have no surface oxygen groups. The higher the amount of hydrogen groups, the lower is the amount of hydrogen uptake by the activated carbon (Bleda-Martinez et al. 2008).

7.1.2 What is the proper procedure to fabricate activated carbon samples, the composite materials and the composite electrodes for this application?

There are three main activation methods: physical activation by CO₂ and steam, chemical activation by KOH, and replica method by silica templates, as reviewed in chapter 4. Among these methods, chemical activation gives more control over porosity and average pore diameter. It is also done at lower temperature compared to physical activation and the processing time is shorter (Yang et al. 2012). The KOH activation method was used in this thesis to fabricate successfully four samples of activated carbon from black coal and charcoal.

The best way to mix activated carbon and nafion solution would be sonication, although many research papers use stirring method. The mixing of activated carbon and nafion solution in this thesis was done at room temperature simply by stirring activated carbon and nafion, as it is the common way of mixing nafion and activated carbon (see, for example, Chien et al. 2012). No literature has been found on the effects of temperature and methods of mixing on the properties of composite materials of nafion and activated carbon. This can be a point of interest for future study to optimise the mixing parameters of nafion and activated carbon.
In the initial attempts to fabricate the full-size electrodes in this thesis, it became obvious that cracks are created in the composite electrodes that diminish electrode structural integrity. Moreover the composite material made was very brittle and could easily break under the compression stress in an experimental cell. To address this issue, a backing layer of carbon cloth was incorporated into the composite electrode. In addition to that problem, the solution casting of the composite electrode showed that, with just a single casting of the composite electrodes, major cracks eventuated. Consequently each composite electrode was coated two times to fill the cracks that were present after casting.

The nafion in the composite electrodes needed to be protonated. To carry out this process, the composite electrodes were boiled successively in distilled water, sulphuric acid, and again in distilled water, to assure that the nafion structure in the composite electrodes had sufficient proton conductivity.

7.1.3 What would be the performance of composite materials of carbon and proton conducting media in different levels of hydration?

The water uptake of the composite electrodes increased with increasing hydration. The samples were kept at a certain relative humidity for at least 42 hours to be in the equilibrium state with its environment. The water uptake of the composite materials in the fully hydrated state was varied from 45 wt % for ACK10 to 85 wt % for ACN. The ratio of the number of water molecules to SO$_3$ groups of the nafion polymer at the fully hydrated state was in the range of 55 (for ACK10) to 105 (for ACN), as shown in Figure 47. The large value of water uptake might be due to water absorption by activated carbon particles and/or the hollow macro volumes in the structure of the composite materials.

The volumetric expansion of the composite electrodes also increased with increasing the level of hydration in the composite electrode. As water is absorbed by nafion, the water channels surrounded on their walls by sulphonic acid groups start to swell (Zhao et al. 2011). The typical value of volumetric swelling for all, except one (ACN), of the composite materials was in the range of 22 % to 33 %. ACN showed an exceptionally high value of expansion of 59 % in the fully hydrated state.
The measured proton conductivity of the composite electrodes increased with increasing the level of hydration in the electrode. In this thesis, the through-plane proton conductivity was measured by EIS. When adding activated carbon to the nafion polymer, two factors were competing simultaneously. By adding activated carbon to the composite, the effective nafion in the cross-sectional area of the composite was reduced, and so the proton conductivity would be expected to decrease accordingly. On the other hand, by adding activated carbon, water uptake of the composite materials increased compared to a nafion membrane, which would tend to enhance proton conductivity. The results of EIS measurements revealed that the proton conductivities of ACN, ACK10, and AC4 in the fully hydrated state were all close to 0.045 S/cm. Fully-hydrated AC3 had a proton conductivity of 0.077 S/cm and ACS 0.089 S/cm. ACK2.5 had the highest proton conductivity when fully hydrated of 0.110 S/cm.

