REVERSIBLE ELECTROCHEMICAL STORAGE OF HYDROGEN IN ACTIVATED CARBONS FROM VICTORIAN BROWN COAL AND OTHER PRECURSORS

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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Declaration

I 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, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Amandeep Singh Oberoi
27 November 2015
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<th>Ampere</th>
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<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of energy</td>
</tr>
<tr>
<td>Exp</td>
<td>Experimental</td>
</tr>
<tr>
<td>E-mode</td>
<td>Electrolyser mode</td>
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<tr>
<td>FC-mode</td>
<td>Fuel cell mode</td>
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<tr>
<td>GHG</td>
<td>Green house gases</td>
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<tr>
<td>MH</td>
<td>Metal hydride</td>
</tr>
<tr>
<td>MSDS</td>
<td>Material safety data sheet</td>
</tr>
<tr>
<td>OC</td>
<td>Open circuit</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton exchange membrane</td>
</tr>
<tr>
<td>SHEL</td>
<td>Sustainable hydrogen energy lab</td>
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<tr>
<td>URFC</td>
<td>Unitised regenerative fuel cell</td>
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<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<tr>
<td>aC</td>
<td>Activated carbon</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>PFB</td>
<td>Proton flow battery</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller</td>
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<td>Dr</td>
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<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
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<td>MEA</td>
<td>Membrane electrode assembly</td>
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<tr>
<td>PFSA</td>
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<td>VED</td>
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</tr>
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</table>
NOMENCLATURE

F Faraday’s constant, 96485 coulomb/mol
V Voltage
m Mass
P Power/Pressure
Q Electrical charge
T Temperature
MPa Mega Pascals

GREEK SYMBOLS

\( \sigma_{\text{proton}} \) Proton conductivity
\( \sigma_{\text{electron}} \) Electron conductivity
PUBLICATIONS

International Journal


International Conferences


EXECUTIVE SUMMARY

Pollution leading to climate change has been the main reason for renewable energy technology development for many decades. But many major technical challenges are still to be met in order to achieve reliable and continuous supply from inherently variable renewable energy sources such as solar and wind. Storing surplus renewable energy as hydrogen is one energy storage option, particularly when long-term, season-to-season storage is required (J. Andrews and B. Shabani, 2012). Hydrogen produced from solar energy by water splitting or other process offers an attractive energy storage option for longer durations and for use as a zero-emission transport fuel. Most work to date has centered on storage of gaseous hydrogen.

K. Jurewicz et al. (2001) showed that sorption of hydrogen produced during the electrochemical decomposition of water in activated carbons can be an efficient method of hydrogen storage. This reversible process is attractive from the point of view of energy efficiency since it associates in a unique step the hydrogen production from water electrolysis and its simultaneous storage in the carbon substrate. The in-situ produced hydrogen easily penetrates into the nanopores of the carbon where it is adsorbed due to the driving force of the negative polarization. In fuel cell mode the stored hydrogen can be released from these nano-pores to supply the fuel cell and produce electricity. Other studies on the reversible storage of hydrogen in activated carbons using a liquid alkaline electrolyte have been conducted by, for example, K. Jurewicz et al. (2002), C. Vix Gutelr and E. Frackowiak et al. (2005), M. J. Blenda-Martinez et al. (2008), and Ningning Liu et al. (2010).

So far all the published work has involved the use of liquid alkaline electrolytes, predominantly concentrated potassium hydroxide solution. Further the optimal characteristics of nanoporous activated carbon materials for hydrogen storage are still to be determined.

Over the past few years, RMIT SAMME work has focused on the potential for reversible storage of hydrogen produced in reversible fuel cells with an acidic solid-state polymer electrolyte, namely nafion.
Professor John Andrews at RMIT, with the assistance of a Master of Engineering by research student – Saeed Seif mohammadi, designed a URFC cell incorporating a solid hydrogen storage electrode based on an AB₅ metal hydride powder. An innovative concept for integrating a metal hydride storage electrode into a reversible proton exchange membrane (PEM) fuel cell was described and investigated experimentally in this project (J. Andrews and S. Mohammadi 2014). This new concept has the potential to increase roundtrip efficiency compared to the conventional hydrogen-based electrical energy storage system by eliminating the intermediate steps of hydrogen gas production, storage, and recovery. Since, in electrolyser mode the input is water that is continuously split into protons which then flow through the system into the storage, the device has been termed ‘a proton flow battery’, which can run as an electrolyser or a fuel cell. In electrolyser mode, hydronium ions emerge from the membrane, and the protons they carry enter into solid metal alloy based storage to form weak chemical bonds with the storage material, that is, a metal hydride, ideally without producing any hydrogen gas. In fuel cell mode, the stored protons come out of the storage material under the influence of an opposite electric potential. These protons then travel back through the membrane as hydronium ions where they react with oxygen and electrons on the oxygen-side catalyst to re-form water and generate electricity.

In the earlier work by Andrews and Seif Mohammadi (2014), a hydrogen storage electrode was fabricated from a novel composite metal hydride-nafion material, and found to have acceptably high proton and electron conductivities. Its 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. These results provide initial confirmatory evidence that the proton flow battery concept is technically feasible, though additional research is still required to enhance both storage capacity and reversibility. Moreover, the uses of metal hydride for composite electrode have certain limitations, namely high cost of the metal alloy powder, its weight, and its availability.

M. J. Jazaeri (2013), also working at RMIT under Prof. Andrews’s supervision, has recently investigated a composite electrode for a proton flow battery made from activated carbon and nafion to check its capability for reversible hydrogen storage. However, Jazaeri found no detectable level of reversible hydrogen storage in such an electrode. A likely explanation of this result identified was that, in the composite nafion-activated carbon
electrode constructed, the relatively large molecular size of the nafion polymer strands would mean that the nafion is unable to penetrate into the ultramicropores (diameter ≤0.7 nm) of the activated carbon particles. Hence there is no medium to conduct the protons right into these ultramicropores, which previously have been identified as the primary sites for electrochemical storage of hydrogen in porous carbons.

In the present study therefore, the use of a liquid proton conductor than can penetrate right into the nanoscale pores of activated carbons has been investigated. The overall aim of this project has thus been to investigate experimentally electrochemical hydrogen storage in porous activated carbon electrodes made from Victorian brown coal and other precursor using sulphuric acid as liquid proton conductor.

The objectives of the project were to:

1. Measure experimentally the physical and electrochemical properties of a number of activated carbon electrodes made from Victorian brown coal and other precursors.

2. Analyse structural features of the fabricated electrodes, and measure their electron and proton conductivities, and other electrochemical properties.

3. Utilise the fabricated electrodes in an electrolytic cell to measure the hydrogen storage capacity in terms of voltammetry and galvanostatic charging-discharging.

4. Incorporate the best-performing electrode into a reversible PEM fuel cell and measure experimentally the hydrogen storage capacities and cell performance in electrolyser and fuel cell mode

5. Recommend further work directed towards achieving a proton flow battery with carbon-based hydrogen storage electrodes of this kind.
The main research questions addressed in this thesis are as follows:

1. How can the proton conductivity of a composite activated carbon - PTFE electrode be maximised?

2. What structure and composition of a carbon-based solid electrode in a reversible PEM fuel cell yield the best performance in terms of sustained hydrogen charge capacity, rates of charge and discharge, and gravimetric and volumetric energy densities?

3. To what extent can hydrogen gas formation in such a hydrogen storage electrode be suppressed?

4. Can a reversible fuel cell with integrated solid-state carbon-based hydrogen storage provide an energy storage that has superior gravimetric and volumetric energy densities, roundtrip energy efficiency, and lifecycle cost than compressed gas hydrogen storage, metal hydrides with gaseous charging and discharging, and the best performing lithium ion or polymer batteries?

Extensive research work has been done during the research candidature by the author of this thesis to answer the above-mentioned research questions.

Specific outcomes of this thesis are:

- Fabrication of thirteen composite aC-PTFE electrodes using PTFE (Polytetrafluoroethylene) and activated carbon (aC) made from different precursors of carbon i.e. charcoal, Victorian brown coal and phenolic resin, with solution casting that have dual proton and electron conductivity.

- Measurement of the properties of the fabricated composite aC-PTFE electrodes:
  - Physical characterisation for example outer dimensions, cross-sectional area and volume. The cross sectional structures of the composite materials were obtained by scanning electron microscopy.
  - Electrochemical characterisation including proton and electron conductivity.

- Development of an experimental set-up to measure proton conductivity of the composite aC-PTFE materials soaked in sulphuric acid using electrochemical impedance spectroscopy.
• Measurement of double-layer capacitance of all the fabricated aC-PTFE electrodes in sulphuric acid electrolyte using split flat coin cell.
• Measurement of electrochemical hydrogen storage capacity of all the fabricated aC-PTFE electrodes using dilute sulphuric acid of 1 mol. concentration as electrolyte in a three-electrode electrolytic cell.
• Design and construction of a special cell for testing the feasible running of the concept of a proton flow battery and testing the aC electrodes in the experimental proton flow battery.
• Some promising indications of the technical feasibility of the proton flow battery with an integrated aC electrode.
• Recommendations for further experimental work to investigate questions arising for the experiments conducted within the present thesis, and to confirm the feasibility of the proton flow battery concept.

An extensive study of the literature related to the concept of the proton flow battery is reported in this thesis. It was found that concept with some similarities, but also some significant differences, to the proton flow battery concept investigated in the present thesis had been patented by GE (General Electrics) in 2007. However, no research work revealing the results on the performance of an actual experimental, system mentioned in the GE patent have yet been reported or published. Earlier work (for example, by REFS) on electrochemical hydrogen storage in activated carbons has primarily been focused on the use of a liquid alkaline electrolyte, rather than a solid-state acidic proton exchange membrane electrolyte as used in the present work. The highest reported hydrogen storage capacity with a KOH electrolyte was an impressive 2 wt%. But very little work has been done to date on the electrochemical hydrogen storage reported in activated carbon electrodes using acidic electrolytes, whether liquid or solid-state.

Considering the outcome of the literature review and the results of the previous research work on electrochemical hydrogen storage at the RMIT University, the reversible hydrogen storage potential of various forms of activated carbon, in conjunction with a liquid acidic electrolyte penetrating into the pores of the aC, has been studied in this thesis. This selection of porous activated carbon with soaked in a liquid acidic proton conductor as the
preferred hydrogen storage electrode in the present project was based on the findings of two earlier studies at RMIT:

- S. Mohammadi and Andrews (2014) study on the use of a composite nafion-metal hydride storage electrode in a proton flow battery, which showed poor reversibility, considerable hydrogen gas production, and involved a high-cost metal hydride,
- J. Jazaeri’s (2013) investigation of a composite activated carbon nafion electrode in a proton flow battery, which found no detectable hydrogen storage in the electrode, for the identified reason that the nafion did not penetrate into the pores of the aC and hence could not conduct the hydronium ions to storage sites within these pores.

The various activated carbon samples employed in the present research project were made from charcoal, Victorian brown coal and phenolic resin. These carbons were activated by adding different proportions of KOH (potassium hydroxide). In total thirteen activated carbon samples were prepared from the mentioned precursors: one from charcoal, five from Victorian brown coal, and the remaining seven samples from phenolic resin. Activated carbon made from charcoal was supplied by Mohammad Javad Jazaeri, a Master of Engineering by Research student at RMIT University, Melbourne. Activated carbon samples made from Victorian brown coal were made available by Lachlan Ciddor, a PhD student at Monash University, Melbourne. The last set of activated carbon samples made from phenolic resin was supplied by Dr M. Karthik, a research associate at CIC Energigune in Álava, Spain.

The sample activated carbons in powdered form were mixed with PTFE to fabricate a solid electrode by solution casting. These electrodes were then tested to measure their proton conductivity, electron conductivity, double-layer capacitance, and reversible electrochemical hydrogen storage capacity.

For proton conductivity measurements, the electrodes were soaked in dilute sulphuric acid employed as a proton conductor within the solid electrode. The proton conductivity of the sample electrodes was found to be in the range of 0.004 – 0.09 S/cm, which reflected the effective conductivity of the acid within the pores. The proton conductivity of the sample electrodes increased with rising average pore volume because with high pore volume
the electrode could accommodate more sulphuric acid leading to enhancement in proton conductivity. The electron conductivity was calculated from the measured electron resistance across opposite faces with a known area of conduct by a standard multimeter. The electron conductivity of the sample activated carbon electrodes was found to be in the range of 5.79 – 14.47 S/cm.

The aC-PTFE electrodes soaked in dilute sulphuric acid that were designed and fabricated in the present project were therefore found to be capable of conducting both protons and electrons, as required for their use as hydrogen storage electrodes in a proton flow battery. This novel electrode design itself is a significant outcome of this research work with potential applications in the field of battery storage, electrochromic windows, chemical sensors, gas separators, and photo catalytic systems that directly use sunlight to split water to hydrogen gas and oxygen gas.

The double-layer capacitance of the sample activated-carbon electrodes was measured using a special-purpose split flat coin cell. Dilute sulphuric acid was again used as the electrolyte in the cell. The capacitance was found to be in the range of 28.3 – 189.4 F/g. The obtained capacitance values were found to be acceptable when compared with the literature (K. Jurewicz et. al 2002). Although the magnitude of current used by K. Jurewicz et al. 2002, was higher than the present work, the current density (amps per unit area) was kept as same.

The reversible electrochemical hydrogen storage capacity of all the fabricated aC-PTFE sample electrodes was measured using a three-electrode electrolytic cell. In the experimental setup, platinum wire was used as the counter electrode, Hg/HgO as reference, and the fabricated aC-PTFE samples as working electrode. Dilute sulphuric acid of 1 mol concentration was used as the electrolyte in the cell. The reversible electrochemical hydrogen storage capacity of the fabricated aC-PTFE electrodes was found to be in the range of 0.36 – 1.6 mass% of equivalent hydrogen in carbon. This equivalent storage capacity was the result of contribution (in hydrogen storage) both from the chemical reaction between hydrogen and storage material (i.e. carbon); and the double-layer capacitance effect. The capacitance contribution was found to be in the range of 0.03 – 0.19 mass% hydrogen equivalent. Individual equivalent electrochemical hydrogen storage capacity of the electrodes was measured as follows:
<table>
<thead>
<tr>
<th>Sample</th>
<th>Reversible Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphitic foam</td>
<td>0.36 wt%</td>
</tr>
<tr>
<td>aCP</td>
<td>0.47 wt%</td>
</tr>
<tr>
<td>Flexible carbon foam</td>
<td>0.51 wt%</td>
</tr>
<tr>
<td>aCS</td>
<td>0.58 wt%</td>
</tr>
<tr>
<td>Mesoporous carbon monoliths</td>
<td>1.04 wt%</td>
</tr>
<tr>
<td>aC'N</td>
<td>1.08 wt%</td>
</tr>
<tr>
<td>aCK7.5</td>
<td>1.22 wt%</td>
</tr>
<tr>
<td>aCK2.5</td>
<td>1.29 wt%</td>
</tr>
<tr>
<td>aCK10</td>
<td>1.36 wt%</td>
</tr>
<tr>
<td>Mesoporous carbon 1:1 KOH</td>
<td>1.43 wt%</td>
</tr>
<tr>
<td>Mesoporous carbon 1:3 KOH</td>
<td>1.48 wt%</td>
</tr>
<tr>
<td>Mesoporous carbon 1:5 KOH</td>
<td>1.56 wt%</td>
</tr>
<tr>
<td>Mesoporous carbon 1:7 KOH</td>
<td>1.60 wt%</td>
</tr>
</tbody>
</table>

Nine out of thirteen tested aC samples were found to have a reversible electrochemical hydrogen storage capacity of more than 1 wt% that is comparable with the gravimetric density of commercially-available MH based solid hydrogen cylinders requiring pressurized hydrogen gas input at pressures of 10 – 20 bar, and also lithium-ion and lithium-polymer batteries.

The volumetric energy density of the tested aC samples were calculated and found to be in the range of 0.26 – 0.52 kWh/litre, which is less than commercially available MH-based hydrogen storage canisters, Li-ion and Li-polymer batteries.

The results of the experimentation showed that there was a monotonic (and fairly linear) relation between BET surface area and reversible electrochemical hydrogen storage capacity of the aC-PTFE sample electrodes, especially for those with higher storage capacities.

A candidate aC sample mesoporous carbon 1:7 KOH (supplied from CIC Energigune in Spain) from all the tested electrodes was selected and employed in an experimental proton flow battery to test its feasible running. This candidate aC was selected since it was the best performer among all the samples in terms of proton conductivity, double-layer capacitance and electrochemical hydrogen storage capacity. The selected aC sample in powdered form was mixed with nafion-117 solution (chemical name is perfluorosulfonic acid) to fabricate
a solid electrode for a proton flow battery. In this case nafion-117 acted as a proton-conducting medium within the storage electrode.

The experimental proton flow battery was designed and fabricated. The end-plates of the PFB were machined out of SS 316 with flow channels and headers to accommodate gas flow. Previous research on the proton exchange membrane (PEM) unitised regenerative fuel cell (URFC) at RMIT University revealed the carbon-based gas diffusion layer (GDL) was attacked in the electrolyser mode. Therefore, in the present study porous sintered titanium felt was used as GDL on the oxygen-side in the PFB. The catalyst loading on oxygen electrode contained 2 mg/cm² of IrRuOₓ and 2 mg/cm² of PtB. In a previous PhD thesis (A. K. Doddathimmaiah 2008), this combination of catalysts was found to have the best performance for the oxygen electrode in a proton exchange membrane unitised regenerative fuel cell (PEM URFC). On the hydrogen side dilute sulphuric acid of 1 mol. concentration was employed instead of a GDL. The hydrogen electrode was soaked in dilute sulphuric acid during operation.

The experiments in the specially designed proton flow battery resulted in the feasible running of the device with an integrated solid carbon-based hydrogen storage electrode. It was shown successfully that hydrogen could go in and out from the activated carbon electrode soaked in dilute sulphuric acid. The URFC with the aC electrode was charged at constant current and constant voltage for nine consecutive cycles to study its performance. The highest discharge value was found to be 1.09 mass% of hydrogen storage, which is comparable to commercially available metal-hydride based hydrogen storage cylinders. The latter further require at least a 10 bar charging pressure of the hydrogen gas. However, a significant amount of drop in the hydrogen storage mass % was observed over various test cycles in the range of 1.09 – 0.97 (from cycle one to cycle nine respectively).

However, some important questions were raised by this preliminary feasibility testing of the concept of a proton flow battery with an acid-soaked aC hydrogen storage electrode. In the experiments conducted to date there were disparities in E-mode between the measured oxygen collection and that calculated using Faraday’s law on the basis of the integrated charge flows; and the measured oxygen consumption in FC mode and that calculated as required again using Faraday’s law.
Possible explanations of these anomalies are the following:

- The experimental cell had some leakage on the oxygen-side gas connections, piping and collection systems. However, testing of both H and O-sides of the cell prior to the experiment, and subsequent testing of the same cell after the experiment, showed no detectable leaks.

- Some of the oxygen evolved on the O-side electrode in E-mode may have reacted with the Pt catalyst, and the sintered Ti GDL, to form an oxide. Then in FC mode this reaction was reversed, allowing the released oxygen to combine with hydronium ions to form water once again.