The measured electron conductivity of the composite electrodes decreased with increasing the level of hydration in the electrode. The electron conductivity significantly decreased with increasing level of hydration, in some cases by about 95% (e.g., ACK10). All the composite materials showed very low electron conductivity when fully hydrated, only about 0.5 - 2.3 S/cm. The reason for this behaviour can be seen in the water uptake and volumetric swelling of the composite materials. By absorbing water and swelling the distance between the carbon particles and the contact between the carbon particles are increased and so the number of contacts between carbon particles in the composite material is reduced. Another reason for the generally low electron conductivity of the composite materials may be that the carbon particles were partially coated with nafion polymer, which may have reduced the effective direct area of contact between the particle surfaces.

In the concept of a proton flow battery with a composite carbon-nafion electrode that has been investigated in this thesis, the composite electrode needs to be both a good electron and proton conductor in the fully hydrated condition. Although the proton conductivity of the carbon-nafion composite with full hydration was shown to be close to the proton conductivity of the nafion membrane itself, the electron conductivity was relatively low and needs to be improved. Higher electron conductivity ensures that electrons can easily be transferred throughout the composite electrode and increases the chance of hydrogen-carbon bonding in the composite electrode.
7.1.4 How does the performance of the URFCs with composite electrodes compare with that of typical standard URFCs?

In the electrolyser mode the URFCs with composite electrodes showed a large overpotential. For instance, a typical MEA with the same catalysts as the URFCs with composite electrodes and 2 mg/cm$^2$ of Pt as the catalysts on hydrogen electrode would draw about 0.2 A/cm$^2$ at a voltage of about 1.9 V (Doddathimmaiah 2008). The URFCs with composite electrodes drew less than 0.01 A/cm$^2$ at the same voltage. The big difference between the current of a normal URFC and the current of the composite URFCs may have been because of the lack of catalysts on the composite electrodes to facilitate the formation of hydrogen gas.

In the fuel cell mode, the behaviour of the URFCs with the composite electrodes was completely different from that of a normal URFC. In fact in the fuel cell mode, the URFCs with the composite electrodes had a very small electrical discharge, which in turn suggests that any reversible storage of hydrogen was itself very low, that is, less than 0.002 wt%.

7.1.5 Is it feasible to incorporate the fabricated composite electrodes into URFCs for direct reversible hydrogen storage?

The results of this research project might be interpreted as an unsuccessful test of the feasibility for direct reversible hydrogen storage in activated carbon electrode in URFCs. But it should be noted that the number of the experiments in this research is far too limited to make any general conclusion about the possibility of direct reversible hydrogen storage in activated carbon electrodes. Many types of activated carbon and proton conducting media should be tested before reaching such a conclusion. On the other hand, this research project has been successful in terms of identifying some limitations and constraints of the concept, and in pointing the way towards improved experimental procedures and electrochemical measuring techniques to find a more conclusive answer to this question.

The lack of observable hydrogen storage in the composite electrodes within the present project has a number of possible explanations, including:
• limited nafion penetration into the smaller pores of the activated carbons, in
  particular into ultramicro-pores, so that proton transfer to hydrogen storage sites
  would have to be though low-proton-conductive bulk water
• presence of oxygen groups on the activated carbon surfaces preventing access to
  hydrogen storage sites
• competitive reactions of hydrogen desorption and hydrogen gas formation that
  prevent hydrogen storage in the activated carbon
• irreversible storage of hydrogen in the activated carbon with a strong bond that
  needed a large activation energy for dissociation to take place in fuel cell mode.

These possible explanations of the results have been explained in more detail in chapter 6.

7.2 THE KEY CONTRIBUTIONS OF THIS THESIS

7.2.1 Activating carbon with KOH chemical activation method

In this thesis the methods of activating carbon have been introduced. Among the methods,
KOH chemical activation has been selected to be the best choice for the present application
because it is done under lower temperatures compared to physical activation method and
gives the operator better control over porosity development in the precursors.