- Hydronium ions from the dissociated dilute sulphuric acid soaking the aC on H-side electrode may enter the electrode and be stored directly, rather than being sourced from water dissociation on the oxygen-side electrode and transit via the nafion membrane to the hydrogen side.

From the findings in this thesis and the hypotheses that were developed to explain these results, the following recommendations are made for future research:

- Further testing of the O-side materials by SEM and XDS need to be performed after E-mode operations to detect the presence of surface oxides and to check for any evidence of oxidation reactions that might have consumed oxygen in E-mode operation.

- The proton flow battery experiments need to be repeated with additional testing before starting for any gas leaks, to see if the results obtained in the present thesis are reproducible.

In other areas, further experiments are required to:

- Obtain more accurate information on the pore structure, pore size distribution, and pore surface chemistry of the activated carbons, in order to gain an improved
• understanding of the mechanisms of reversible electrochemical hydrogen storage in these materials.

• Investigate the use of other proton conducting media to sulphuric acid, such as protic ionic liquid, proton conducting gels and oils, which may give better results.

• Study any corrosive effect on aC of the acid used as the proton conductor within the pores of the material. Also, different concentrations of sulphuric acid need to be tested.

In conclusion, this thesis has been successful in meeting its objectives and answering the research questions. The thesis has reported on the procedure of fabrication of the aC-PTFE and aC-nafion composite electrodes using aC samples made from Victorian brown coal and phenolic resin. The physical and electrochemical properties of the sample aC electrodes were measured and reported in this thesis.

The samples aC made from Victorian brown coal have shown the acceptable values of proton conductivity, double-layer capacitance and reversible electrochemical hydrogen storage capacity. The Victorian brown coal samples have shown the gravimetric density of more than 1 mass%, which is comparable with commercially available MH based compressed hydrogen cylinders. However no information was provided on macro and meso porosity of these samples. As the samples from Victorian brown coal have shown some promising results, it is clearly a very attractive research area where further work is required.

Other aC samples were supplied by CIC Energigune in Spain with their structural data including micro porosity, but no information was provided on ultramicro porosity which is a limitation of the reported work.

The contribution of the double-layer capacitance and reaction of hydrogen ions with carbon to equivalent electrochemical hydrogen storage capacity has been described. A monotonic relation was found between the BET surface area and reversible electrochemical hydrogen
storage capacity of sample aC electrodes. One of the sample aC electrodes was selected and employed in the proton flow battery to test its feasible running.

The thesis has reported on the successful running of the proton flow battery with an integrated solid carbon-based electrode in both electrolyser and fuel cell modes. It has identified specific follow-up experiments that are now needed to seek to explain a number of anomalies in the data obtained in these preliminary experiments. Overall, this thesis has thus taken a major step towards a full demonstration of the technical feasibility of a proton flow battery with a carbon-based hydrogen storage electrode.
CHAPTER 1

1. INTRODUCTION

1.1 BACKGROUND

For many centuries past, exhaustible fuels formed the basis of meeting most of the world’s energy demand. The continuous elevation of the world’s population and development has led to an extensive and increasing utilisation of fossil fuels (M. J. Khan and M. T. Iqbal, 2005). According to the US Department of Energy, in less than 10 years (2021) the delivery rate of world oil will reach its peak, while others argue that oil production’s maximum global rate has already been reached (The Oil Drum, 2008). In any case, the remaining oil supplies and oil prices will face immense pressure due to rapidly growing demand of the developing economies across the world.

On the other hand, the climate science community says that the increasing concentrations of the greenhouse gases in earth’s atmosphere due to human activities result in global warming and related climate change (Intergovernmental Panel on Climate Change, 2007). Burning of fossil fuels is one of the major activities leading to emission of greenhouse gases. Therefore, these reasons generate a need of transition from fossil fuels to renewables over the coming decades.

Indeed, one of the biggest challenges facing humankind over the next few years is decreasing dependence on fossil fuels and their by-products (such as petrol and diesel), and controlling the emission of greenhouse gases responsible for climate change. In other words, it is necessary to make a shift towards a sustainable energy economy. In this historical revolution of technological change, a generally accepted fact is that renewable energy sources and energy efficiency have the key role to play in the near future. Yet increasing dependency on various renewable sources of energy will give rise to a need for energy storage systems to provide a continuous and secure supply. So in order to store and transport renewable energy on land, sea and air, some sought of energy carrier will be required, as the majority of renewables are not in a form to replace petroleum fuels directly in the transport sector. In order to meet this need, production of hydrogen from renewables and storing this hydrogen for later reuse in fuel cells to supply electricity was proposed (J.
Bockris, 1975). Hydrogen generated from renewables not only acts as an alternative to petroleum fuels, but also leads to a zero-emission transportation system (J. Andrews, 2011; J. Andrews and B. Shabani, 2011). Moreover, hydrogen obtained from renewables can be utilised in electricity supply systems as long-term energy storage.

The development of efficient, compact and low-mass hydrogen storage is a major barrier for the more widespread applications of hydrogen in transport and other sectors (A. Züttel, 2008). Storage of hydrogen is possible in many ways, such as chemical compound with metal and chemical hydrides, as a cryogenic liquid and as a pressurised gas (B. Sakintuna et al., 2007; US DoE, 2009; F. Askri et al., 2009). The results achieved so far in the field of hydrogen storage in terms of volumetric (energy per unit volume) and gravimetric (hydrogen energy stored per unit mass) densities are well below the set targets for the implementation in the hydrogen-powered vehicles. Potentially high energy storage densities and safety are few of many inherent advantages of hydrogen storage in metal hydrides (in solid-state). However, gravimetric energy density of 0.47 kWh/kg is the best-recorded hydrogen storage in metal hydrides so far which is well lower than 1.08 kWh/kg – the US DoE target for 2015 (US DoE, 2009; J. Andrews, 2011; J. Andrews and B. Shabani, 2011). Moreover, in order to make the required alloys for storing hydrogen, the available metal hydrides utilise scarce and costly earth elements, which make them quite expensive. Relatively low (typically 40-45% through electrolyser, gas storage unit and fuel cell) round trip energy efficiency compared to batteries (70-80% when going from electricity in to electricity out), is yet another obstacle in the way of using hydrogen storage systems (E. Gray et al., 2011).

Previous research at RMIT University (A.K. Doddathimaiah and J. Andrews, 2009; A. K. Doddathimmaiah, 2008) developed the concept of a unitised regenerative fuel cell. In this concept, a single Proton Exchange Membrane (PEM) cell utilizes an integrated solid hydrogen electrode that could operate as an electrolyser to split water or as a fuel cell to generate electricity, that is, a unitised regenerative fuel cell (URFC).

Reversible PEM URFCs are still at the research and development stage, and have yet to reach the commercial market.
Professor John Andrews at SAMME, RMIT University, in 2011 with the assistance of Master of Engineering by research student named ‘S. Mohammadi’ developed a solid composite hydrogen storage electrode using metal hydride-AB₅ and a proton conducting medium – nafion. In electrolyser mode, hydrogen ions in form of protons emerge at membrane and then enters the solid storage directly where they react with electrons and storage material atoms to form a chemical bonding as a hydride without producing hydrogen gas. They termed this novel device a ‘proton flow battery’, and pointed to its numerous potential applications across many fields. When the developed composite electrode was employed in a PEM URFC for testing its storage capabilities, it showed quite promising results. This new concept has the potential to increase roundtrip efficiency compared to the conventional hydrogen-based electrical energy storage system by eliminating the intermediate steps of hydrogen gas production, storage, and recovery. A hydrogen storage electrode was fabricated from a novel composite metal hydride-nafion material, and found to have acceptably high proton and electron conductivities. Its 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. These results provide initial confirmatory evidence that the proton flow battery concept is technically feasible, though additional research is still required to enhance both storage capacity and reversibility. Moreover, there were some limitations of using this metal hydride-nafion composite electrode which involved: production of hydrogen gas, AB₅ metal hydride is quite expensive and some other carbon based materials or CNTs may be more suitable for hydrogen storage.

Using a solid oxide (ceramic) in a reversible fuel cell at high temperature with a similar concept was proposed by J. B. Condon and Schober (1995 and 1994). A general patent by C. Wang and Wei (2007) also referred about the concept of integrating fuel cells with hydrogen storage. K. Jurewicz et al. (2002) had reported about various materials as a medium of reversible hydrogen storage such as liquid alkaline electrolyte and activated carbons. Alkaline solutions were used as electrolyte in the earlier experiments for storage of hydrogen in solid metal hydride electrodes (e.g. G. Bronoel et al., 1976). Development of NiMH batteries in the early 1990s was a result of further research in this field. Solid electrolytes were also investigated by researchers from Fiat Company, but they failed to
demonstrate direct storage of protons from acid-based membranes (C. Folonari et al., 1980).

Another Master of Engineering by research student in RMIT SAMME, J. Jazaeri, in 2013 optimized the method of production of activated carbon from different precursors of carbon by treatment with nitrogen and CO\textsubscript{2} gases (J. Jazaeri 2013). Jazaeri provided the following possible explanations for not detecting any reversible hydrogen storage in the composite electrodes made from nafion and activated carbon that were integrated in a PEM URFC experimental cell:

- 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.

Present research work at RMIT, including this thesis, is focussing on the development of number of activated carbon (aC) electrodes for hydrogen storage within a proton flow battery from different precursors of carbon using a commercial PTFE solution as a binder. These fabricated aC electrodes were first tested in an electrolytic cell with a liquid acid electrolyte for their hydrogen storage capacity by cyclic voltammetry and galvanostatic charging-discharging. The best performing aC electrode was then tested in an experimental proton flow battery.

The previous RMIT experiments provide initial confirmatory evidence of the technical feasibility of the proton flow battery concept using a composite MH-nafion electrode. However, further research is now needed to explore proton-conducting media within the electrode other than nafion, in particular liquid acid proton conductors, in order to achieve a much greater level of hydrogen discharge in fuel-cell mode, and boost the level of charge in electrolyser mode. The earlier RMIT work has also led to a focus on activated carbons for the electrochemical storage of hydrogen storage in composite electrodes, to suppress hydrogen gas formation, and avoid costly metal hydrides.
The present PhD project thus involves the utilisation of composite aC electrode with sulphuric acid (as a proton conducting medium) within the composite electrode in PEM fuel cell for generation of electricity.

1.2 AIM AND OBJECTIVES OF THIS PROJECT

The overall aim of this PhD project has been to determine experimentally the electrochemical hydrogen storage capacity of activated carbons made from different precursors and investigate feasible running of a proton flow battery with integrated activated carbon storage electrode.

The objectives of this PhD project have been thus to:

- Fabricate number of carbon electrodes from different precursors of carbon using a commercial PTFE binder.
- Identify through cyclic voltammetry experiments suitable porous carbon-based materials with the potential for reversible storage of protons generated by electrolysis in a reversible Proton Exchange Membrane (PEM) fuel cell.
- Measure experimentally the physical and electrochemical properties of the selected candidate carbon electrodes.
- Incorporate these carbon electrodes into a reversible PEM fuel cell and measure experimentally the hydrogen storage capacities and cell performance in electrolyser and fuel cell mode.
- Recommend further work directed towards achieving a proton flow battery with carbon-based hydrogen storage electrodes of this kind.

1.3 RESEARCH QUESTIONS

The main research questions addressed in this thesis are:

- How can the proton conductivity of an activated carbon electrode be maximised?
• What structure and composition of a carbon-based solid electrode in a reversible PEM fuel cell yield the best performance in terms of sustained hydrogen charge capacity, rates of charge and discharge, and gravimetric and volumetric energy densities?

• To what extent can hydrogen gas formation in such a hydrogen storage electrode be suppressed?

• Can a reversible fuel cell with integrated solid-state carbon-based hydrogen storage provide an energy storage that has superior gravimetric and volumetric energy densities, roundtrip energy efficiency, and lifecycle cost than compressed gas hydrogen storage, metal hydrides with gaseous charging and discharging, and the best performing lithium ion or polymer batteries?

1.4 SCOPE

The scope of this project is limited to electrodes made from activated carbons and carbon nanotubes. The principal proton-conducting materials used in experiments with activated carbon electrodes will be H₂SO₄, other acids, protic ionic liquids (Tamar L. Greaves et al. 2008), and nafion-117. Experimental reversible fuel cells will all be Proton Exchange Membrane cells with a relatively small active membrane area of less than 10 cm². The project is seeking just to investigate the basic processes taking place in, and the technical feasibility of, the proton flow battery concept, rather than develop any pre-commercial prototype systems.

1.5 OUTCOMES

The deliverables and outcome of this research work have been:

1. One or more identified porous carbon materials, particularly suited to electrochemical storage of hydrogen.

2. A practical method for fabrication of composite activated carbon-PTFE electrodes with dual proton and electron conducting capability.

3. Experimental data on the performance of a Proton Flow Battery (PFB) comprising a reversible PEM fuel cell with an integrated carbon-based storage electrode.
1.6 GUIDE TO THESIS

In chapter 2, the method used for present research project is discussed. Since the major part of this study involves 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.

In chapter 3, a comprehensive background on electrochemical storage of hydrogen is discussed in details. The earlier work on this concept conducted at RMIT University is disclosed and its findings are presented.

In chapter 4, a detailed documentation is provided for fabrication of activated carbon, activated carbon-PTFE composite electrode.

In chapter 5, characterisation of all the fabricated activated carbon (aC) electrodes is covered. The method and equipment used to measure various characteristics of aC electrodes is described.

In Chapter 6, the double-layer capacitance and hydrogen storage capacity measurements of aC electrodes are elaborated. Testing procedure is discussed in detail.

In Chapter 7, the concept of proton flow battery 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 aC electrode in charge and discharge mode is reported.

Finally, chapter 8 analyses all experimental results and summarises the findings. The answers obtained to the research questions from all the work conducted in thesis are presented. 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 thesis project is a step towards feasible running of a ‘proton flow battery’ that can run reversibly as an electrolyser or fuel cell and form a key link between the fields of hydrogen fuel cell technology, hydrogen storage and battery technology. The project also adds to current understanding of materials science by fabricating and characterising a new energy storage material that is both proton and electron conductive. This new low-cost carbon based material has been used in a three-electrode electrolytic cell with sulphuric acid as liquid electrolyte (proton conducting medium), and their capacity for electrochemical hydrogen storage has been investigated and compared.

In this chapter, the basic method followed to achieve the objectives of the thesis is presented along with the main phases and activities conducted.

2.2 BASIC METHODOLOGICAL APPROACH

This thesis project is predominantly an experimental study, with critical analysis of research results using existing theoretical frameworks to explain and understand the implications of the results obtained. An extensive literature review of previous works on electrochemical hydrogen storage in porous carbons is conducted to determine an initial selection of suitable candidate forms of activated carbon for study in our own experiments. Samples of activated carbon material will be made from a number of precursors by treatment with KOH, and various gases under pressure and at high temperatures. Various physical and electrochemical properties of these samples of activated carbon are measured experimentally at different conditions (mainly varying the relative humidity). Activated carbon samples with the preferred properties for hydrogen absorption are used to fabricate electrodes. Sulphuric acid is used as an electrolyte to serve as a proton-conducting medium for the transfer of protons (in the form of hydronium, $\text{H}_3\text{O}^+$, from the reference electrode to the working electrode or storage electrode. These electrodes are characterised by
measuring various physical and electrochemical properties, for example, BET surface area, electron and proton conductivities, and SEM images of their surfaces. The activated carbon electrode is incorporated into a specially-designed reversible PEM fuel cell for testing in electrolyser and fuel cell mode to measure hydrogen storage and cell performance. The goal has been to find one or more practical designs for the activated electrode that demonstrates hydrogen storage and discharge, and hence prove the technical feasibility of the proton flow battery concept with a carbon-based storage electrode.

**2.3 EXPERIMENTAL PROCEDURES**

**2.3.1 Carbon-based material as medium for electrochemical hydrogen storage**

As indicated from literature, carbon-based materials favour suppression of hydrogen gas formation in electrolysis process (A. Zuttel et al. 2008). Hence activated carbon (aC) was chosen as an appropriate candidate material to investigate for its electrochemical hydrogen storage capacity. Another strong reason for choosing aC as candidate material is its high surface area, light weight, low cost and availability offered by carbon based materials. Moreover, a composite MH-nafion and aC-nafion electrodes used in previous studies (S. Mohammadi 2013 and J. Jazaeri 2013 respectively) had shown some the ability to work as required within a proton flow battery, but the degree of reversible hydrogen storage measured and energy density achieved in both cases were much lower than the desired values. The present project has thus sought to overcome some of the limitations of these previous studies. Samples from Victorian brown coal, charcoal, and other precursors have been employed in this study because of their high carbon content, availability, low-cost and economic interests in brown coal in the State of Victoria in Australia.

**2.3.2 Fabrication and characterisation**

Activated carbon powders made from Victorian brown coal were supplied by Professor Alan Chaffee of Monash University, Melbourne, Australia, and activated carbon samples made from phenolic resin by Dr M. Karthik, CIC Energigune, Miñano, Álava, Spain. These
powders were activated after potassium hydroxide (KOH) addition, and the percentage of KOH was varied to obtain different samples with a range of micropore volumes and surface areas. Each sample aC powder was weighed using a digital weighing scale and mixed with 5 wt% PTFE solution. The PTFE was to act as a binder to hold the aC particles together in the electrode. The volume of solution added was set so that after evaporation of the solvent the mass of PTFE in the electrode was 10 wt% of the mass of the aC powder. The mixture was thoroughly mixed and stirred in a glass beaker. The solution was then stirred on hot plate surface using magnetic stirrer to obtain even mixing of aC powder and PTFE. The slurry was poured into a mould of the desired shape and heated in an electric oven for 2 hours at 110º C to evaporate the solvent from mixture.

After two hours, the mould was removed from the oven and allowed to cool down for a further two hours under ambient temperature conditions. The solid porous aC electrode was then removed from mould and lightly pressed onto a gold foil backing to act as a current collector. A similar procedure was followed to fabricate other aC electrodes. The fabricated sample electrodes were named graphitic carbon foam, aC_P, flexible carbon foam, aC_S, mesoporous carbon monolith, aC_N, aC_K2.5, aC_K7.5 and aC_K10, mesoporous carbon 1:1 KOH and mesoporous carbon 1:5 KOH. For characterisation of these sample electrodes their BET (S. Brunauer Emmett Teller) surface areas and limiting micropore volumes were measured by N₂ and CO₂ isotherm adsorptions.

2.3.3 Measurement of proton conductivity of acid-saturated electrodes

Proton conductivity was calculated by measuring proton resistance using Electrochemical Impedance Spectroscopy (EIS). Before testing the sample aC electrodes, the proton conductivity of 1 mol (M) dilute sulphuric acid was measured. Sulphuric acid (known volume) was contained between two nafion-117 membranes backed by two gold plated metal plates. An AC voltage was applied across the gold plated metal plates to measure the total series resistance of the whole setup using a Nyquist plot. The electrical resistance of the metal plates and the nafion-117 membranes were measured separately by a similar procedure, and subtracted from the total series resistance of the whole setup to obtain the proton resistance of the acid.
The proton resistance of the sample electrodes saturated with 1 M sulphuric acid was measured using the same experimental setup. The aC electrode was sandwiched between two nafion-117 membranes backed by two gold plated metal plates. The Nafion-117 membranes, being proton but not electron conductors, were used to ensure that only protons were available to pass through the aC electrodes via the sulphuric acid. AC power in the frequency range of 0.1 to 10⁶ Hz was supplied across the gold plate electrodes. The proton resistance was obtained in the form of a Nyquist plot of impedance on the real and imaginary axes, and was used to calculate proton conductivity given the known area and thickness of the electrodes.