The samples of activated carbons were fabricated from coal and charcoal precursors. The
methods to characterise the precursors have been identified. The precursors were powdered
and scanning electron microscopy technique has been used to monitor the structure and
grain size of the powders. Energy-dispersive electron spectroscopy (EDS) has been used to
determine the elemental composition and the carbon content of each precursor. The
powders of carbon have been carbonised, chemically treated with KOH, and activated
under nitrogen gas in a horizontal tube furnace. The parameters that could affect the
porosity of the activated carbons like final activation temperature, rate of temperature
increase, and ratio of carbon to KOH have been identified. The chemical mechanism of
KOH activation process was also explained and the reactions in each temperature range
have been identified in chapter 4. The necessary of washing step to remove potassium from
the activated carbons was highlighted.
The methods of characterising activated carbons were also presented in chapter 4. EDS was used to do the elemental analysis of the composition of the activated carbons. The adsorption isotherm was conducted with CO\textsubscript{2} at 273 K and N\textsubscript{2} at 77 K. The methods of interpreting the adsorption isotherm data, that are Brunauer-Emmett-Teller equation, Dubinin-Radushkevich equation, and Dubinin–Astakhov equation, have been explained in chapter 4 and the calculations to compute surface area from adsorption isotherm data and with those equations.

In summary, four samples of activated carbon were made from black coal and charcoal precursors and the samples were characterised by scanning electron microscopy, EDS, CO\textsubscript{2} adsorption isotherm at 273 K, and N\textsubscript{2} adsorption isotherm at 77 K.

### 7.2.2 Fabricating composite materials from activated carbon and nafion

In this thesis, the procedure of mixing nafion and activated carbon has been described. The method of fabrication was solution casting of the mixture in a mould. The activated carbon was stirred with nafion solution under room temperature and when most of the solvent in the mixture was evaporated the mixture was poured into a mould. The mould was placed in an oven over night and was post annealed at 120°C for two hours and then cooled down to the room temperature. The parameters of fabrication of composite material such as ratio of carbon to nafion, heat treatment temperature, and post annealing temperature have been presented and discussed in this thesis.

The composite materials were protonated by sulphuric acid. The procedure of protonation is necessary to ensure proper proton conductivity in the nafion of the composites. The composite materials were boiled in water, boiled in sulphuric acid, and boiled in water again. To ensure that the composite materials are free of sulphuric acid, the composite materials were rinsed under distilled water until the pH paper indicator showed no sign of acidity in the rinsed water. To investigate the structure of the composite materials, they have been observed under a scanning electron microscope. The surface and the cross sectional images of the samples were obtained. The cross-sectional images of the composite materials showed that a majority of the volume of the composite materials are
hollow spaces. This finding helped to explain some of the characteristics of the composite materials, i.e. water uptake and volume swelling.

7.2.3 Characterising the composite materials under various relative humidities

A method to obtain and maintain different values of relative humidities of the composite electrode samples has been developed and applied in this thesis. A desiccator jar was used for 0% relative humidity. For the 100% RH, the samples were placed in an open jar which was placed in a closed jar with water in it. The water was not in contact with the samples, but the samples were exposed to the saturated water vapour.

An apparatus was designed and manufactured for 75% relative humidity. The standard E104-02 of American society for testing and materials (ASTM) was used to design the apparatus that can create and maintain a constant relative humidity by using saturated salt solutions. Sodium chloride was used in a humidity chamber to create 75% relative humidity. The dimensions and amount of salt in the chamber was designed by the author in accordance with the ASTM standard. A digital hygrometer-thermometer was incorporated in the humidity chamber to monitor the relative humidity and temperature in the chamber.

7.2.4 Dual proton and electron conductivity of the fabricated composite materials

The proton and electron conductivities of the composite materials were measured by using EIS. A special EIS cell was designed and manufactured by the author to measure the through-plane proton and electron conductivity. The effect of the size of the composite materials on the EIS measurement has been explained in chapter 4. The shortcomings of the typical method of measuring proton conductivity of mixed proton and electron conductive materials have been described. The equivalent circuit proposed by Associate Professor John Andrews from RMIT University was used to address those shortcomings. The method to identify the resistance of the EIS cell by using an EIS test and using a multimeter has been described.

The proton and electron conductivities of six composite materials have been measured at five different relative humidities. The experimental results showed that the proton conductivity of composite materials increased with increasing relative humidity. The
reason is the increased water uptake of the nafion in the composite materials with rising relative humidity, which led to a corresponding increase in proton conductivity of the nafion. The electron conductivity was found to decrease with increasing relative humidity. The possible reason for that is the volumetric swelling of the composite materials that moves the carbon particles away from each other and decreases their effective contact area.