2.3.4 Measurement of double-layer capacitance

Double-layer capacitance of all aC sample electrodes was measured by cyclic voltammetry at constant potentials monitored in terms of scan rate. A typical split flat coin cell was employed with a non-conducting separator between the two fabricated working electrodes made from porous activated carbon and PTFE binder. The electrolyte used was 1 mol sulphuric acid within the split flat coin cell. The amount of electrolyte added was enough to soak in working electrodes separated by a separator. A voltammogram was obtained for each fabricated activated carbon-PTFE electrode and the peak current and voltage scan rates were used to calculate double-layer capacitance. Later the measured double-layer capacitance was used to analyse its contribution toward the equivalent hydrogen weight percent stored in the activated carbon electrodes.

2.3.5 Measurement of hydrogen storage capacity

Hydrogen storage capacity of all aC sample electrodes was measured by galvanostatic charging and discharging at constant currents. A typical 3-electrode electrolytic cell was employed with platinum wire as counter electrode, Hg/HgO as reference electrode, and fabricated aC samples as working electrode. The electrolytic cell was filled with 1 mol sulphuric acid to act as an electrolyte, and connected with CH Instruments EIS workstation for power supply.
Separate graduated cylinders were used to collect gas (as produced) from the working electrode and counter electrode. Hydrogen gas was collected from working electrode side and its volume was used in calculation of stored hydrogen.

2.3.6 Testing activated carbon electrodes in proton flow battery

The activated carbon electrodes with optimum performances in terms of proton conductivity, electron conductivity, double-layer capacitance and electrochemical hydrogen storage capacity were selected and employed in the modified unitised regenerative fuel cell (URFC) that comprised, the proton flow battery, to test its feasible working and hence its performance in both electrolyser and fuel cell mode.

2.4 INSTRUMENTATION AND COLLECTION OF DATA

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. These tests and associated results, particularly for the activated carbon samples from phenolic resin were performed and supplied by Dr M. Karthik, Research Associate at CIC Energigune, Álava Spain. S. Brunauer-Emmett-Teller (BET) equation and Dubinin-Radushkerich (DR) equation were used by Lachlan Ciddor (PhD student, Monash University) to interpret the values of gas adsorption and determine the surface area of activated carbon samples from Victorian brown coal. The characterisation of charcoal sample was done by Mohammad Javad Jazaeri (Master Engg. student, RMIT University) and School of Applied Science, RMIT University. Elemental composition of the activated carbon samples were acquired by the author of this thesis using EDX technique available in Australian Microscopy and Microanalysis Research Facility (AMMRF) at RMIT University.

Activated carbon and PTFE were mixed using a hot-plate and the mixture was stirred manually. Before mixing with PTFE, 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. The proton conductivity of the composite material was measured using EIS. The equivalent circuit for interpreting the results of the EIS was developed by 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 during the discharge mode were measured. Produced hydrogen and oxygen gases were stored in graduated cylinders.

2.5 ACTIVITIES

The main activities conducted to achieve the objectives of the project and address the research questions are set out in Table 1:

Table 1. The main activities carried out in the present project

<table>
<thead>
<tr>
<th>Step No.</th>
<th>Title of Activity</th>
<th>Activity Description &amp; Relation to Objectives and Research Questions</th>
</tr>
</thead>
</table>
| 1        | Literature survey on electrochemical hydrogen storage. | • Extensive literature surveys on electrochemical hydrogen storage systems.  
• Extensive literature surveys on carbon based materials used for hydrogen storage.  
*Addresses Objective 1 and Research questions 1,2* |
| 2        | Preparation of experimental test rig for testing proton conductivity using electrochemical impedance | • Setup for experimental test rig includes: -  
• Two gold plated metal electrode  
• Nafion-117 membranes  
• Electrode holder, and  
• E.I.S. workstation |
<table>
<thead>
<tr>
<th>Step No.</th>
<th>Title of Activity</th>
<th>Activity Description &amp; Relation to Objectives and Research Questions</th>
</tr>
</thead>
</table>
| 3       | Selection of candidate activated carbon samples | - Selection of candidate activated carbon samples from different precursors of carbon based upon selecting factors like – large surface area, high ultra-micro pore volume and availability.  
  *Addresses Objective 1, 2 and Research questions 1, 2* |
| 4       | Fabrication of Activated Carbon – PTFE composite electrode. | - Activated carbon and PTFE solution will be mixed.  
  - The mixture of activated carbon and PTFE will be poured into a mould for desired shape.  
  - The composite electrode will be obtained from mould.  
  *Addresses Objective 3 and Research questions 2, 3* |
| 5       | Measurement of physical and electrochemical properties of the composite electrode. | - The activated carbon-PTFE composite electrode will be treated with sulphuric acid.  
  - The gold plated metal electrodes will be cleaned using Acetone and Methanol  
  - MEA (nafion membrane-electrode assembly) including composite electrode sandwiched between two nafion membranes will be prepared.  
  - The Proton conductivity will be measured using E.I.S. technique.  
  - Other properties will be measures for example – BET surface area, electron conductivity and TEM.  
  *Addresses Objective 1, 3, 4 and Research questions 3, 4* |
| 6       | Testing the composite electrode in PEM (Proton Exchange Membrane) fuel cell for storage of hydrogen. | - The activated carbon-PTFE composite electrode will be used in an electrolytic cell and will be tested for galvanostatic charging and discharging; cyclic voltammetry using different electrolytes viz. sulphuric acid, ionic protic liquids, and proton conducting gel.  
  - The candidate aC-PTFE electrode will be employed in PEM (Proton Exchange membrane) fuel cell to split water in an electrolyser mode and to generate electricity in the fuel cell mode.  
  *Addresses Objective 5 and Research questions 4, 5* |
| 7       | Data Analysis | - Identify areas of improvement.  
  - Compare the performance of selected aC electrodes under different electrolytes.  
  *Addresses Objective 5 and Research questions 4, 5* |
<table>
<thead>
<tr>
<th>Step No.</th>
<th>Title of Activity</th>
<th>Activity Description &amp; Relation to Objectives and Research Questions</th>
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</table>
| 8       | Publications and Thesis Write Up      | • A formal presentation of research results and interpretations will compiled in the thesis  
|         |                                       | • Journal and conference publications will be ongoing process throughout the period of candidature upon achieve new experimental results  
|         |                                       | *Addresses Objective 5 and Research questions 5*                        |

An extensive literature survey on electrochemical storage of hydrogen and other topics was conducted, focussing particularly on the research work on electrochemical storage of hydrogen from the last decade. A test rig was prepared for the measurement of proton conductivity and double-layer capacitance using electrochemical impedance spectroscopy. Assembly of the electrochemical cell was done in order to test the samples for cyclic voltammetry and galvanostatic charging-discharging processes. Based upon the findings of an earlier master's thesis at RMIT (S. Mohammadi 2014) samples of metal-hydride-nafion composite electrodes were prepared. These fabricated electrodes were tested with electrochemical impedance spectroscopy in order to measure their proton conductivity at different level of hydration. The electron conductivity of these samples was also measured at different level of hydration using ohm meter. The results were recorded, compared, analysed and published in J. Andrews and S. Mohammadi (2014). Jazaeri (2013) reported on the fabrication and testing of composite activated carbon-nafion electrodes for a reversible PEM fuel cell, but did not detect any significant hydrogen storage within the composite electrode. The same aC-nafion samples were used to measure the double-layer capacitance and hydrogen storage capacity using 1 mol sulphuric acid as electrolyte. The results were compared with aC_PTFE sample under same conditions in the present project and were reported in a paper published in proceeding of the Grand Renewable Energy Conference held at Tokyo in July-August 2014 (A. Oberoi and J. Andrews 2014).

Various activated carbon samples from different precursors of carbon were selected based upon large surface area, high ultra-micro pore volume and availability. The selected aC samples were used to fabricate composite aC-PTFE electrodes named as graphitic carbon foam, aC_P, flexible carbon foam, aC_S, mesoporous carbon monolith, aC_N, aC_K2.5,
aC_K7.5, aC_K10, mesoporous carbon 1:1 KOH and mesoporous carbon 1:5 KOH. The characterisation of these aC-PTFE electrodes was done by measuring various physical and electrochemical properties. Hydrogen storage capacities of these fabricated aC-PTFE samples were measured and correlated with surface area. The best performing aC-PTFE electrodes in terms of proton conductivity, electron conductivity, double-layer capacitance and electrochemical hydrogen storage capacity, were then employed in the proton flow battery to test its performance.
3. ELECTROCHEMICAL STORAGE OF HYDROGEN – STATE OF ART REVIEW

3.1 COMPONENTS OF A HYDROGEN SYSTEM

3.1.1 Overview

A normal hydrogen system consists of an electrolyser to split water into hydrogen and oxygen, storage for hydrogen, and a fuel cell to consume the produced hydrogen from storage and oxygen from atmosphere to give water and electricity (Figure 1). All these components are explained in detail in section 3.1.1 to 3.1.3.

Figure 1. Schematic of a hydrogen system.

3.1.2 PEM electrolysers

Anthony Carlisle and William Nicholson in 1800 introduced the method of water decomposition into its constituent elements using electricity. Two conducting wires were connected to a Volta battery through its poles and immersed in salt water, which resulted in gas formation around the wires (J. M. Andujar and Segura, 2009).
The proton exchange membrane (PEM) electrolyser is a device that splits water electrochemically by using DC electricity to generate hydrogen and oxygen (Matt Grasson, 2010). The proton exchange membrane (PEM) electrolyte is capable of conducting protons produced by water splitting on positive electrode (B. M. Gallant 2008). Oxygen is liberated on this electrode, and the protons, as hydronium (H$_3$O$^+$ ions), combine in pairs with two electrons on the negative electrode to form hydrogen gas. There are many membranes available for this type of electrolyser; however, the most commonly used PEM is based upon nafion polymer or perfluorosulfonic acid (PFSA). PEM electrolyser is capable of operation at current densities up to three times higher than alkaline electrolysers (Ito et al. 2011; M. Carmo et al. 2013). Although a PEM electrolyser is much costlier than its alkaline counterpart, its higher cost can be recoup by its higher current density and energy efficiency (N. Briguglio et al. 2013). PEM electrolysers can be smaller and lighter than alkaline electrolysers with the same capacity because of a thinner solid electrolyte (Garcia-Valverde et al. 2012; M. Carmo et al. 2013). 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 are few more advantages of PEM electrolysers (O. Atlam and Kolhe 2011).

A schematic of a PEM electrolyser is presented in Figure 2. In the electrolyser, at anode the water enters and split electrochemically into oxygen gas, hydrogen protons or H$^+$, and electrons by using DC electricity. The H$^+$ gets conducted through the solid electrolyte and emerges at the membrane while the electrons move through the electric circuit towards cathode. At the cathode, the H$^+$ and electrons blend together to give hydrogen gas.
The chemical reaction in the cell is (Ito et al. 2011):

\[ 2\text{H}_2\text{O} + \text{electricity} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^- \]  
\[ \text{Eq. 1} \]

On the hydrogen side, the reaction is:

\[ 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \]  
\[ \text{Eq. 2} \]

The overall reaction in the PEM electrolyser is:

\[ \text{H}_2\text{O} + \text{electricity} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2. \]  
\[ \text{Eq. 3} \]
3.1.3 PEM fuel cell

A fuel cell is an electrochemical device capable of converting chemical energy of the reactants into electricity (F. Zhang 2012). Sir William Grove used principles of electrolyser to compose water electrochemically, and then recombined hydrogen and oxygen atoms in a device that he called a *gaseous voltaic battery* subsequently this device became known as a fuel cell (W. R. Grove, 1839; W. R. Grove, 1842).

PEM fuel cells have an operating temperature between 50 and 100°C and their efficiency lies between 40-60% (F. Zhang 2012). A solid electrolyte, low operating temperature and quick start-up are some of the main advantages of PEM fuel cells (F. Zhang 2012).

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

$$ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- $$  \hspace{1cm} Eq. 4

The protons move towards oxygen electrode (cathode) through the membrane and electrons pass through an external load to produce electric current. Water is produced at cathode by combining protons, electrons and oxygen:

$$ 2\text{H}^+ + 2e^- + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} $$  \hspace{1cm} Eq. 5

PEM fuel cells are employed by many car manufacturers as their technology of choice: namely General Motors (Chevrolet Equinox), Honda (FCX Clarity) Hyundai-Kia (Kia Borrego SUV), Toyota (FCHV-adv), Volkswagen (Passat Lingyu) and Nissan (Xterra FCV) (C. Wang *et al.* 2011). Further review of PEM fuel cells in automobile is available in J. M. Andujar and Segura (2009).
3.1.4 Hydrogen storage systems

3.1.4.1 High-pressure hydrogen storage

High-pressure hydrogen storage involves the storage of hydrogen gas in a pressure vessel at high pressure (Hua et al. 2011). Hydrogen gas can be produced in compressed form by three different ways (B. Bensmann et al. 2013). The first one employs a multi-stage compressor to compress hydrogen gas; the second adopts pressurised water supply in high-pressure electrolysis; and the third involves pressurising hydrogen gas produced within the cell. In the latter method, hydrogen gas keeps accumulating within the cell leading to increased pressure of gas within the cell. Compressed hydrogen gas escapes the cell through a safety valve and is stored in a high-pressure cylinder when the pressure reaches the desired value. Since there is a pressure difference between oxygen side and hydrogen side, the latter method is dependent on the ability of a membrane, supported by the oxygen-side gas diffusion layer, to withstand the resulting mechanical stresses (B. Bensmann et al. 2013).

Higher volumetric densities can be achieved with elevated pressures depending upon the strength of the material used for the storage cylinder. However, greater wall thickness is required to withstand the elevated pressures, leading to an increase in mass of the cylinder and reducing the gravimetric densities (Andreas Zuttel 2003). Therefore, the increase in volumetric density is usually compromised to achieve acceptable value of gravimetric density in pressurised hydrogen gas storage systems.

Another concern is the safety of pressurised storage cylinders. The future hydrogen gas cylinders are; likely to have three layers: a carbon fibre layer wrapped around inner polymer layer and an outer layer to withstand corrosion and mechanical damage (Andreas Zuttel 2003). These future cylinders would allow achieving gravimetric storage density of up to 6 mass% and volumetric storage density of 30 Kg/m$^3$ (Andreas Zuttel 2003). Toyota have recently launched a fuel cell powered car which uses compressed hydrogen gas at the pressure of 700 bar in a cylinder with total gravimetric density of 5.7 wt% (B. Fay et al. 2014).
It is to be noted that relatively low hydrogen storage density with high gas pressure in the system are some important shortcomings of the high-pressure hydrogen storage system.

### 3.1.4.2 Liquid hydrogen

The boiling point of the liquid hydrogen is as low as 21.2 K at atmospheric pressure (Andreas Zuttel et al. 2008). Therefore, liquid hydrogen storage incurs two major challenges: the first is the energy expenditure required to attain low temperature of 21 K; and the second is heat insulation method with high adiabatic efficiency required to maintain the low temperature. About 30% of the heating value of the stored hydrogen is needed to liquefy hydrogen (G. Walker 2008).

Liquid hydrogen vaporises very quickly if stored in an uninsulated vessel. Both thermal radiation and thermal conduction contributes to heat transfer to the vessel (Hanada T. et al. 1995; G. Walker 2008; U. Eberle et al. 2009). The evaporated hydrogen increases the pressure inside vessel. Therefore, gas has to be removed from the vessel in order to keep the vessel pressure within safe limits (M. Hosseini et al. 2012). A major safety concern with vehicles left unattended is related to the removal of gas, particularly when the vehicle is confined in a closed space like garage (G. Walker 2008, S. Brennan and Molkov 2013).

It is possible to store hydrogen in liquid form but high energy expenditures and an efficient insulation system are the key challenges to be met in this area of energy storage. Moreover, safety limitations of this type of storage make it inappropriate to be carried onboard of the light vehicles.

### 3.1.4.3 Hydrogen sorption in solid state

Hydrogen storage in the solid-state can be categorised into two forms: chemisorptions and physisorptions. The first one (Chemisorptions) is based upon strong chemical bonding between hydrogen and the host material (H. Yang et al. 2010a), whereas the latter depends upon weak Van der Waals attraction between molecular hydrogen and surface of the host.
material. However, both the methods have advantages in terms of safety over pressurised hydrogen gas storage and cryogenic liquid hydrogen storage (K. L. Lim and Z. Yaakob et al. 2010). Extensive research to develop this kind of hydrogen storage system has been going on, which includes materials like metal hydrides, zeolites, metal organic framework, doped polymers and carbon based materials (K. L. Lim and Z. Yaakob et al. 2010).

Chemisorption (i.e. in form of metal hydrides) is known for adsorbing large amount of gases, while in physisorption is known for higher energy efficiency and faster adsorption/desorption cycles (K. L. Lim and Z. Yaakob et al. 2010).

Metal hydrides and carbon materials have received high attention of researchers as possible hydrogen storage materials for solid-state storage (Y. Yurum et al. 2009). However, less than 2 wt% of hydrogen storage has been recorded in metal hydrides. Moreover, metal hydrides being made from rare earth metals are quite heavy, which is a major limitation in achieving high gravimetric energy density of a solid-state hydrogen storage system using metal hydrides (U. Eberle et al. 2009). Carbon on the other hand is a promising material for solid-state hydrogen storage because of low cost, availability, environmentally-friendly recycling, low density, and good chemical stability. Also, carbon materials are available in range of porosity and surface areas in form of carbon nanotubes, carbon nanofibers, and activated carbon (Y. Yurum et al. 2009). This form of storage is the focus in the present thesis, with the emphasis on electrochemical methods of forming the C-H bonds.

3.1.4.4 Chemically bonded hydrogen storage liquids

Liquid hydrogen storage materials like N-ethylcarbazole and methanol have shown some initial promising results for chemically bonded hydrogen storage. Scientists are working to find out a liquid-phase material rich in hydrogen with appropriate thermodynamic properties to support reversible hydrogen storage (Maciej Gutowski et al. 2006; Andreas Zuttel et al. 2008). Another storage medium capable of chemical hydrogen storage is ammonia (C. Weidenthaler and Felderhoff 2011). Hydrogen gas could be easily released from ammonia gas by using conventional ammonia decomposition catalysts (Maciej Gutowski et al. 2006). When compared with hydrocarbons, thermodynamic characteristics of hydrogen release from ammonia are more advantageous with less production of heat.
and emission (Macieji Gutowski et al. 2006; G. Walker 2008). However, ammonia is toxic and corrosive, and therefore there are issues concerning safety of people and apparatus (G. Walker 2008). The production of hydrogen on board by a chemical reaction is followed by removal of the reaction products and recycling off-board (J. Alfonso Alonso et al. 2012).

3.2 CONVENTIONAL HYDROGEN SYSTEMS

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

A conventional hydrogen system powered by renewable energy is usually made up of: photovoltaic cell, an electrolyser, a hydrogen storage system, and a fuel cell, as shown in the schematic in Figure 3.

![Figure 3. Schematic of a conventional hydrogen system (modified from A. K. Doddathimmaiah, 2008).](image-url)
In the conventional hydrogen system, surplus solar energy is utilised to generate hydrogen through water electrolysis. Water is split in hydrogen and oxygen through an electrolyser powered by DC electricity from photovoltaic cells. The hydrogen produced is stored in a separate storage and later recovered to use in a fuel cell to produce electricity and water by recombinining hydrogen and oxygen into water (B. Paul and J. Andrews 2008). In order to achieve higher energy densities, hydrogen is compressed before storage. However, when the stored hydrogen is recovered the pressure is reduced before using it in the fuel cell. Power supply for remote areas is one of the possible applications for such systems (A. K. Doddathimmaiah, 2008; B. Paul and J. Andrews 2008). Hydrogen production from water splitting is a well-known and commercially-developed method employed in industries (S. Koumi Ngoh and Njomo 2012).

Zero green-house gas emissions, scalability, and silent operation are main advantages of the conventional hydrogen system (S. Koumi Ngoh and Njomo 2012). A major advantage of this system over commercially-available batteries is that unlike normal batteries the hydrogen storage system does not get self-discharged over time (K. Agbossou et al., 2001). Therefore, normal batteries are known for storing energy for short span of time only, whereas hydrogen energy could be stored until used.

Conventional hydrogen systems also have many disadvantages. The number of devices involved in the system is more than in batteries. The recorded roundtrip efficiency of conventional hydrogen system when going from electricity in to electricity out is only 40 – 45 % compared to 70 – 80 % in batteries (E. Gray et al. 2011). Another disadvantage of the system is its relatively large size, though not necessarily larger than an equivalent battery system, which limits its deployment for mobile applications.

3.2.2 A hydrogen system employing a URFC and storage unit

A unitised regenerative fuel cell or URFC is an individual unit capable of running in both electrolyser and fuel cell mode (J. Andrews and A. K. Doddathimmaiah 2008). This single URFC unit can replace electrolyser and fuel cell in the conventional hydrogen system because electrolyser and fuel cell never work simultaneously in the conventional system. In this hydrogen system, the URFC splits water into hydrogen and oxygen by using DC
electricity from renewable when working in an electrolyser mode. The hydrogen produced in electrolyser mode is pressurised and stored in a separate storage unit. When working in fuel cell mode, the URFC combines hydrogen and oxygen to produce electricity and water (U. Wittstadt et al. 2005). The hydrogen required in the URFC is supplied from the storage unit. The schematic of this hydrogen system with a URFC is shown in Figure 4. Since the system has less number of components compare to the conventional hydrogen system, it has the potential to have a lower mass and volume for the same net electrical energy stored.

Figure 4. Schematic of a hydrogen system with URFC (modified from A. K. Doddathimmaiah, 2008)

It is worth noting that the URFC employed in the system should be compatible, both in efficiency and lifetime, to a dedicated electrolyser and fuel cell (A. K. Doddathimmaiah, 2008). The purchase of a single URFC cell could save the expenses of a separate electrolyser and fuel cell, which is a financial advantage (A. K. Doddathimmaiah and J. Andrews 2006). Many researchers have been working to enhance the efficiency of the URFC both in electrolyser and fuel cell modes (J. Pettersson et al. 2006; A. K. Doddathimmaiah, 2008).
Doddathimmaiah 2008; A. K. Doddathimmaiah and J. Andrews 2009). It is possible to achieve the performance of PEM URFCs close to the dedicated electrolysers and fuel cells, but URFCs are associated with certain limitations of short lifetime and degraded performance after few hundred cycles (P. Millet et al. 2011).

One of the concerns with use of a hydrogen system with URFC is that it still requires an external hydrogen storage unit to store the produced hydrogen. The present research project seeks to overcome the shortcomings of this system by adding a storage electrode within a PEM URFC capable of storing hydrogen electrochemically, while retaining the advantage of a single reversible cell capable of operating in both electrolyser and fuel cell modes.

3.3 INTEGRATED HYDROGEN STORAGE IN A PEM URFC

3.3.1 The concept of the proton flow battery

The proton flow battery concept involves a solid hydrogen storage electrode 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) with an integrated storage (A. K. Doddathimmaiah and J. Andrews, 2008, 2009). A schematic of the concept is shown in Figure 5.
Figure 5. Schematic of integrated hydrogen storage in PEM URFC (J. Andrews & S. Mohammadi 2014)

In electrolyser mode, water is split, hydronium ions (or H\(^+\) ions) emerge from the membrane, and the protons they carry enter into solid storage electrode to form weak chemical bonds with the storage material, ideally without producing any hydrogen gas. The oxygen gas produced in E-mode flows through the channels in oxygen-side end plate and exits the cell. The electrons generated are made to pass through the external circuit. Since in electrolyser mode the input is water that is continuously split into protons, which then flow through the system into the storage, the device has been termed ‘a proton flow battery’ (J. Andrews and S. Mohammadi 2014). The reactions of E-mode operation of the proton flow battery are shown in equation 6 and 7: -

\[
\text{H}_2\text{O} + \text{electricity} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^-.
\]  
Eq. 6

\[
\text{H}^+ + \text{e}^- + \text{M} \rightarrow \text{M-H}
\]  
Eq. 7

where, M is the material of the hydrogen storage electrode.

In the first experimental proton flow battery, the solid hydrogen storage electrode was made of a metal with formation of a hydride on charging (S. Mohammadi and Andrews, 2014). But other materials may also be used, such as various forms of porous carbon as explored in the present thesis.

In fuel cell mode, the stored protons come out of the storage material under the influence of opposite negative and hence attractive electric potential. These protons then travel back through the membrane as hydronium ions where they react with oxygen and electrons on the oxygen-side catalyst to re-form water and generate electricity. The associated reactions are presented in equation 8 and 9:

\[
\text{M-H} \rightarrow \text{M} + \text{H}^+ + \text{e}^-.
\]  
Eq. 8
2H⁺ + ½ O₂ + 2e⁻ → H₂O + electricity  

Eq. 9

The proton flow battery concept has thus managed to eliminate a number of steps involved in the conventional hydrogen system. By comparing Figures 2, 3 and 4 it can be observed that in proton flow battery, unlike the conventional system, there is no need to convert protons produced in E-mode into hydrogen gas, compress the produced hydrogen gas in a separate compressor, store this gas in a separate storage, and split the gas molecules to release protons again in fuel cell mode to generate electricity once again. This cutting out of energy-losing steps leads to the potential of the proton flow battery to have increased round-trip energy efficiency from electricity in to electricity out as compared to the conventional hydrogen system (J. Andrews and S. Mohammadi 2014).

3.3.2 Benefits and potential applications of a proton flow battery

The proton flow battery may be more suitable for mobile applications as compared to the conventional hydrogen system and the URFC hydrogen system because of its more compact structure with a single device serving as an electrolyser, storage and fuel cell all combined. The proton flow battery thus has the simplicity and convenience of a battery: electricity in and electricity out. The energy expenditures associated with running an electrolyser, a compressor and a fuel cell could be saved with the proton flow battery as compared to the conventional hydrogen system. Therefore, it is likely to be possible to achieve overall higher round trip efficiency at low cost with proton flow battery than conventional hydrogen system.

In a proton flow battery, the highly-reactive protons (as H₃O⁺) diffuse directly into the solid storage material where they form weak chemical bonds with the storage material. This concept has opened the way for relatively light and ample materials (for example carbon, graphite, and aluminium) to be used as electrochemical storage for hydrogen, which otherwise requires high pressure and temperatures to react and form strong chemical bonds with hydrogen. Hence, with use of such materials, it promises higher gravimetric and volumetric energy densities, and lower costs per unit mass of hydrogen stored, than commercially available metal hydride-based hydrogen cylinder that employ heavier and very costly rare-earth metals.
3.3.3 Recent work on electrochemical hydrogen storage and the concept of a proton flow battery at RMIT University

The idea of the proton flow battery was first proposed by Professor John Andrews when he was working on URFCs. The research on this concept was initiated in early 2010 by a Master of Engineering (by research) student of Prof. J. Andrews and lead to the first paper articulating the concept and reporting on some initial experiments in 2013 (J. Andrews and S. Mohammadi 2014).

S. Mohammadi in his research work designed and developed a modified PEM URFC cell with an integrated metal hydride based solid hydrogen storage electrode. The device consisted of nafion-117 (perfluorosulfonic acid) as solid polymer electrolyte and was tested with a number of metal hydride (MH) powder electrodes (S. Mohammadi, 2013; J. Andrews and S. Mohammadi 2014).

The research conducted by S. Mohammadi and Andrews (S. Mohammadi, 2013; J. Andrews and S. Mohammadi 2014) provided preliminary experimental evidence on the technical feasibility of the proton flow battery with an integrated solid MH storage electrode and solid polymer electrolyte. It was clearly shown in the research that hydrogen could go in and come out of the MH electrode and could be stored electrochemically in the MH electrode. However, although the reported electrochemical hydrogen storage capacity was measured to be 0.6 wt% of hydrogen in E-mode (reasonable for a first attempt), the amount of hydrogen recovered to run the device in fuel cell mode was much lower (S. Mohammadi, 2013; J. Andrews and S. Mohammadi 2014). Since that time, research and development at RMIT, including the present thesis, has concentrated on enhancing both the storage capacity and the reversibility of the storage electrodes within a proton flow battery.

3.3.4 Limitations of metal hydride storage electrodes

All the tested MH electrodes have shown a significant rate of hydrogen gas production along with formation of chemical bonds in form of hydride within the proton flow battery.
system. One of the reasons reported was the presence of nickel in the metal alloy powder employed to make the hydrogen storage electrodes, which is known to be a good catalyst of hydrogen gas production (S. Mohammadi 2014).

Another important finding that was reported in this research was of water accumulation in the metal hydride electrode, which was drawn steadily from the oxygen-side electrode across the nafion-117 membrane in E-mode operation. This phenomenon is referred to an ‘electro-osmotic’ drag of water molecules (in the form of hydronium, Eigen and/or Zuntel captions). So the water content increases continuously in the hydrogen storage electrode and it eventually gets flooded. Hence, this water logging tends to vary the current over time from the start of applying the charging voltage, even when the other variables are held constant.

3.4 ELECTROCHEMICAL STORAGE OF HYDROGEN IN ACTIVATED CARBON

3.4.1 Review

Electrochemical storage of hydrogen in activated carbon has been extensively researched upon by a European research group including Krzysztof Jurewicz and Elzbieta Frackowiak from Poznan University of Technology, Poland; and Francois Beguin from CNRS-University France, as lead researchers.

In an early publication by this research group (K. Jurewicz et al. 2001), the ability of activated carbon for storing hydrogen electrochemically was reported. This early publication in 2001 revealed that it was possible to store electrochemically more hydrogen in the selected forms of aC than has been achieved with pressurised hydrogen gas, both in aC and using carbon nanotubes. The authors investigated the electrochemical hydrogen storage in activated carbon electrode using potassium hydroxide (liquid KOH) of 6 mol.L\(^{-1}\) concentration as an electrolyte. They tested their hypothesis by employing selected samples of activated carbon in galvanostatic charging discharging. The surface functionality of activated carbons was modified by treating the samples with nitric acid and NaOCl. The
sample activated carbon electrodes were charged and discharged at a constant current in a liquid alkaline electrolyte (i.e. KOH). The amount of hydrogen released from carbon during oxidation process was reported to be as 1.5 wt%, which was higher than the amount absorbed under ambient gas atmosphere.

Another research paper published by K. Jurewicz et al. (2002) reports on reversible storage of hydrogen in activated carbon in a liquid alkaline electrolyte (KOH) and acidic electrolyte (H$_2$SO$_4$). The cell was charged at a high current of 500 mA/g to split water and produce hydrogen, followed by discharging at constant current. The authors reported the hydrogen capacity to be 1.8 wt% in the alkaline electrolyte, which was four times higher than the hydrogen adsorption capacity under 700 bar pressure for the same activated carbon sample. The hydrogen storage capacity in liquid acidic electrolyte was also measured and reported as half that of the alkaline electrolyte. Unlike in the liquid alkaline electrolyte, no distinct discharge plateau was observed in the acidic electrolyte. However, it was clearly shown that activated carbon in acidic electrolyte was capable of storing hydrogen electrochemically. But the authors concentrated almost exclusively on alkaline electrolytes for their later research in electrochemical storage of hydrogen, rather than acidic electrolytes.

In the next publication by these authors, the electrochemical hydrogen storage capacity of a nano-structured carbon electrode in KOH and H$_2$SO$_4$ (aqueous solutions) was investigated using process of galvanostatic charging and discharging and voltammetry techniques (K. Jurewicz et al. 2004). In this paper, the CO$_2$ adsorption isotherm and N$_2$ adsorption isotherm were used for characterisation of the sample of activated carbon. The procedure for charging and discharging the cell was similar to the previous publications by this research group. The paper revealed that the molecular hydrogen evolution through the electrochemical reaction was less favoured in KOH electrolyte than H$_2$SO$_4$. Due to the higher over-voltage of KOH ($\eta$=0.55 V) than H$_2$SO$_4$ ($\eta$=0.32 V), the authors reported a meaningful sorption of hydrogen in basic electrolyte with reversible capacity of 1.3 wt% corresponding to 350 mAh/g. Initially the reported ratio between discharge and charge was 92%, but the discharge capacity or hydrogen storage was only 194 mAh/g (i.e. 0.71 wt %) compared to a charge capacity of 211 mAh/g. To achieve higher discharge values the cell was charged at 14 000 mAh/g, and then the corresponding discharge value reached to 475
mAh/g (1.74 wt %), but the ratio between discharge and charge dropped to about 3%. After this publication, the authors focussed on the investigation of the use of alkaline media.

The relationship between porosity and hydrogen storage capacity of activated carbon was investigated and reported by C. Vix-Guterl et al. (2005). The procedure for charging and discharging the cell was similar to the previous publications by the authors. At room temperature the optimum pore size of the sample activated carbon was estimated by Monte-Carlo simulation and reported to be below 1 nm. A linear relationship was found between the volume of ultra-micro pores (less than 0.7 nm in diameter) and hydrogen capacity). The volume of the ultra-micropore was measured by using the CO₂ adsorption isotherm method. Further, in this paper the contribution of electric double-layer capacitance to hydrogen storage was reported along with hydrogen adsorption on the surface involving a charge transfer. The method of cyclic voltammetry was employed to estimate the electrical double-layer capacitance. For a particular tested sample, the total discharge value was reported to be 432 mAh/g, out of which 54 mAh/g was contributed by the electrical double-layer and the remaining 388 mAh/g by hydrogen discharge from the activated carbon, i.e. 1.44 wt%.

F. Beguin et al. (2006a) examined and reported on the effects of pore size distribution on electrochemical hydrogen storage capacity of activated carbon. It was found in this paper that the ultramicropores with diameter less than 0.7 nm contribute most of the active sites for hydrogen storage. Further it was concluded that larger pores (with diameter more than 0.8 nm) do not play a significant role in storing hydrogen in the activated carbon. Another research fact revealed in this paper was that the hydrogen forms a weak (but stronger than physisorption) chemical bond with carbon in the active storage sites. Further it was reported that the reversible hydrogen storage capacity of nanoporous carbons increased with increased operating temperature to 60 °C.

F. Beguin et al. (2006b) explored the procedure and attributes of the bonds formed between activated carbon and hydrogen. The authors reported on the formation of weak chemical bonds between carbon and hydrogen during electrolysis of water within KOH electrolyte. It was shown that the hydrogen capacity of activated carbon rises with temperature from
room temperature to 60° C. One reason suggested for this relationship was that the increased thermal energy with rising temperature assisted in overcoming the activation energy for bond formation between the carbon material and hydrogen.

K. Jurewicz *et al.* (2008) explained the method of construction of activated carbon from lignin based coal. The manufactured activated carbon was employed for fabricating electrode for a capacitor and not to test electrochemical hydrogen storage capacity. Even so, because the method of preparation of activated carbon from lignin (as the precursor) was explained in details, this paper was of interest to the author of this thesis. The lignite samples were activated by KOH chemical activation in inert atmosphere using argon gas. The porosity of the sample was measured by N₂ adsorption isotherm at 77 K. The result showed that the average pore diameter decreases from 2.3 to 2.0 nm with increase in the final activation temperature from 500°C to 700°C. The authors have identified lignin as a suitable candidate for the fabrication activated carbon.

K. Babel and K. Jurewicz (2008) tested a highly porous carbon sample with surface area as high as 2000 m²/g, micropore volume equal to 31% of total volume and pores with diameter between 0.5 nm to 0.64 nm for its electrochemical hydrogen storage capacity using KOH as electrolyte. The authors have reported to have achieved electrochemical hydrogen storage capacity of 1.89 wt%. It was therefore concluded that the electrochemical hydrogen storage capacity of activated carbon could be enhanced with large micropore volume and small mesopore volume.

K. Jurewicz (2009) examined that how electrochemical hydrogen storage capacity of activated carbon is affected by charge current density and duration of charge. The precursor and procedure of activation of carbon sample were identical to the earlier publications by K. Babel and K. Jurewicz (2008), except that the final activation temperature was 700°C as compared to 900°C in the previous paper. It was found that a large over-charge, leading to a very low coulomb efficiency, was required to attain the maximum hydrogen capacity, in this case a very high value of 2.17 wt %. The discharge value of electrochemical hydrogen storage was not distinguished from electrical double-layer by the author. Infact, the electrical double-layer was considered as an additional advantage and equally useful as the charge in enhancing the electrochemical hydrogen storage capacity of activated carbon.
storage capacity of the activated carbon. Further it was concluded that the reversible hydrogen storage capacity was not separately dependent upon the charge current density or the charging time, but only on the amount of supplied charge.

A design concept for a secondary battery based on reversible hydrogen storage in an activated carbon electrode using a liquid alkaline KOH electrolyte was proposed by K. Jurewicz et al. (2009). A schematic of this type of rechargeable fuel cell is shown in Figure 6.

![Schematic representation of the rechargeable fuel cell (K. Jurewicz et al. 2009)](image)

While charging, the porous carbon electrode was set as the positive pole, and the auxiliary electrode, nickel gauze in this paper, as the negative pole. The reactions in this mode were as follows:

\[
\text{Carbon electrode: } C + xH_2O \rightarrow CH_x + xOH^- + xe^- \quad \text{Eq. 10}
\]

\[
\text{Auxiliary electrode: } xOH^- \rightarrow (x/2)H_2O + xe^- + (x/4)O_2 \quad \text{Eq. 11}
\]
In recharging, carbon electrode was set as negative and air electrode, which was activated carbon layer with platinum black in this case, as positive. The reactions in this mode were as follows:

\[
\text{Air electrode: } (x/2)\text{H}_2\text{O} + xe^- + (x/4)\text{O}_2 \rightarrow x\text{OH}^- \quad \text{Eq. 12}
\]

\[
\text{Carbon electrode: } \text{CH}_x + x\text{OH}^- \rightarrow \text{C} + x\text{H}_2\text{O} + xe^- \quad \text{Eq. 13}
\]

The auxiliary electrode was employed in charging to facilitate the oxygen gas evolution on carbon electrode, which could lead to oxidation of carbon. The electrochemical hydrogen storage capacity of carbon electrode was reported to be 1.44-1.66 wt%. The discharge capacity of the cell was found to be 450 mAh/g, which correspond to 1.65 wt% hydrogen storage capacity.