The composite aC-nafion material designed and fabricated within this project itself constitutes a novel material with the very interesting property of being capable of conducting both electrons and protons at the same time. This form of material alone is a significant discovery. Such a dual proton and electron conductor has potential applications in devices such as battery electrodes, chemical sensors, gas separators, electrochromic windows, and membranes (Liu et al. 2012). One of the most interesting applications is in photocatalytic systems that directly use sunlight to split water to hydrogen gas and oxygen gas (Tortello et al. 2012). The dual conductor can transfer the photo-generated protons and electrons from the anodic to the cathode. The composite materials that were fabricated in this thesis showed the same level of proton conductivity, and an electron conductivity three orders of magnitude higher, than the corresponding conductivities of the nafion and carbon nanotubes composites made by Tortello et al. (2012).

7.2.5 Casting of full-size composite electrodes

The mass ratio of activated carbon in the aC-nafion composite was 50 wt%. Although there have been published research papers on composite membrane of nafion and activated carbon, the ratio of carbon to nafion was only as high as 20 wt% (Chien et al. 2012), well below the 50 wt% investigated in this thesis. The initial try to fabricate a full-size composite electrode revealed the practical problems associated with the fabrication. The most significant problem was that during solution casting of the electrodes, cracks are created in the electrode that breaks the electrode and destroy its structural integrity. To address this issue, a backing layer of carbon cloth has been incorporated into the composite electrodes to reinforce the structure of the composite electrodes.
Moreover, the composite electrodes were very brittle and could easily break under slightest pressure. It should be noted that the composite electrodes would have to go under a large pressure during hot-pressing procedure and also the composite electrodes would be under moderate pressure in the experimental PEM URFC cell, because of the clamping forces and expansion of the membrane and composite electrode itself. The backing layer of carbon cloth can ensure that the structural integrity of the composite electrode has been saved under pressure.

The aluminium backing layer proved to be a poor choice since it became corroded after only a few electrolyser-fuel cell cycles in the PEM URFC experimental cell. The effect of the corrosion was shown in Chapter 5.

7.2.6 Testing the composite electrodes in a PEM URFC experimental cell

A special PEM URFC cell was designed in this project to test electrochemical hydrogen storage in the composite electrodes. The cell was modified to contain flow channels in the oxygen-side end-plate. The end-plate on the hydrogen side did not have any flow channels since it had been assumed that the activated carbon may prevent hydrogen gas formation in the electrolyser mode. For safety reasons, a channel was designed on the hydrogen end-plate that was located around the composite electrode to allow hydrogen gas formed in the electrolyser mode escape from the cell.

A test set-up was constructed to test the performance of the URFCs with composite electrodes on the hydrogen side. In the electrolyser (charge) mode, the URFCs with composite electrodes showed a behaviour similar to normal URFC, but with a much higher overpotential. The performance of the URFCs with composite electrodes in the fuel cell (discharge) mode showed no sign of hydrogen storage. The experiments provided valuable data on the performance of the composite electrodes and the limits and constraints of the test and the set-up.

The main limitations of the experiments were the low accuracy of the DC power supply (±0.01A), low accuracy of the gas storage cylinders (± 5ml), and testing the composite electrodes over only few charge-discharge cycles. In future it will be important to study the
performance of the composite electrodes with more accurate instrumentation and over a much larger number of charge-discharge cycles.

7.3 CONCLUSIONS

The goal of this thesis has been to investigate the feasibility of reversible electrochemical storage of hydrogen in a carbon-nafion composite electrode that had been integrated in a PEM URFC. In the course of this research project, a novel set of composite materials capable of conducting electrons and protons at the same time has been fabricated. In addition to using this composite material in the present application, it can also be used in direct solar electrochemical splitting of water to produce hydrogen.