It is to be noted that, in all the published research papers by the Jurewicz group, the total charge flow in the charging cycle was much higher than the charge flow during the discharge cycle. Hence a large over-charge was required to achieve the maximum electrochemical hydrogen storage capacity of hydrogen in the activated carbon electrodes (K. Jurewicz et al. 2004; K. Jurewicz 2009). Hence, it was likely that the majority of charge was consumed in formation of hydrogen gas (H\textsubscript{2}) rather than the hydrogen that entered the aC storage sites as atomic hydrogen. In the case of the proposed rechargeable fuel cell (K. Jurewicz et al. (2009), there was no mechanism mentioned to vent-out the hydrogen gas produced in the cell. Importantly, however, the publications by this research group presented early evidence that activated carbon can act as a medium for electrochemical storage of hydrogen, achieving gravimetric densities even above 2 wt%. Hence these findings pointed the way towards a proton flow battery with an integrated carbon-based hydrogen storage electrode.

E. Frackowiak (2010) critically examined the bond between hydrogen and carbon acting as a host material. The author reported the binding energy of H\textsubscript{2}C bond to be 110 kJ/mol and considered electrochemical storage of hydrogen in carbon as chemisorptions, as it was suggested in F. Beguin et al. (2006b).
G. Lota et al. (2011) studied that how the electrochemical hydrogen storage is affected by the charge parameters. An interval method for charging the electrodes was employed, involving periodic charging of the electrode for few seconds (the ‘pulse’), resting for few seconds without charging (the ‘pause’), and then a charging pulse again. Pulse-pause charging was done for 9 minutes (6 mins. charging followed by 3 mins. of pause), which resulted in charging of electrode with 1.08 wt% of hydrogen. The effect of temperature on electrochemical hydrogen storage capacity of activated carbon was also investigated by the authors. It was concluded that the hydrogen storage capacity was improved by 10% when temperature was elevated from 25°C to 60°C that confirms the result of F. Beguin et al. (2006b).

K. Babel et al. (2012) mentioned details of the fabrication of various activated carbons from different precursors. One of the fabricated activated carbons that were made from blackthorn stone was found to have a 2.31 wt% electrochemical hydrogen storage capacity. However, in this paper the validity of the previously proposed linear relationship between volume of ultra-micro pores and hydrogen storage capacity was challenged.

A. Weselucha-Birczynska et al. (2012) used Raman spectroscopy to get a better understanding of the structure of activated carbons. Since there was not a straight-forward relationship between surface area (and even ultra-micro pore volume) and electrochemically stored hydrogen in activated carbon mentioned in the literature, it lead the author into this investigation of structure of carbon. It was revealed from the data of the Raman spectroscopy that activated carbons of different precursors have different phases and even different forms within a certain phase. Therefore, in addition to pore volume, pore size distribution, and surface area, phases of carbon can be another important parameter affecting the electrochemical hydrogen storage capacity.

3.4.2 Mechanism of electrochemical storage of hydrogen in activated carbon

V. Jiménez et al. 2012 reported that hydrogen has a better accessibility to the internal pore surface of highly amorphous carbons compared to more graphitic carbon materials. This research paper reports on the comparison of hydrogen adsorption capacity of activated
carbons and non-activated carbons. Further, the effect of activation on BET surface area and pore volume of carbons was evaluated and reported in this publication.

In an alkaline environment, Volmer reaction forms the base for hydrogen adsorption (K. Jurewicz et al. 2004; Qu 2008), which is given as:

\[ C + e^- + H_2O \rightarrow CH_{ads} + OH^- \]  \hspace{1cm} \text{Eq. 14}

Thereafter the adsorbed hydrogen moves into the interlayer spaces and nanopores of the carbon (Qu et al. 2012). The adsorbed hydrogen may be evolved to hydrogen molecule through the Tafel reaction (K. Jurewicz et al. 2004; Qu 2008):

\[ 2CH_{ads} \rightarrow H_2 + 2C \]  \hspace{1cm} \text{Eq. 15}

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

\[ CH_{ads} + H_2O + e^- \rightarrow H_2 + OH^- + C \]  \hspace{1cm} \text{Eq. 16}

If the energy involved in hydrogen adsorption is lower than the energy required for Tafel or Heyrovsky reactions, then hydrogen gas is evolved (K. Jurewicz et al. 2004). The micro spaces of the imperfect structure of carbon are considered as major storage sites for hydrogen (Qu 2008).

Qu (2008) reported about the some indication that ambient conditions are not suitable for molecular hydrogen storage in activated carbon. Instead, the hydrogen has to be in atomic form in order to get stored electrochemically in carbon. The existence of atomic hydrogen in activated carbon was experimentally proved by C. S. Tsao et al. (2011). The authors have revealed the state of hydrogen in Pt-doped activated carbon using the inelastic neutron scattering method.

Furthermore, it was shown that C-H bond energy for electrochemically-stored hydrogen in KOH environment is only about 110 kJ/mol and hence this bond can be categorised as a weak chemical bond (F. Beguin et al. 2006b and E. Frackowiak 2010).
3.4.3 Activated carbon as hydrogen storage medium at RMIT University

Professor John Andrews at RMIT University have proposed the idea of the proton flow battery and started a research project with his master of engineering by research student named S. Mohammadi in 2010. The thesis published in 2013 has showed the feasible running of the proton flow battery with an integrated metal-hydride (MH) storage electrode (S. Mohammadi 2013; J. Andrews and S. Mohammadi 2014). However, the evolution of H$_2$ (hydrogen gas) was reported while testing the experimental proton flow in electrolyser mode. The possible explanation for the formation of hydrogen gas was reported as the transition of metal particles in the metal hydride electrode that might act as a catalyst in gas generation. In fact, it is mentioned in the literature that metal hydride has an advantage to act as both storage and catalyst for hydrogen (D. Chartouni et al. 2002). Unlike transition metals, carbon does not have d-electrons to facilitate hydrogen association or dissociation and therefore it is a poor catalyst for hydrogen gas generation (Andreas Zuttel et al. 2008). Therefore, the research focus at RMIT University shifted from metal-hydride to carbon to test the concept of the proton flow battery. Moreover, availability, low cost and light weight of carbon compared to metal hydrides are few additional reasons for selection of carbon to test the feasibility of the concept of proton flow battery. Also K. Jurewicz, E. Frackowiak, and F. Beguin (see section 3.4.1) have revealed in their research publications that activated carbon has the potential to achieve high capacity of hydrogen storage (about 2 wt%).

Jazaeri (2013), also working at RMIT, has investigated a composite electrode for a proton flow battery made from activated carbon and nafion to check its capability for reversible hydrogen storage. However, Jazaeri found no detectable level of reversible hydrogen storage in such an electrode. A likely explanation of this result he identified was that, in the composite nafion-activated carbon electrode constructed, the relatively large molecular size of the nafion polymer strands would mean that the nafion is unable to penetrate into the ultramicropores (diameter ≤0.7 nm) of the activated carbon particles. Hence there is no medium to conduct the protons right into these ultramicropores, which previously have
been identified as the primary sites for electrochemical storage of hydrogen in these porous carbons.

### 3.5 CONCLUSIONS

#### 3.5.1 Limitations of previous studies and areas requiring R&D

The General Electric Company has researched on metal hydride electrodes for fuel cell application. These metal-hydride electrodes being made from rare earth metals are very expensive as compared to other energy storage materials. Moreover, gravimetric hydrogen density, recycling of metal hydride materials, and heat management related to metal hydrides are few areas requiring further research for widespread application of such materials. Carbon has emerged as a suitable candidate for energy storage applications because it is easily available, cheap, and easy to recycle. Another important attribute of carbon favouring hydrogen storage is its lower density compared to metal hydrides that may promise a higher gravimetric hydrogen capacity.

The research done by K. Jurewicz, E. Frackowiak, and F. Beguin was focussed on electrochemical storage of hydrogen in alkaline liquid electrolyte. But, there were few issues related to the use of alkaline electrolyte, these are the need to purify and pump electrolyte, safety issues related to leakage of electrolyte, low current density of alkaline electrolyte, and sensitivity to CO₂.

The research of S. Mohammadi (2013) revealed that metal hydride act as a catalyst for hydrogen gas formation and thus majority of electrochemically produced protons leave the electrode without making bond with the metal hydride electrode and forms hydrogen gas instead. Carbon on the other hand, does not have d-electrons and may therefore restrict the formation of hydrogen gas in the electrolyser mode.

Mohammad J. Jazaeri (2013) reported on using composite activated carbon-nafion electrode with nafion-117 as solid electrolyte and proton conducting medium in proton flow battery. He found no detectable signs of stored hydrogen in carbon-nafion composite electrode. Nafion being a polymer have larger molecules than pores of activated carbon
and did not penetrate into ultramicropores of activated carbon that are known as potential hydrogen storage sites.

3.5.2. Gaps in knowledge and understanding in this area of research, and focus in present thesis

Building on the earlier work of S. Mohammadi (2013) and Mohammad Javad Jazaeri (2013), the present research focuses on using activated carbon electrodes for hydrogen storage with a liquid proton conducting medium, instead of a metal hydride or activated carbon with solid electrolyte (nafion-117 polymer). A liquid electrolyte penetrating into the aC electrodes has been used with the aim of facilitating the conduction of protons (in the form of hydronium ions) right into the deepest pores of activated carbon. Carbon has been selected rather than a metal alloy as the hydrogen storage medium with the aim of hindering the formation of hydrogen gas, since carbon does not have d-orbital electrons like transient metals in metal hydrides. Moreover, carbon, an abundant and light weight material, used as the hydrogen storage electrode in a proton flow battery has the potential of both reducing the total weight of the cell and increasing its gravimetric hydrogen storage capacity.

The present research differs from the work of K. Jurewicz, E. Frackowiak, and F. Beguin in using an acidic proton exchange membrane instead of an alkaline (KOH) electrolyte. Proton exchange membranes promise higher charge density. The solid proton exchange membrane may also increase the hydrogen storage capacity by transferring highly-reactive protons into liquid electrolyte and then into deepest pores of 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 PTFE (polytetrafluoroethylene) has been fabricated and tested in a specially designed PEM URFC using 1 mol. H₂SO₄ as liquid acidic electrolyte 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 PTFE is also described in the chapter 4. The method of characterisation of the fabricated electrodes in terms of their physical and electrochemical properties is presented in Chapter 5. Chapter 6 gives details of experimental setup, testing procedures and experimental results.
4 FABRICATION OF ACTIVATED CARBON ELECTRODES

4.1 ACTIVATED CARBON

4.1.1 Preparation of precursors

4.1.1.1 Precursors

Carbon is readily available in nature in multiple forms that may serve as precursors for making activated carbon, such as brown and black coals, corn cob, banana peel, pistachio-nut shell, oil sands coke, wood sawdust and fruit stones (C. F. Chang et al. 2000; A. C. Lua and H. Yang 2004; S. Mopoung, 2008; H. Chenand Hashisho 2012; K. Y. Foo and Hameed 2012; B. Y. Venhryn et al. 2013; Jazaeri 2013). In the present project, initially charcoal was used as the precursor for making activated carbon. Subsequently, vitreous carbon from phenolic resin and Victorian brown coal were used as precursors. Sample carbon powder from charcoal was activated and supplied by Mohammad Javad Jazaeri, an earlier Master of Engineering by research student at RMIT University, Melbourne. Various samples of activated carbon powder made from phenolic resin were prepared and supplied by Dr M. Karthik, a Research Associate at CIC Energigune, Spain. Samples of activated carbon powder made from Victorian brown coal was prepared and supplied by Lachlan Ciddor, a PhD student in the School of Chemistry, Monash University, Melbourne, Australia. Hence to date only a relatively small selection of possible activated carbon samples – from particular precursors and employing particular activation procedures – have been investigated in this project for electrochemical hydrogen storage and suitability for the proton flow battery application. A much more extensive search for the best-performing carbons for these applications is thus necessary in the future.

Burning wood in a deficient oxygen atmosphere is the conventional method to obtain charcoal (Agirre et al. 2013). Across the globe, millions of tonnes of charcoal are produced.
annually (L. C. Zulu and Richardson 2013). Decomposition of vegetation in presence of heat and pressure under water bodies for millions of years lead to formation of coal (Australia Institute of Energy 2013). The density of coal (~1300 kg/m³) is typically more than six times that of charcoal at around 200 kg/m³ (G. Walker 2011; J. G. Speight 2013). Commercially-available charcoal (Diggers charcoal made from lump hardwood) was purchased by Jazaeri from the market for this project (J. Jazaeri, 2013). Photographs of charcoal, brown coal and vitreous carbon made from phenolic resin, the precursors for making activated carbon in the present study, are shown respectively in Figures 7, 8 and 9.

Figure 7: The morphologies of charcoal sample (Xiaojun Ma et al. 2015).

Figure 8. The morphologies of Victorian brown coal sample (R. Durie 1991).
It is worth noting that the structure of an activated carbon remains broadly similar to its precursor during the process of fabrication and activation, as the precursor is ‘hollowed out’ to form a porous material of much lower density (J. Jazaeri 2013). In certain literature the activated carbon is referred as a ‘pseudo-morph’ of its precursor (Marsh & Rodriguez-Reinoso 2006). Hence the properties of the final activated carbons are affected by structure of the precursor. Therefore, it becomes necessary to find the most suitable candidate for the proton flow battery application by employing various different precursors and activation procedures. As mentioned before, this project is just a part of a much more comprehensive research effort required to review a full range of activated carbons for this application.

4.1.1.2 Morphology of precursors

The precursor carbon samples were crushed in a crucible to form fine powder, which later was also used for elemental analysis. The elemental analysis was done to check for any unwanted impurity mixed in carbon powder. The grain size of sample carbon powders was studied using Scanning Electron Microscopy (SEM). SEM can also be employed for the
study of surface texture, dimensional changes and structural changes of the carbon sample (P. J. M. Carrott et al. 2002; B. G. Kutchku et al. 2013). In SEM, electrons from the electron gun (usually a tungsten filament) are shot onto the carbon sample and the image is formed by detecting back-scattered electrons and secondary electrons emitted by the material (Cazaux 2012). The initial testing of samples showed that all were electrically conductive. Hence, no electrically-conducting coating was used on or before imaging the samples in the SEM machine.

Two SEM machines available in Australian Microscopy and Microanalysis Research Facility (AMMRF) at RMIT University − a FEI Quanta 200 ESEM, and Philips XL30 SEM − were employed for imaging the carbon samples used in this research project. High vacuum was used, when imaging the carbon samples with a high accelerating voltage of 20 kV. A sticky double-sided conductive carbon tape was used to mount the carbon samples on stubs in the SEM.

Figure 10. SEM image of the activated charcoal powder taken by Philips XL30 SEM

Figure 10 presents an SEM image of the charcoal powder. The charcoal powder had particle sizes ranging from a few µm to 70 µm with most of them tending towards the
lower end of this range. It is to be noted that fine charcoal powder was obtained by grinding several lumps of charcoal; therefore, the structure of the final powder is an average over these lumps (J. Jazaeri 2013). The diversity of porous structures within this charcoal can clearly be seen in Figure 11.

![Figure 11. Different structures observed in the charcoal powder using the Philips XL30 SEM (J. Jazaeri 2013).](image)

**4.1.1.3 Elemental analysis of precursors**

Elemental composition of the samples was investigated by Energy-Dispersive X-ray spectroscopy (EDX). EDX is an effective, reliable and fast technique for elemental analysis of a sample. The distribution of metals in a sample can also be investigated by EDX (Y.
Sun et al. 2011). Figure 12(a) shows a schematic and 12(b) a photograph of an EDX system.

Figure 12. (a) Schematic of an EDX apparatus (modified from www.thermo.com)
(b) Photograph of SEM machine with EDX tool (located at RMIT University) used in the present project.
In EDX, the specimen material is exposed to a beam of X-rays that excites electrons from atoms in the material to higher energy levels. Energy from the excited electrons is emitted in the form of photons (in the X-ray region of the spectrum) as they go back to their ground states. The energy and hence frequency of the emitted photon corresponds to the energy difference between the excited and ground states, which is unique for each element. The X-ray energy is converted into voltage signals by an X-ray adaptor and these voltage signals form the horizontal axis of the spectrum. At each characteristic energy/voltage, the X-ray count indicates the concentration of the atoms in the sample that have this signature.

An EDX feature is an inherent part of most scanning electron microscopes. It is to be noted that the source energy for excitation is different for a stand-alone EDX and SEM-EDX, because of the use of the electron beam in the latter for this purpose instead of an X-ray beam (Y. Leng 2008). SEM-EDX is also known by the name of Energy Dispersive Spectroscopy (EDS). In the present project, the Philips XL30 SEM with Oxford Si (Li) detector at the RMIT University Microscopy and Microanalysis Facility (RMMF) was used for the elemental analysis of all the carbon-based specimens.

In the EDS spectra results, ‘counts’ refer to the number of emitted X-rays from the sample, plotted on the vertical axis. The elemental composition of the samples is defined by the relative intensities of the reflected electrons given by these counts. The mass percent of each element is determined by comparing the relative heights of the peaks. In the process of the elemental analysis, there are certain periods when no emission is counted, which are known as Dead Times. The EDS spectrum obtained for the charcoal powder is presented in Figure 13.
Figure 13. EDS result for the activated charcoal powder using EDX tool in Philips XL30 SEM (J. Jazaeri, 2013).

For this aC sample, the results show that 66 wt% of the sample was carbon, 29 wt% was oxygen, and from rest of the elements 1.5 wt% was calcium. The principal elements and their weight percent in the aC sample are presented in Table 2.

Table 2. The elemental composition of activated charcoal powder measured by SEM-EDX

<table>
<thead>
<tr>
<th>Element</th>
<th>(wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>66</td>
</tr>
<tr>
<td>Oxygen</td>
<td>29</td>
</tr>
<tr>
<td>Calcium</td>
<td>1.5</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1.34</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.30</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.86</td>
</tr>
</tbody>
</table>

From the elemental analysis it was found the oxygen to carbon ratios in the charcoal were in the range of 0.2-0.4, which corresponds with the literature (S. Brodowski et al. 2005). Both the EDS and EDX techniques have one major limitation: that they cannot detect
elements lighter than boron. Therefore, if the sample consists of hydrogen, it cannot be detected by the EDS method (J. Jazaeri 2013). No elemental analysis data were supplied on the other two precursors – Victorian brown coal and phenolic resin.

4.1.2 Activation techniques

4.1.2.1 Main types
Carbon activation techniques can be classified into two main categories: physical activation and chemical activation.

Pores in carbon structure are classified according their respective diameters (Marsh and Rodriguez-Reinoso 2006; O. W. Achaw 2012):

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

4.1.2.2 Physical activation

The activation process that involves creation of voids in a precursor by removal of carbon material so as to increase porosity is known as physical activation.

In physical activation (also known as thermal activation) carbonisation of the carbon-rich precursor takes place in an inert atmosphere (or in the absence of air). Steam or CO₂ or both are used as activating agents in the process of activation at temperatures in the range of 800-1200°C (J. E. Vargas et al. 2010; S. X. Zhao et al., 2013; Sachin and Saka, 2013). Some research papers have reported on tests on fibre and coke samples that indicated CO₂ activation creates less porosity than steam activation (M. A. A. Zaini et al. 2010).

During the physical activation process, oxygen is supplied in a controlled amount, and its reaction with the carbon generates the heat to drive the reaction for carbon removal. Hence pores are created and the precursor becomes activated carbon. It is obvious that, in this
process of activation, the mass of the carbon sample decreases. The difference between the mass of the carbon sample before and after activation is termed 'burn-off' or 'yield', and is dependent on activation time (C. F. Chang et al. 2000). Specifically the yield is the ratio of the mass of activated carbon to the mass of precursor (K. Y. Foo and Hameed 2012b). Physical activation of carbon involves two steps: first formation of pores, until 60% burn-off is reached; and second widening of the existing pores and converting them into mesopores (Marsh and Rodriguez-Reinoso, 2006; O. Sahin and Saka, 2013).

The physical activation is affected by various factors such as structure of the carbon, reacting temperature, and partial pressure of the reacting gas (Marsh and Rodriguez-Reinoso 2006). On the other hand, the size and volume of microspores is mainly dependant on the activation agent, the amount of oxygen surface complexes, activation equipment, and the structure and elemental composition of the initial carbonaceous precursor (Marsh and Rodriguez-Reinoso 2006).

4.1.2.3 Chemical activation

In chemical activation, the precursor carbon-based material is subjected to chemical treatment followed by heating to a high temperature in an inert atmosphere or in absence of oxygen. Advantages of this activation technique over physical activation are higher yields, lower temperatures required and less activation time (C. Wang and Kaskel 2012).

The chemicals most commonly used for chemical activation are potassium hydroxide, zinc chloride, sodium hydroxide, and phosphoric acid (Marsh and Rodriguez-Reinoso 2006; A. Linares-Solano et al. 2012). The KOH activation involves a very complex mechanism and is still not completely understood (D. Lozano-Castello et al. 2001). However, C. Wang and Kaskel (2012) have reported the following steps in the KOH activation process.

- Reactions that take place in the temperature range of 400-600 °C:
2KOH $\rightarrow$ K$_2$O + H$_2$O  \hspace{1cm} \text{Eq. 17}

C + H$_2$O $\rightarrow$ CO + H$_2$ \hspace{1cm} \text{Eq. 18}

CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$  \hspace{1cm} \text{Eq. 19}

CO$_2$ + K$_2$O $\rightarrow$ K$_2$CO$_3$ \hspace{1cm} \text{Eq. 20}

- Reactions occurring at temperatures higher than 700 ºC are:

K$_2$CO$_3$ $\rightarrow$ K$_2$O + CO$_2$ \hspace{1cm} \text{Eq. 21}

CO$_2$ + C $\rightarrow$ 2CO. \hspace{1cm} \text{Eq. 22}

- Metallic potassium is also produced at temperature above 700ºC via these reactions:

K$_2$CO$_3$ + 2C $\rightarrow$ 2K + 3CO \hspace{1cm} \text{Eq. 23}

C + K$_2$O $\rightarrow$ 2K + CO. \hspace{1cm} \text{Eq. 24}

The chemical activation by adding KOH is composed of three phases: first, pure chemical activation, as shown in equations 17-20; second, physical activation, as shown in equations 21 and 22; and third, the expansion of carbon lattices via the entry of metallic K into the carbon matrix, as shown in equations 23 and 24. The pores created in the chemical activation process by adding KOH are usually blocked by potassium after the activation. So, potassium is needed to be removed to clear this blockage (D. Lozano-Castello et al. 2001).

Chemical activation technique possesses the advantage of controlling the pore size in activated carbon; whereas the disadvantages of this techniques involves the additional washing step needed to remove the activating agent, and the use of corrosive chemicals.

4.1.2.4 Activation technique used for present samples
All the samples used in the present project were activated by chemical activation technique because of the control it affords over pore size and temperature of each stage. Further, KOH was used as the activation agent because of its wide usage in activating of carbon for hydrogen storage application (e.g. K. Babel and Jurewics 2008; Bleda Martinez et al. 2008; Jurewics 2009; A. Minoda et al. 2013). Another reason for choosing KOH as the activating agent was that it could produce more porosity as compared to steam activation for same precursor (M. Song et al. 2013). One of thirteen activated carbon samples was made from charcoal powder (named as ‘aC_P’) and supplied by RMIT Master of Engineering by research student, Mohammad Javad Jazaeri. Other samples were supplied by CIC Energigune, Spain and Monash University (refer Table 3 for details).

Table 3. Name and detail of aC samples used in the present research work

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of aC sample</th>
<th>Precursor</th>
<th>Activation method</th>
<th>Person/Organisation that supplied the samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>aCP</td>
<td>Charcoal powder</td>
<td>Chemical activation by adding KOH</td>
<td>Mohammad Javad Jazaeri, RMIT University</td>
</tr>
<tr>
<td>2</td>
<td>aCN</td>
<td>Commercial aC Nitro 50</td>
<td>Not given</td>
<td>Lachlan Ciddor, Monash University.</td>
</tr>
<tr>
<td>3</td>
<td>aCS</td>
<td>Brown Coal</td>
<td>Chemical activation by adding KOH</td>
<td>Lachlan Ciddor, Monash University.</td>
</tr>
<tr>
<td>4</td>
<td>aCK 2.5</td>
<td>Brown Coal</td>
<td>Chemical activation by adding KOH</td>
<td>Lachlan Ciddor, Monash University.</td>
</tr>
<tr>
<td>5</td>
<td>aCK7.5</td>
<td>Brown Coal</td>
<td>Chemical activation by adding KOH</td>
<td>Lachlan Ciddor, Monash University.</td>
</tr>
<tr>
<td>6</td>
<td>aCK10</td>
<td>Brown Coal</td>
<td>Chemical activation by adding KOH</td>
<td>Lachlan Ciddor, Monash University.</td>
</tr>
<tr>
<td>7</td>
<td>Mesoporous carbon monolith</td>
<td>Phenolic resin</td>
<td>Chemical activation by adding KOH</td>
<td>Dr M. Karthik, CIC Energigune, Spain</td>
</tr>
<tr>
<td>8</td>
<td>Mesoporous carbon 1:1 KOH</td>
<td>Phenolic resin</td>
<td>Chemical activation by adding KOH</td>
<td>Dr M. Karthik, CIC Energigune, Spain</td>
</tr>
<tr>
<td>9</td>
<td>Mesoporous carbon 1:3 KOH</td>
<td>Phenolic resin</td>
<td>Chemical activation by adding KOH</td>
<td>Dr M. Karthik, CIC Energigune, Spain</td>
</tr>
</tbody>
</table>
4.1.3 Activated carbons from CIC Energigune, Spain

Seven samples of activated carbon made from phenolic resin and activated by chemical activation technique using KOH were provided by Professor Bruno D’Aguanno and Dr M. Karthik from CIC Energigune, Spain for testing in this project. The samples were named: graphitic carbon foam, flexible carbon foam, mesoporous carbon monolith, mesoporous carbon 1:1 KOH, mesoporous carbon 1:3 KOH, mesoporous carbon 1:5 KOH and mesoporous carbon 1:7 KOH. The data on surface area and porosity were supplied to the author by CIC Energigune and are reported in chapter 5.

4.1.4 Activated carbons from Monash University

Five samples of activated carbon were provided by Professor Alan Chaffee and PhD candidate Lachlan Ciddor from the School of Chemistry, Monash University, for testing in this project. The samples were named: AC_N, AC_S, ACK2.5, ACK7.5, and ACK10. The precursor of all supplied sample was Victorian brown coal and the activation process used to produce these samples was chemical activation by KOH. The porosities of the samples were disclosed and reported in Jazaeri 2013 and mentioned in section 5.3.6 (Table 9) of this thesis.

4.2 FABRICATION OF ACTIVATED CARBON-PTFE ELECTRODES
4.2.1 Weighing and mixing

All the activated carbon samples were weighed separately using the digital weighing scale shown in Figure 14 to measure their density, and the specific amounts needed to fabricate electrodes. The specifications of the weighing scale used are listed in Table 4. Calibration of the scale was checked using a standard dead weight of known mass and all possible errors were taken into account while calculating the amount of electrochemical hydrogen storage in carbon in chapter-6 of this thesis.

Table 4. Specifications of the digital weighing scale

<table>
<thead>
<tr>
<th>Model</th>
<th>LWS-3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Display</td>
<td>16.5mm digital high LCD display</td>
</tr>
<tr>
<td>Capacity</td>
<td>3000 g</td>
</tr>
<tr>
<td>Readability</td>
<td>0.002 g</td>
</tr>
<tr>
<td>Pan size</td>
<td>Ø 120 mm</td>
</tr>
<tr>
<td>Keyboard</td>
<td>7 membrane keys</td>
</tr>
<tr>
<td>Housing</td>
<td>ABS plastic</td>
</tr>
<tr>
<td>Attachment</td>
<td>Wind shield</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>5º C ~ 40º C</td>
</tr>
<tr>
<td>Power</td>
<td>AC adapter (12V/500mA), Rechargeable battery (6V/1.2A)</td>
</tr>
<tr>
<td>Gross weight</td>
<td>2 Kg</td>
</tr>
</tbody>
</table>

A commercial polytetrafluoroethylene (PTFE) solution was added into already weighed activated carbon (aC) powder and mixed thoroughly on a hot plate to remove solvent of PTFE as shown in Figure 15. The PTFE was to act as a binder to hold the aC particles together in the electrode. The volume of solution added was set so that after evaporation of the solvent the mass of PTFE in the electrode was 10 wt% of the mass of the aC powder.
Aqueous polytetrafluoroethylene (PTFE) resin solutions available commercially are hydrophobic containing PTFE particles with diameter ranging from 0.05 to 0.5 µm suspended in water (Jiri George Drobny 2009). Commercial products have a resin content of approximately 60% by weight. Most PTFE dispersions typically contain 6% to 10% of the weight of the resin of non-ionic wetting agent and stabilizer (essentially a surfactant). The specific gravity of such dispersion is about 1.50 (Jiri George Drobny 2009).
PTFE resin dispersions are milky-white liquids, with viscosity of approximately 20 cP and pH about 10 (Jiri George Drobny 2009). The specifications of commercial PTFE solution used in the present project are listed in Table 5.

Table 5. Specifications of the PTFE solution used in the present project

<table>
<thead>
<tr>
<th>Model</th>
<th>3M™ Dyneon TF 5035 GZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Water-based fluoropolymer dispersion</td>
</tr>
<tr>
<td>Appearance</td>
<td>Milky-white</td>
</tr>
<tr>
<td>Solids content</td>
<td>58%</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>Emulsifier content</td>
<td>5%</td>
</tr>
<tr>
<td>Particle size</td>
<td>200 nm</td>
</tr>
<tr>
<td>pH value</td>
<td>&gt;9</td>
</tr>
<tr>
<td>Viscosity</td>
<td>12 mPas</td>
</tr>
<tr>
<td>Density</td>
<td>2.2 g/ml</td>
</tr>
</tbody>
</table>

4.2.2 Moulding

Slurry of activated carbon powder mixed with commercial PTFE was obtained after evaporation of the solvent contained in PTFE. The slurry was poured into a mould of 25 mm x 25 mm x 2 mm to attain the desired shape of the electrode as shown in Figure 16. The mould was made from two stainless steel plates of grade SS 310 with depression of desired dimensions in one of the plates. The two plates were fastened together with bolt sand wind nuts. The slurry was poured into the mould and the mould was closed by tightening the bolts.
Figure 16. Slurry mixture of activated carbon powder and commercial PTFE in a mould.

4.2.3 Heating and cooling

The mould was heating in an electric oven as shown in Figure 17 for 2 hours at a temperature of 110º C to remove all solvent from the electrode. It was then cooled under ambient conditions for another two hours. The specifications of the electric oven are given in Table 6.

Figure 17. Electric oven used in the present project.
Table 6. Specifications of the electric oven used

<table>
<thead>
<tr>
<th>Model</th>
<th>JSEO-150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber volume (capacity)</td>
<td>150 L</td>
</tr>
<tr>
<td>Heating type</td>
<td>Forced convection</td>
</tr>
<tr>
<td>Range</td>
<td>Ambient +10º C ~ 250º C</td>
</tr>
<tr>
<td>Accuracy</td>
<td>± 0.2 ºC at 120 ºC</td>
</tr>
<tr>
<td>Uniformity</td>
<td>± 1.0 ºC at 120 ºC</td>
</tr>
<tr>
<td>Heat up time to 120 ºC</td>
<td>Within 15 minutes</td>
</tr>
<tr>
<td>Heater</td>
<td>1.7 KW</td>
</tr>
<tr>
<td>Sensor</td>
<td>Pt 100</td>
</tr>
<tr>
<td>Inner dimensions W x D x H mm</td>
<td>500 x 500 x 600</td>
</tr>
<tr>
<td>Outer dimensions W x D x H mm</td>
<td>890 x 650 x 860</td>
</tr>
<tr>
<td>Clearance W x D x H mm</td>
<td>895 x 660 x 870</td>
</tr>
<tr>
<td>Internal material</td>
<td>Stainless steel 0.8 T Polished (SUS 304)</td>
</tr>
<tr>
<td>External material</td>
<td>Steel 1T with epoxy powder coating</td>
</tr>
<tr>
<td>Insulation</td>
<td>Mineral wool 50 mm/w woven aluminum barrier</td>
</tr>
<tr>
<td>Ventilation damper</td>
<td>1</td>
</tr>
<tr>
<td>Power consumption by damper</td>
<td>8.7 A</td>
</tr>
<tr>
<td>Electrical requirement</td>
<td>220 VAC 50/60 Hz or 120 VAC 60 Hz</td>
</tr>
<tr>
<td>Net weight</td>
<td>63 Kg</td>
</tr>
</tbody>
</table>

4.2.4 Fabricated activated carbon electrode

The solid porous aC electrode was then removed from mould and lightly pressed onto a gold foil backing to act as a current collector as shown in Figure 18. A similar procedure was followed to fabricate all other aC electrodes.
Figure 18. Fabricated activated carbon-PTFE solid electrode.

The fabricated sample activated carbon-PTFE electrodes were named as aCP, aCN, aCS, aCK2.5, aCK7.5, aCK10, graphitic carbon foam, flexible carbon foam, mesoporous carbon monolith, mesoporous carbon 1:1 KOH, mesoporous carbon 1:3, mesoporous carbon 1:5, and mesoporous carbon 1:7, after the forms of aC used in them. (The definitions of these aC forms were provided earlier in section 4.1.3 and 4.1.4). All these activated carbon-PTFE electrodes were used in electrochemical experiments to measure their double-layer capacitance in a flat split coin cell using cyclic voltammetry and electrochemical hydrogen storage capacity in a 3-electrode electrolytic cell using galvanostatic charging-discharging respectively. The electrolyte used in both tests was 1 mol H₂SO₄ (sulphuric acid). The detail on the characterisation of these electrodes and experimental procedure is given in chapter 5 and 6.

4.3 FABRICATION OF ACTIVATED CARBON ELECTRODES WITH NAFION BINDER

4.3.1 Ingredients for activated carbon electrodes

4.3.1.1 Nafion solution
For aC electrodes tested in a proton flow battery, a nafion binder was employed rather than PTFE.

Dr Walter Grot was the first to discover nafion in late 1960s when working for DuPont (Grot 1994, cited in C. Heitner-Wirguin 1996). Nafion is a perfluorosulfonated polymer that possesses hydrophobic tetrafluoroethylene backbone with perfluoroalkyl ether side chains terminated by hydrophilic sulfonic acid groups (S. X. Zhao et al. 2011; Q. Duan et al. 2012). Figure 19 shows the chemical structure of nafion. The hydrophilic domains are responsible for the water and proton transport (Figure 19 right) (E. Fontananova et al 2012).

![Chemical Structure of Nafion](image)

\[
[(\text{CF}_2-\text{CF}_2)_x-(\text{CF}_2-\text{CF})]_y
\]

The average equivalent weight per sulfonic group in nafion is considered as a defining factor while reporting properties of nafion. The most commonly available nafion has equivalent weight of 1100 g mol\(^{-1}\) SO\(_3\)H, correspond to \(m\) equal to 6, \(n\) equal to 1, and \(z\) equal to 1 in Figure 18 (Li et al. 2006; D. K. Paul et al. 2013). In the above-mentioned structure, the length between CF and CF\(_2\) (called side chains) is in the order of 0.8 nm, between CF\(_2\) and CF\(_2\) (called backbone space) of 0.6-1.2 nm, and the length of a single extended molecule (Figure 19 left) is in order of 100 nm (D. K. Paul et al. 2013).
Nafion solution (perfluorosulfonic acid-PTFE copolymer, 5% w/w solution) used in the present project was obtained from Sigma Aldrich, Australia, for use in making the composite electrodes with the activated carbon samples. The nafion solution specifications are listed in Table 7 (Sigma Aldrich, 2015).

Table 7. Specifications of the nafion-117 solution used in the present project

<table>
<thead>
<tr>
<th>Make</th>
<th>Sigma Aldrich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>Nafion® perfluorinated resin solution</td>
</tr>
<tr>
<td>Model</td>
<td>274704 ALDRICH</td>
</tr>
<tr>
<td>Eq. wt.</td>
<td>1,100</td>
</tr>
<tr>
<td>Water content</td>
<td>15-20 %</td>
</tr>
<tr>
<td>Concentration</td>
<td>5 wt % in lower aliphatic alcohols and water</td>
</tr>
<tr>
<td>Refractive index</td>
<td>n20/D 1.379</td>
</tr>
<tr>
<td>Density</td>
<td>0.874 g/mL at 25 °C</td>
</tr>
<tr>
<td>1-propanol</td>
<td>45 % w/w</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5 % w/w</td>
</tr>
</tbody>
</table>

4.3.1.2 Activated carbons

The best-performing activated carbon sample based upon electrochemical hydrogen storage capacity (as reported later in Chapter 6) was selected to be mixed with nafion solution and fabricate composite aC-nafion electrode for testing in the proton flow battery. Unlike other studies (for example, D. Gharibi et al. 2011; H. C. Chien et al. 2012), the activated carbons were not functionalised. One reason for not functionalising was that it has been reported in the literature (Bleda Martinez et al. 2008) that the hydrogen storage capacity reduces with the presence of surface oxygen groups. However, this finding may not be a general one, so that in future a thorough investigation of the effect of various surface groups on storage capacity is merited.
4.3.2 Mixing nafion and selected activated carbon samples

A solution casting method was chosen to fabricate the composite activated carbon-nafion electrode because it has been extensively employed for fabrication of membranes from nafion (Li et al. 2006, Molla and Compan 2011). Activated carbon powder in a weighed quantity was mixed with measured quantity of nafion solution in a beaker at room temperature. The mixture was stirred continuously for 10-15 minutes to obtain an even mixture, followed by heating on a hot plate surface until most of the solvent had evaporated and a uniform thick slurry mixture was obtained, as shown in Figure 20.