Chapter 4 was dedicated to fabrication and characterisation of the composite materials from activated carbon and nafion. The first section of this chapter detailed the fabrication of activated carbon in KOH chemical activation process. It was followed by characterisation of the activated carbon samples by CO$_2$ and N$_2$ adsorption isotherm methods. The surface area of the activated carbons included a wide range, for example the range of CO$_2$ surface area was from 126 m$^2$/g (AC4) to 870 m$^2$/g (ACS). The selected activated carbons were used to fabricate composite materials with nafion. The methods of obtaining different relative humidity including the method of using saturated salt solutions were explained. Physical properties, water uptake and volumetric swelling, of the composite materials under different relative humidity conditions were determined. The results showed that the water uptake of the composite materials increased with increasing relative humidity. The values increased from 5-12 wt% at 35% relative humidity to 45-85 wt % at fully hydrated in water. The measurements of volumetric swelling of the composite materials showed that it increased with increasing relative humidity. The volumetric swelling ranged from 20 % AC4 to 60 % for ACN. The electrochemical properties, proton and electron conductivity, of the composite materials under different relative humidity conditions were measured. The proton conductivity at fully-hydrated state is in the range of 0.04 S/cm (AC4) to 0.11 S/cm (ACK2.5).

Chapter 5 started with the details of fabrication of the full-size composite electrodes. It was noted in this chapter that the cracks were created in the fabrication of the full-size
composite electrodes and prevented the possibility of scaling up the size of the composite. To address this issue, a backing layer was incorporated in the composite electrode. The nafion 115 membrane was used as nafion membrane. For oxygen electrode the catalyst composition of 2 mg/cm$^2$ of IrRuO$_x$ and 2 mg/cm$^2$ of PtB were used. The membrane-electrode-assemblies were manufactured by hot-pressing the composite electrodes, oxygen electrodes and nafion 115 membrane. The design and manufacturing of the experimental cell that was specially modified for the application of this research project were described. The experimental rig and the equipment that were used to the cells were presented in this chapter. The experimental results of the cells were presented. The results showed that the cell did not work as expected in fuel cell mode, since the overall electrical energy supplied was very low. The discharge values of the cells were very small, less than 0.7 mAh per gram of activated carbon in the aC-nafion composite electrodes.

Chapter 6 provided an analysis of the results and provided possible hypotheses and explanations for the results of the experiments. These hypotheses were also included in section 7.2.6. The most plausible explanation of the results was that nafion could not penetrate into the ultramicropores of the activated carbon, which are the main hydrogen storage sites. From these macropores that nafion has penetrated, protons rely on bulk water to be transport to the ultramicro-pores. Because the low proton conductivity of bulk water, protons are unlikely to reach the ultramicro-pores to form hydrogen-carbon bonds.

In summary, this thesis was successful in addressing the objectives of the project and answering the research questions set in chapter 1. The thesis has documented the procedure of activating carbon with KOH chemical activation and used activated carbon to fabricate a set of activated carbon – nafion composite materials that are capable of dual proton and electron conductivity. The physical properties of the composite materials including water uptake and volumetric swelling were tested in different relative humidities. A special EIS cell was designed and manufactured to test the effects of relative humidities on electron and proton conductivity. A novel equivalent circuit was developed and used to interpret the EIS results. Some of the selected composite materials were used to fabricate full-size composite electrodes and the procedure and manufacturing limitations and difficulties have been documented in this thesis. The composite electrodes were used in a specially designed URFC cell to test their hydrogen storage capacity.
Although the results showed no observable hydrogen storage in the activated carbon, several hypotheses have been developed to set a pathway towards future work. The most likely reasons for lack of observed reversible hydrogen storage in the activated carbon samples to date results are thought to be limited penetration of nafion in activated carbon, saturation of the hydrogen storage sites with oxygen groups; the competitive desorption and gas formation reactions; and irreversible hydrogen storage.

7.4 RECOMMENDATIONS

7.4.1 Computer simulation on proton conductivity within the composite materials and rate of sorption and desorption reactions in various conditions

As discussed in Chapter 6, one of the findings of this thesis was that nafion cannot penetrate into activated carbon particles. Nafton can coat the activated carbon particles and might even penetrate macro pores, but is unable to go into meso, micro, and ultra-micro pores. In fact, it is very likely that protons rely on bulk water within the activated carbons to be transferred to the ultra-micro-pores. However the proton conductivity of the bulk water is lower than naftion. A computer simulation with molecular dynamics can investigate if bulk water can transfer protons to the ultra-micro-pores. The simulation can also investigate to what extend water can penetrate into the pores of activated carbon.

Molecular Dynamics computer simulation might also be used to explore the possible sorption and desorption reactions on the activated carbon and find the proper conditions for bond formation between hydrogen and activated carbon, e.g. charge density, temperature, to encourage sorption reactions. The possible reactions with naftion as a solid proton conducting electrolyte between protons and activated carbon need to be investigated further. Some of the possible reactions have been proposed in Chapter 6. The molecular dynamic method can investigate the rate of such reactions at different voltages and temperatures.
7.4.2 The relationship between water uptake of composite materials and meso-porosity

From the results in Chapter 4, it was noticed that the order of the composite materials with high water uptake is as the same as the order of meso-porosity of their activated carbon. However, the number of samples was too few to make any general conclusion.

An experimental study with activated carbons with different porosity from a single precursor should be conducted to show the relationship between water uptake and porosity and check the hypothesis that is suggested in Chapter 6 that the water uptake might be related to meso-porosity and possibly average pore diameter, not the ultra-micro-porosity of the samples.

7.4.3 New aC-nafion composite materials with different carbon to nafion ratio

An experimental study should be conducted to find the optimum ratio of activated carbon to nafion in the composite to get the maximum proton conductivity. As described in Chapter 4, two competing factors affect the proton conductivity of the composite materials; by increasing the ratio of activated carbon to nafion in the composite: (a) water uptake increases and hence the proton conductivity increases, (b) effective Nafion polymers reduces in the cross sectional area of the composite material and hence proton conductivity decreases.

Therefore, there might be an optimum ratio that proton conductivity reaches its maximum. A set of composite materials can be made ranging from 0 wt% carbon content (nafion membrane) to 99 wt% carbon content (almost no nafion content). The composite materials can be tested by EIS technique and the proton conductivity and electron conductivity of the composite materials can be determined.

7.4.4 Investigating irreversible hydrogen storage in the composite electrodes

As suggested in Chapter 6, one of the possible explanations of the experimental results is that the hydrogen is stored in the composite electrode, but because the bond between
hydrogen and carbon is strong or because the proton conductivity of bulk water prevents proton transfer, the stored hydrogen is unable to be released from the composite electrode. As was noted the instruments that were used in this thesis had a large error that prevented detecting hydrogen storage in electrolyser mode. The available storage tanks in this thesis had the accuracy of ± 5 ml.

To test if there is any irreversible hydrogen storage in the activated carbon electrode during electrolyser mode, it is recommended that more accurate measuring cylinders for storing hydrogen gas and oxygen gas are employed in future experiments. The X-ray photoelectron spectroscopy (XPS) can be used to determine the existence of C-H bonds after the electrolyser mode. The existence of such bonds may suggest that the activated carbon is storing hydrogen in the electrolyser mode, but the conditions in the fuel cell mode are not suitable for hydrogen (or protons) release.

7.4.5 Doping activated carbon to encourage sorption reaction in the electrolyser mode

The possibility of doping activated carbon to facilitate hydrogen sorption is suggested to be studied. Although in the composite material of nafion and activated carbon, protons were expected to be directly stored, the hydrogen gas formation indicates that the sorption reaction needs to be facilitated. Doping materials such as copper (Li et al. 2005), TiO2 (Yu et al. 2012), nickel (Liu et al. 2010), and Fe (Reyhani et al. 2009) have been used to increase the electrochemically hydrogen storage in carbon based materials. An experimental study may be conducted to test the effects of these doped particles on the hydrogen storage in the activated carbon electrodes.
REFERENCES


IPCC, Renewable Energy Sources and Climate Change Mitigation, 2012, Intergovernmental Panel on Climate Change.


Leng, Y 2008, Materials characterization: introduction to microscopic and spectroscopic methods, John Wiley and Sons (Asia), Singapore.


Shakun, JD, Clark, PU, He, F, Marcott, SA, Mix, AC, Liu, Z, Otto-Bliesner, B, (...) & Bard, E 2012, ‘Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation’, Nature, vol. 484, pp. 49-54.