Figure 20. A mixture of nafion and activated carbon in the beaker

The earlier fabricated aC electrodes (mentioned in section 4.2.4 of this thesis) included commercial PTFE as binder. These electrodes were later tested in three electrode electrolytic cell with liquid electrolyte (dilute 1 mol. H₂SO₄), to determine their electrochemical hydrogen storage capacity. The role of acid was to penetrate in the spaces within the fabricated aC electrode and in the pores of carbon particles in order to provide proton conduction. The aC sample that demonstrated highest hydrogen storage capacity amongst all the tested samples, were used to fabricate a new solid electrode for proton flow battery (PFB) experiments. The reason for choosing nafion instead of PTFE as binder was to obtain additional proton conduction, beside the liquid electrolyte. Since in this case,
nafion was to act as binder only and not the main proton conduction medium (which was dilute acid), the amount of nafion added was less than 10 wt% of carbon powder.

In future it would be important to find out the optimum values of proton and electron conductivity by testing various numbers of carbon-based materials from different precursors suitable for the proton flow battery application and different proton conducting medium e.g. proton conducting gels and protic ionic liquids.

A similar procedure (as used in fabrication of aC-PTFE electrode) was followed to cast the composite aC-nafion electrode from the prepared slurry mixture. In this case, nafion-117 (Perfluorosulfonic acid) acted as binder (instead of PTFE) and proton conducting medium within the aC electrode. The fabricated composite activated carbon-nafion electrodes interspersed in 1 mol H₂SO₄ (sulphuric acid) were used in reversible PEM (proton exchange membrane) hydrogen fuel cell to test the performance of the proton flow battery.

4.4 CONCLUSION

This chapter has described the fabrication method for activated carbon — PTFE (Polytetrafluoroethylene) sample electrodes and composite activated carbon — nafion electrodes. The fabricated samples were named as aCP, aCN, aCS, aCK2.5, aCK7.5, aCK10, mesoporous carbon monolith, mesoporous carbon 1:1 KOH, mesoporous carbon 1:3 KOH, mesoporous carbon 1:5 KOH, and mesoporous carbon 1:7 KOH. These samples have been used in the subsequent experiments to measure proton conductivity, electron conductivity, double-layer capacitance, electrochemical hydrogen storage capacity and performance of the proton flow battery.
CHAPTER 5

5. CHARACTERISATION OF ACTIVATED CARBON ELECTRODES

5.1 OVERVIEW

This chapter gives the characteristics of the activated carbons measured in the present project. The basic structures of the activated carbons are described, and methods used to measure various characteristics are elaborated. Typical characteristics of activated carbon include porosity, BET surface area, pore volume, proton conductivity, and electron conductivity.

5.2 PHYSICAL MEASUREMENTS OF THE ACTIVATED CARBON ELECTRODES

Physical properties of all activated carbon sample electrodes were measured for use in subsequent experiments to calculate double-layer capacitance and electrochemical hydrogen storage capacities. All the physical dimensions were measured using a standard digital vernier calliper. The basic physical characteristics of the fabricated activated carbon electrodes are listed in Table 8 below.

Table 8. Physical characteristics of all fabricated activated carbon electrodes made from samples listed in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Width of Sample (cm)</th>
<th>Length of Sample (cm)</th>
<th>Area (cm²)</th>
<th>Thickness (cm)</th>
<th>Mass of PTFE solution (grams)</th>
<th>Total mass of electrode (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aCP</td>
<td>2.4</td>
<td>2.4</td>
<td>5.76</td>
<td>0.2</td>
<td>0.1</td>
<td>1.18</td>
</tr>
<tr>
<td>aC'N</td>
<td>2.4</td>
<td>2.4</td>
<td>5.76</td>
<td>0.2</td>
<td>0.2</td>
<td>2.15</td>
</tr>
<tr>
<td>aCS</td>
<td>2.4</td>
<td>2.4</td>
<td>5.76</td>
<td>0.2</td>
<td>0.2</td>
<td>2.2</td>
</tr>
<tr>
<td>aCK2.5</td>
<td>2.4</td>
<td>2.4</td>
<td>5.76</td>
<td>0.2</td>
<td>0.2</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>2.4</td>
<td>5.76</td>
<td>0.2</td>
<td>0.2</td>
<td>2.22</td>
</tr>
<tr>
<td>----------------</td>
<td>-----</td>
<td>-----</td>
<td>------</td>
<td>-----</td>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>aCK7.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aCK10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon monoliths</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon powder – MC 1:1 KOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon powder – MC 1:3 KOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon powder – MC 1:5 KOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon powder – MC 1:7 KOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphitic carbon foam</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexible carbon foam</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 5.3 POROSITY MEASUREMENT

#### 5.3.1 Structure of activated carbon

In the literature, activated carbon has been defined in many forms: for example, as a crude form of graphite with a random or amorphous structure, a simplified model of crumbled segments of graphene layers with different degree of perfection, and a modified form of graphite-like structure resulting from the presence of microcrystallines (also known as cellulose beads out of which activated carbon is formed, Georgios D. Karles and Shuzhong
Zhuang 2007) etc. The segments involved in the structure of activated carbon are present in different sizes, shapes and orientation. The random bonding of these segments results in formation of three-dimensional spaces with certain gaps between them because of imperfect packing. These empty spaces between the segments are known as pores (Marsh and Rodriguez-Reinoso 2006). The microcrystallines present in the activated carbon, created in the process of carbonisation, get their bonding disturbed during activation process causing free valencies, which are very active.

Porosity of activated carbons is quite often obtained by measurement of secondary data from which the requisite pore parameters are estimated. But direct methods are also available to measure the pore size distribution of activated carbons (Osei-Wusu O. W. Achaw 2008). Optical microscopy and scanning electron microscopy (SEM) are examples of direct methods. These methods are known for their ability to directly view the micro-structure of activated carbons (Manocha et al., 2010; Lazslo et al., 2009; O. W. Achaw & Afrane, 2008). However, the direct pore measurement method has only been applied in a very limited capacity in the past. Researchers and industries, rather, rely on the indirect methods to determine the pore sizes in activated carbons. The indirect methods give the estimation of pore size distribution by measuring other parameters that are generally related to the properties of interest (Osei-Wusu O. W. Achaw 2008). Adsorption measurements and related mathematical models are the most commonly used amongst the indirect methods, which provides information regarding the pore structure of an activated carbon. Porosity measurements using indirect methods reveal various pore characteristics including pore volume, surface area, pore size distribution and average pore diameter. Indirect methods utilise information on the adsorbate employed and an adsorption isotherm to estimate pore size distribution. Besides adsorption measurements, several other indirect methods are also available to estimate the pore characteristics of activated carbons, such as immersion calorimetry, small-angle scattering of X-rays (SAXS), small-angle scattering of neutrons (SANS), and mercury porosimetry (Rigby & Edler, 2002; F. Stoeckli et al, 2002; Daley et. al., 1996).
5.3.2 Adsorption isotherm analysis method

5.3.2.1 Classification of methods

The adsorption isotherm method is used to determine the pore size distribution, surface area and adsorption capacity (mol/g) of the sample activated carbon. In the adsorption process, the adsorbate (mainly CO\textsubscript{2} or N\textsubscript{2} gas) enters the adsorbent (pores of the activated carbon) and gas molecules try to formulate weak chemical bonds with the inner surfaces of the pores of the activated carbon sample. Some of the gas is retained under the effect of enhanced van der Waals forces between the gas and the pores of activated carbon. In the whole process of adsorption, an isothermic equilibrium condition is maintained (Marsh and Rodriguez-Reinoso 2006). The molecules of gas retained within the pores of activated carbon do not remain stationary; in-fact they maneuver within the pores at an average of more than a thousand times per second, according to Marsh and Rodriguez-Reinoso (2006). This motion of gas molecules is temperature dependent, and varies in terms of amplitude and frequency according to temperature. However, under equilibrium conditions, the number of gas molecules leaving the pores is same as the number of gas molecules entering the pores.

Typical adsorption isotherm methods are classified as under:

1. Volumetric adsorption
2. Gravimetric adsorption
3. Pulse adsorption
4. Dynamic adsorption

In the present research work, the volumetric method was employed because of its advantage of separating the apparatus for sample pre-treatment to achieve the high throughput measurement of surface area and porosity. The testing for Victorian brown coal samples was done by Lachlan Ciddor, PhD student in the department of chemistry at Monash University,
Melbourne, Australia. The testing for phenolic resin samples was done by Dr M. Karthik, research associate at CIC Energigune, Spain.

5.3.2.2 Volumetric adsorption isotherm method

The apparatus for the volumetric method consists of pressure sensors, valves, and a vacuum system, as shown in the Figure 21. As a mandatory requirement of preparation, the inner volume is calibrated before measurement. The adsorption amount is calculated by subtracting the number of remaining molecules at the adsorption equilibrium from the number of introduced molecules by using the ideal gas equation. However, the volumetric method has the disadvantage that it needs to account for the non-ideal gas behaviour for high-density gas and thermal transpiration for the low-pressure measurements (Marsh and Rodriguez-Reinoso 2006).

Figure 21. Volumetric adsorption apparatus (adapted from Marsh and Rodriguez-Reinoso 2006)
The result of the adsorption isotherm test is generally expressed in terms of the amount of adsorbate in mol/g of activated carbon at known relative pressure (ratio of equilibrium vapour pressure to the saturation vapour pressure) at the set temperature within the chamber (Marsh and Rodriguez-Reinoso 2006). The amount of adsorbate required to cover the total pore surface with one layer of adsorbate is termed as the monolayer (March and Rodriguez-Reinoso 2006). The adsorbed volume of gas is used to plot the BET (S. Brunauer, Emmett and Teller) value against $P/P_0$ (i.e. relative pressure) which normally results a linear plot. The slope and intercept from the plot is used to determine the volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface. It is from this value that surface area is calculated using equation 26. Next, the most common models to obtain the latter from the measured volumetric adsorption, namely the S. Brunauer-Emmett-Teller (BET) equation and Dubinin-Radushkevich equation, are briefly explained in the following subsection.

5.3.3 Brunauer, Emmett and Teller (BET) theory

5.3.3.1 Overview of BET theory

The BET theory, proposed by Brunauer, Emmett and Teller in 1938, states that the specific area of a porous structure can be determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbed gas comparable to a monomolecular layer on the surface (S. Brunauer et al. 1938; A. K. Ladavos et al. 2012). Physical adsorption results from relatively weak van der Waals forces between the gas molecules and the inner surfaces of the pores of the activated carbon. The adsorption process is usually carried out at the temperature of liquid nitrogen. Continuous flow or a volumetric procedure can be employed to determine the amount of gas adsorbed.

5.3.3.2 BET theory and specific surface area determination by multi-point measurements

The Brunauer, Emmett and Teller (BET) equation is given as:
\[
\frac{1}{V_a\left(\frac{P_0}{P} - 1\right)} = \frac{C-1}{V_m\, C} \times \frac{P}{P_0} + \frac{1}{V_m\, C}
\]  

Eq. 25

where,
P → partial vapour pressure of adsorbate gas in equilibrium with the surface at 77 K (boiling point of liquid nitrogen) in Pascals.
P₀ → saturated pressure of adsorbate gas at constant temperature (the temperature at which the isotherm is taken), in Pascals
Vₐ → volume of gas adsorbed at standard temperature and pressure (STP), in millilitres.
Vₘ → volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in millilitres.
C → dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas and can be calculated from Figure 22.

The value of \( V_a \) is measured at three values of \( P/P_0 \), and then the BET value \( \left[ \frac{1}{V_a\left(\frac{P_0}{P} - 1\right)} \right] \) is plotted against \( P/P_0 \) according to equation 25. This plot (as shown in Figure 21) should yield a straight line in the approximate relative pressure range 0.05 to 0.3. The data are considered acceptable if the correlation coefficient, \( r \), of the linear regression is not less than 0.9975; that is, \( r^2 \) is not less than 0.995.

Figure 22. BET plot from the results of adsorption isotherm (adapted from Marsh and Rodriguez-Reinoso 2006).
From the resulting linear plot, the slope (A), which is equal to \((C - 1)/V_mC\), and the intercept (I), which is equal to \(1/V_mC\), are evaluated by linear regression analysis. From these values, \(V_m\) is calculated as \(1/(\text{slope} + \text{intercept})\), while \(C\) is calculated as \((\text{slope}/\text{intercept}) + 1\) (S. Brunauer et al. 1938; A. K. Ladavos et al. 2012). From the value of \(V_m\) so determined, the specific surface area, \(S\), in \(m^2/g\), is calculated by the equation:

\[
S = \frac{V_m N_a a}{m \times 22400}
\]  
Eq. 26

where,

\(N_a\) → Avogadro constant \((6.022 \times 10^{23} \text{ mol}^{-1})\)

\(a\) → effective cross-sectional area of one adsorbate molecule, in square metres \((0.162 \text{ nm}^2\) for nitrogen)

\(m\) → mass of porous sample, in grams

\(22400\) → volume occupied by 1 mol of the adsorbate gas at STP, in millilitres.

5.3.3.3 BET theory and specific surface area determination by single-point measurements

Normally, at least three measurements of \(V_a\) each at different values of \(P/P_0\) are required for the determination of specific surface area by the dynamic flow gas adsorption technique or by volumetric gas adsorption. However, under certain circumstances described below, it may be acceptable to determine the specific surface area of a powder from a single value of \(V_a\) measured at a single value of \(P/P_0\) such as 0.300 (corresponding to 0.300 mole of nitrogen), using equation 26 for calculating \(V_m\). The specific area is then calculated from the value of \(V_m\) by equation 26 (S. Brunauer et al. 1938; A. K. Ladavos et al. 2012).
The single-point method may be employed directly for a series of powder samples of a given material for which the material constant $C$ is much greater than unity. These circumstances may be verified by comparing values of specific surface area determined by the single-point method with that determined by the multiple-point method for the series of powder samples. Close similarity between the single-point values and multiple-point values suggests that $1/C$ approaches zero (S. Brunauer et al. 1938; A. K. Ladavos et al. 2012).

5.3.4 The Dubinin-Radushkevich (DR) equation

In 1967, Dubinin described adsorption on microporous adsorbents and proposed a new theory known as the Theory of Volume Filling of Micropores (TVFM) (A. Kumar 2011). TVFM postulates that, in micropores, the adsorbate occupies the pore volume by the mechanism of volume filling, and does not form discrete layers in the pores (A. Kumar 2011). The gas gets adsorbed in pores by quasi-vaporisation adsorption mechanism (K. Kaneko et al. 1996). Total micropore volume is an essential characteristic of activated carbon and can be determined using the isotherm method by means of the Dubinin-Radushkevich (DR) equation (C. Nguyen et al. 2001):

$$\frac{W}{W_O} = \exp \left[ - \frac{BT^2}{\beta^2} \ln^2 \left( \frac{p_0}{p} \right) \right]$$

where,

$W$ → volume of the pores that has been filled at a relative pressure of $p/p_0$, in cm$^3$/g

$W_O$ → total volume of the micropore system, in cm$^3$/g

$B$ → structural constant related to the width of the Gaussian pore distribution, in K$^{-2}$

$T$ → temperature at which the isotherm has been taken, in K

$\beta$ → similarity constant known as affinity coefficient, depending solely on adsorbate (dimensionless)

$p_0/p$ → inverse of the relative pressure of the adsorbate, in pascals.
The validity of equation 27 for a given adsorption process should be tested by plotting $\ln^2 \frac{p_0}{p}$ versus $\ln [W]$ (refer Figure 23) at different temperatures to check for a linear relationship with a negative slope proportional to $T^2$ in absolute terms (L. Verhoeven and P. Lodewyckx 2001). As most of the active sites are situated inside the micropore system, the total volume is obtained from the DR plot (refer Figure 22). It is to be noted that the amount of gas adsorbed through specific bonding inside the micropores plus the amount of gas adsorbed through micropore filling of the remaining micropore volume should correspond to the real total micropore volume of the activated carbon (L. Verhoeven and P. Lodewyckx 2001). A comparison between experimental data obtained from the N$_2$ and CO$_2$ adsorption isotherm methods is shown in Figure 23. At low relative pressures DR theory is applicable where as BET theory applies at high pressures (W. Rudzinski et al. 1992). The intercept on the vertical axis in Figure 22 is considered as $\ln [W]$ which further could be used to calculate surface area. In certain cases when no intercept is obtained (e.g. in case of CO$_2$), the curve is back drawn to estimate the value of $\ln [W]$ as shown in Figure 23.

![Diagram](image)

**Figure 23.** Comparison between experimental data obtained from N$_2$ and CO$_2$ adsorption isotherm method (modified from Marsh and Siemieniewska, 1967 cited in Marsh & Rodriguez-Reinoso 2006, p. 168, J. Jazaeri 2013 p. 89).
5.3.5 Porosity analysis using CO₂ and N₂ adsorption isotherms

The porosity of carbon is a critical parameter for hydrogen storage applications. Porosity is usually measured by using both CO₂ at 273K and N₂ at 77 K in adsorption isotherm methods (Lozano Castello et al. 2004). The convenience in availability of CO₂ and N₂ is the main reason behind the selection of these adsorptive gases (Marsh and Rodriguez-Reinoso 2006; J. Jazaeri 2013). The critical size of molecules of both gases is in the range of 0.33 - 0.36 nm (F. Beguin et al. 2006; Jazaeri 2013).

The processes of CO₂ and N₂ adsorption on carbon surfaces within pores are different from each other. The higher kinetic energy and higher quadrupole moment of CO₂ molecules at lower relative pressures results in a higher quantity of carbon dioxide adsorption compared to N₂. On the other hand the amount of N₂ adsorption increases steeply at higher relative pressures and this phenomenon is known as filling of mesopores. It is reported in the literature that filling of mesopores is suppressed by the quadrupole moment of the CO₂ molecules (Marsh and Rodriguez-Reinoso 2006; J. Jazaeri 2013).

Different results are obtained from the tests with these two adsorptive gases. In the porosity analysis, finite activation energy is required for CO₂ and N₂ adsorption. Nitrogen adsorption in micropores at 77 K, gets very slow and is undetectable even within span of a day (Marsh and Rodriguez-Reinoso 2006). On the other hand, the diffusion of carbon dioxide within micropores at 273 K is far better due to the higher kinetic energy of the CO₂ molecules at this temperature compared to N₂ at 273 K (C. Vix-Guterl et al. 2005). Therefore, it can be concluded that if CO₂ adsorption is higher than N₂ adsorption there is a higher proportion of ultra-microporosity but lower mesoporosity and microporosity. If CO₂ adsorption is approximately equal to N₂ adsorption there is likely to be a relatively homogeneous distribution of mesoporosity, microporosity and ultra-microporosity. If CO₂ adsorption is less than N₂ adsorption, mesoporosity and microporosity can be expected to be more prevalent than ultramicroporosity (J. Garido et al. 1987; Marsh and Rodriguez-Reinoso 2006).
Hence the extent of microporosity and mesoporosity can be assessed using the N\textsubscript{2} adsorption isotherm; and that of ultra-microporosity using the CO\textsubscript{2} adsorption isotherm (J. Garido \textit{et al.} 1987; Lozano Castello \textit{et al.} 2004). In other words, the information on porosity that the N\textsubscript{2} adsorption isotherm is not able to provide is obtained by using the CO\textsubscript{2} adsorption isotherm, and vice versa. Since ultramicropores are considered of utmost importance in applications like hydrogen storage in activated carbon, their porosity determination by CO\textsubscript{2} adsorption isotherm should be an additional measurement over and above N\textsubscript{2} adsorption isotherm (D. Lozano-Castello \textit{et al.} 2004; C. Vix-Guterl \textit{et al.} 2005, Jazaeri 2013).

5.3.6 Summary of porosity tests on the activated carbons

In the present research project, measurement of N\textsubscript{2} adsorption isotherms and CO\textsubscript{2} adsorption isotherms for the charcoal sample was conducted earlier by Mohammad Javad Jazaeri, a Master of Engineering by research student at RMIT University (J. Jazaeri 2013, M Engg. thesis). For the N\textsubscript{2} and CO\textsubscript{2} adsorption isotherm measurements Micromeritics\textsuperscript{®} ASAP 2000 and Micromeritics\textsuperscript{®} ASAP 2010 instruments were used respectively. Both measuring techniques involved the static volumetric method to obtain the inner surface area of the sample carbon particles. Tests to determine porosity were done by Frank Antolasic, the Senior Technical Officer at the RMIT School of Applied Sciences, on request of Mohammad Javad Jazaeri, in 2013. Tests specifications as reported by Jazaeri (2013) were 77 K for N\textsubscript{2} and 273 K for CO\textsubscript{2}. The porosity, surface area and other characteristic results for the five Victorian brown coal samples were provided by Lachlan Ciddor, PhD candidate from Monash University, Australia, by personal communications. The physical and surface characteristics of the seven activated carbon samples made from phenolic resin were provided by Dr M. Karthik, research associate at CIC Energigune, Spain. The pore surface area and volume characteristics of all the samples are presented in Table 9.
Table 9. Porosity of the activated carbon samples obtained from volumetric adsorption isotherm method with CO\(_2\) and N\(_2\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area [m(^2)/g]</th>
<th>Micropore Volume [cm(^3)/g]</th>
<th>Mesopore volume [cm(^3)/g]</th>
<th>Average micropore size (nm)</th>
<th>Average mesopores size (nm)</th>
<th>Total Pore volume [cm(^3)/g]</th>
<th>Bulk Density (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aCP</td>
<td>208.9</td>
<td>0.131</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>aC'N</td>
<td>902.3</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>aCS</td>
<td>646.1</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>aCK2.5</td>
<td>610.6</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>aCK7.5</td>
<td>751.6</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>aCK10</td>
<td>639</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mesoporous carbon monoliths</td>
<td>619</td>
<td>0.221</td>
<td>0.398</td>
<td>1.08</td>
<td>3.88</td>
<td>0.619</td>
<td>~0.57</td>
</tr>
<tr>
<td>Mesoporous carbon powder – MC 1:1 KOH</td>
<td>989</td>
<td>0.285</td>
<td>0.45</td>
<td>0.67</td>
<td>3.27</td>
<td>0.734</td>
<td>~0.64</td>
</tr>
<tr>
<td>Mesoporous carbon powder – MC 1:3 KOH</td>
<td>1271</td>
<td>0.392</td>
<td>0.48</td>
<td>0.73</td>
<td>3.26</td>
<td>0.872</td>
<td>~0.50</td>
</tr>
<tr>
<td>Mesoporous carbon powder – MC 1:5 KOH</td>
<td>1658</td>
<td>0.513</td>
<td>0.686</td>
<td>0.81</td>
<td>3.63</td>
<td>1.199</td>
<td>~0.42</td>
</tr>
<tr>
<td>Mesoporous carbon powder – MC 1:7 KOH</td>
<td>1922</td>
<td>0.586</td>
<td>0.804</td>
<td>0.93</td>
<td>3.69</td>
<td>1.39</td>
<td>~0.36</td>
</tr>
<tr>
<td>Graphitic carbon foam</td>
<td>150</td>
<td>0.04</td>
<td>0.082</td>
<td>Less than 1</td>
<td>3.6</td>
<td>0.122</td>
<td>~0.35</td>
</tr>
<tr>
<td>Flexible carbon foam</td>
<td>230</td>
<td>0.07</td>
<td>0.062</td>
<td>Less than 1</td>
<td>-</td>
<td>0.132</td>
<td>~0.008</td>
</tr>
</tbody>
</table>
Although the same coal powder sample was used in both the $\text{N}_2$ and $\text{CO}_2$ isotherm adsorption tests, the sample could not be degassed in the $\text{CO}_2$ test. It could have been because of a leak in the apparatus, or due to the composition of the coal sample. Further investigation was terminated to prevent damaging the apparatus. However, this is clearly an area that requires further research investigation.

5.4 SCANNING ELECTRON MICROSCOPY IMAGING OF ACTIVATED CARBON SAMPLES

A commercial PTFE (polytetrafluoroethylene) solution was used in the fabrication of all aC electrodes to act as a binder to hold the aC particles together. The volume of solution added was set so that after evaporation of the solvent the mass of PTFE in the electrode was 10 wt% of the mass of the aC powder. These aC electrodes and their application require uniform dispersion of PTFE between the aC particles to ensure that the carbon particles are not clustered together in particular regions.

It is desirable to have minimal hollow spaces within the aC electrode as these spaces increase electrode volume without adding to hydrogen storage, thus reducing the overall volumetric capacity. Also these hollow spaces may favour hydrogen gas formation. To check the uniformity of the distribution of PTFE within the aC electrode and potential hollow spaces, images of all aC sample electrodes were taken under a scanning electron microscope. The SEM images of samples aCP, aCN, aCS, aCK2.5 and aCK7.5 are shown as examples in Figures 24 to 28.
Figure 24. SEM image of sample aCP

Figure 25. SEM image of aCN

Figure 26. SEM image of aCS
The SEM images captured for all the fabricated aC electrodes clearly showed the porous structure of activated carbon powder. Further, it was found that aC powder was evenly mixed with the binder and distributed evenly.

5.5 MEASUREMENT OF ELECTRON AND PROTON CONDUCTIVITY OF THE ACTIVATED CARBON ELECTRODES SOAKED IN DILUTE SULPHURIC ACID

5.5.1 Electrochemical impedance spectroscopy
Electrochemical processes can be investigated by fitting an equivalent circuit to experimental data points after conduct of electrochemical impedance spectroscopy (EIS). EIS is widely used as a diagnostic and characterisation technique in battery and fuel cell technology (S. Buller et al. 2005; Yuan et al. 2007; M. Tliha et al. 2010). A small-amplitude alternating current (AC) voltage is applied to the system and the response is recorded in form of a phase-shifted AC voltage. The measured amplitude and phase shift of the response are used to estimate the impedance of the equivalent circuit expressed as a complex number (S. C. Page et al. 2007). The EIS method is classified into two-probe or four-probe methods. The four-probe method requires more sophisticated equipment than two-probe method and is more accurate (R. Yadav and Fedkiw 2012). The two-probe method is accurate enough to be used in conductivity measurement of composite and normal membranes (T. Soboleva et al. 2008; R. Yadav and Fedkiw 2012). In the present project, the two-probe method was employed to obtain through-plane proton conductivity of the activated carbon electrodes.

Since proton conductivity of the membrane depends on temperature (B. Choi et al. 2005; R. Yadav and Fedkiw 2012), tests in the present project were conducted at room temperature. A two-probe test set-up was designed and manufactured to measure through plane conductivity as shown in Figure 29. All the EIS tests were performed at School of Applied Sciences, RMIT University by the author using the electrochemical workstation of make - CH Instruments Incorporation, Austin, TX, USA.
Figure 29. Schematic of proton conductivity measurement set-up using electrochemical impedance spectroscopy.

5.5.2 Design and manufacture of the test cell for EIS method

The EIS test cell to measure the bulk proton conductivity of the aC electrodes soaked in 1M sulphuric acid comprised two gold-coated ceramic plates as the outer electrodes and a clamp, as shown in Figure 28. Gold coating on ceramic plates ensured no involvement of the EIS in any chemical reaction with samples. The arrangement was such made that the sample aC electrode was sandwiched between two nafion-117 membranes backed by two gold-coated ceramic plates. The whole setup was pressed gently between the jaws of the clamp. Nafion-117 membranes were used as proton conductors to prevent the passage of electrons through them. In the absence of these membranes on both main faces of the electrode, the electrical
resistance between the faces would have been very low because of the high electron conductivity of the aC material, and electron current flow would have been very dominant, many orders of magnitude greater than any proton current. The presence of the solely proton conducting membranes ensured that only proton current flowed through the electrode, allowing bulk proton conductivity of the aC electrode plus acid to be measured.

The clamping force needed to be high enough to reduce the contact resistance between the EIS electrodes and the samples to a low level. However, too much pressure will compress the membrane and might change the EIS results (Yun et al. 2012). 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 (T. Soboleva et al. 2008; Yun et al. 2012).

5.5.3 Equivalent circuit

An equivalent electrical circuit is always required to model the response of an electrochemical system in EIS (R. A. Huggins 1999). An equivalent circuit representation of the chemical processes and mechanisms taking place in the material is valid only if the observed experimental data exhibit the same response to the alternating excitation signals as the equivalent circuit (Yuan et al. 2010). In other words, the equivalent circuit elements need to represent all the possible physical and chemical processes in terms of their response to an AC input signal with minimum disparity to experimental results (S. Buller et al. 2005).

The test configuration and equivalent circuit for the EIS test method used in the present study to measure bulk proton conductivity of the electrodes are presented in Figures 30 and 31 respectively.
Figure 30. Test configuration for measurement of proton resistance with EIS (J. Jazaeri 2013).

Figure 31. Equivalent circuit for measurement of proton resistance with EIS (J. Jazaeri 2013).

The electrical resistance of the outer metal electrodes are represented as $R_{e1}$ and $R_{e2}$ in Figure 31. The double-layer capacitance phenomena at the interfaces of the nafion membrane and the metal electrodes are represented by two sets of straight capacitor and resistance in parallel. The resistance offered by the nafion membrane for ion transfer is given as $R_{mem}$. The total effective impedance for the equivalent circuit shown in Figure 31 is given by equation 28.

$$Z = R_{e1} + \frac{R1 \times \frac{1}{j\omega C_1}}{R1 + \frac{1}{j\omega C_1}} + R_{mem} + R_{composite} + R_{mem} + \frac{R2 \times \frac{1}{j\omega C_2}}{R2 + \frac{1}{j\omega C_2}} + R_{e2}$$

Eq. 28
R represents resistance and C represents capacitance. Z is a function of angular frequency (\( \omega \)) so as:

\[
\omega \to 0, \quad Z \to R_{e1} + R_1 + R_{mem} + R_2 + R_{e2}
\]

and as:

\[
\omega \to \infty, \quad Z \to R_{e1} + R_{mem} + R_{e2}
\]

Therefore, in the majority of the literature, the high frequency intercept of Z on the real axis of the Nyquist plot (-Zim vs Zreal) is considered to be the sum of proton resistances in series of the whole setup, plus all the series electron resistances, since the impedances of the capacitive elements tends to zero (A. M. Affoune et al. 2005; T. Soboleva et al. 2008; V. Ijeri et al. 2010; A. Anis et al. 2011):

\[
Z = R_{e1} + R_{mem} + R_{composite} + R_{mem} + R_{e2}
\]

Eq. 29

where \( R_{e1} \) and \( R_{e2} \) are ohmic resistances to electron flow, and \( R_{mem} \) and \( R_{composite} \) are ohmic resistance to proton flow through the nafion membranes and the composite aC plus acid electrode.

It is worth noting that there are many equivalent circuits available that could be fitted to EIS spectra but all the available equivalent circuits for nafion membrane tend to produce similar spectra (P. D. Beattie et al. 2001; R. Yadav and Fedkiw 2012; Yun et al. 2012). The circuit employed in the present research project was found to provide a good fit to the experimental data.

5.5.4 Electrochemical characterisation of the test set-up

5.5.4.1 Identifying values of EIS test rig
The total series ohmic resistance of the test rig includes the resistance of the gold-coated end plates and the connecting wires to the EIS cell, that is, $R_{e1}$ and $R_{e2}$. This total series DC resistance to electron flow of the EIS set-up was measured separately simply by connecting together the EIS electrodes as shown in Figure 31. The nyquist plot obtained for the corresponding EIS test is shown in Figure 32.

![EIS electrode](image)

Figure 32. Setup and result of DC electrical resistance of the EIS (J. Jazaeri 2013)

The result obtained from the EIS test showed that the equipment possessed a typical behaviour for a pure electrical conductor with a DC electric resistance of only 0.8 ohm (that is, 0.4 ohm for each side or $R_{e1} + R_{e2} = 0.8$ ohm).

### 5.5.4.2 Proton conductivity of Nafion 117 membrane

Next the proton resistance of each of the two nafion membranes was required, assumed to be the same value, $R_{\text{mem}}$. Before measuring the proton conductivity of the nafion 117 membrane, it was treated with hydrogen peroxide ($H_2O_2$) and sulphuric acid ($H_2SO_4$) to remove the dust and impurities if any. The membrane was successively boiled in $H_2O_2$ for one hour rinsed
under flowing water; boiled in distilled water for one hour and rinsed under water; boiled in H$_2$SO$_4$ for one hour and rinsed under water; boiled in distilled water for one hour; and finally stored in demineralised water for 48 hours (R. Yadav and Fedkiw 2012; S. X. Zhao et al. 2011; M. B. Satterfield et al. 2006). The membrane was stored in water for such a long time to allow absorption of sufficient water to become fully hydrated. The treatment and storing of the membrane was followed by cutting it into required dimensions and testing in the EIS cell. The nyquist plot obtained from the EIS workstation for a single nafion membrane sandwiched between the two outer gold electrodes is shown in Figure 33 (a) and its zoomed version in Figure 33 (b).

Figure 33. (a) Nyquist plot of nafion 117 soaked in water.
The equivalent circuit shown in Figure 30 was employed and the intercept of the real axis at the high frequency end (REQ) gave the resistance of 10.9 ohm. According to equation 28, the resistance at high frequency is given as:

\[ R_{EQ} = R_{mem} + R_{e1} + R_{e2} = 10.9 \text{ ohm} \]

Substituting the value for \( R_{e1} + R_{e2} \) from the previous section, we have:

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

A uniform current distribution was assumed while calculating the through-plane proton conductivity of the nafion membrane from the equation given by R. Yadav and Fedkiw 2012, and H. C. Chien et al. 2013:

\[ \sigma_{bulk} = \frac{t}{R_{mem}l_w} \quad \text{Eq. 30} \]
where

\[ \sigma_{\text{bulk}} \rightarrow \text{is the proton conductivity of the nafion membrane in S/cm,} \]
\[ t \rightarrow \text{is the thickness of the sample in cm,} \]
\[ l \rightarrow \text{is the length of the sample in cm,} \]
\[ w \rightarrow \text{is the width of the sample in cm, and} \]
\[ R_{\text{mem}} \rightarrow \text{is the protonic resistance of the membrane that has been measured by EIS as above.} \]

The face area of the sample electrode was fully covered by the EIS electrodes. The thickness of the dry and fully hydrated nafion 117 was measured to be 125 μm and 180 μm respectively using a digital vernier calliper. To ensure good proton conductivity the nafion membranes used in the EIS tests were fully hydrated.

The proton conductivity of fully hydrated nafion membranes used in the test rig was thus found to be:

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

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

5.5.5 Proton conductivity of the activated carbon electrodes soaked in acid

The EIS tests were done on an electrochemical workstation of CH Instruments make. The frequency applied was in the range of 1 Hz - 1 MHz and 5 mV was amplitude of the applied AC voltage. The quiet time (or the sample rest time) was set to 10 seconds.

Before calculation of proton resistance \( R_{\text{composite}} \) of the aC \( R_{\text{bulk}} \) has to be determined. The area of the nafion membrane affects its resistance because there is an inverse relationship
between the area of the membrane and its face-to-face resistance. The area of the nafion membrane was kept equal to that of sample aC electrode and it was assumed that there was a uniform current distribution in the membrane that was parallel to the cross section of the aC electrode. In this case, the bulk membrane resistance is given by:

\[ R_{\text{bulk}} = \frac{t_{\text{bulk}}}{\sigma_{\text{bulk}} lw} \]  \hspace{1cm} \text{Eq. 31}

where
- \( t_{\text{bulk}} \rightarrow \) is the thickness of nafion membrane (=0.18 mm),
- \( l \rightarrow \) is the length of aC electrode, and
- \( w \rightarrow \) is the width of aC electrode. The proton resistance of the composite aC-PTFE material was then calculated from the equation:

\[ R_{\text{comp}} = R_{\text{EQ}} - R_{e1} - R_{e2} - 2R_{\text{bulk}} \]  \hspace{1cm} \text{Eq. 32}

where,
- \( R_{\text{EQ}} \rightarrow \) is the value obtained from the intercept at high frequency end shown on the Nyquist plot and equivalent circuit. The proton conductivity of the composite aC-PTFE was hence calculated from:

\[ \sigma_{\text{comp}} = \frac{t}{R_{\text{comp}} lw} \]  \hspace{1cm} \text{Eq. 33}

\subsection*{5.5.6 Electron conductivity of the composite materials}

The electron conductivity of the composite materials was measured by a multimeter. The aC-PTFE sample electrode was sandwiched between gold-coated ceramic plates, which 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 gold coated ceramic plates. The clamping force on the composite material was sufficient to provide a good contact.

The electron conductivity was calculated using the standard formula:

$$\sigma_E = \frac{t}{R_E l w}$$  \hspace{1cm} \text{Eq. 34}

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. All the sample aC-PTFE electrodes were tested in the same way.

The experimentally-determined values for the proton conductivity of composite materials made from the range of aC samples are presented in Table 10.

Table 10. Experimentally measured proton and electron conductivities of the aC-PTFE electrodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proton conductivity of the sample in S/cm ($\sigma_p$)</th>
<th>Electrical conductivity of the sample in S/cm ($\sigma_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aCP</td>
<td>0.0043</td>
<td>12.86</td>
</tr>
<tr>
<td>aC’N</td>
<td>0.0110</td>
<td>8.90</td>
</tr>
<tr>
<td>aCS</td>
<td>0.0083</td>
<td>11.20</td>
</tr>
<tr>
<td>aCK2.5</td>
<td>0.0161</td>
<td>11.97</td>
</tr>
<tr>
<td>aCK7.5</td>
<td>0.0110</td>
<td>11.57</td>
</tr>
</tbody>
</table>
It was observed that the aC samples made from phenolic resin have higher proton conductivity (max. obtained proton conductivity is 0.0965 S/cm) than the ones made from brown coal (max. obtained proton conductivity is 0.0299 S/cm). One possible reason for this is that aC samples from phenolic resin were activated by adding more KOH than brown coal samples which resulted in more pore volume. The aC samples were soaked in dilute sulphuric acid before measuring their proton resistance and aC samples with higher pore volume would have contained more acid which as a medium for proton conduction. The relation between pore volume and proton conductivity is given later in chapter 8 of this thesis.

The phenolic resin based aC sample also performed well in terms of electron conductivity. The highest recorded electron conductivity among the entire lot of tested sample was 14.47 S/cm for sample mesoporous carbon powder – MC 1:7 KOH. The obtained electron conductivity is comparable with graphite which normally have electron conductivity >100 S/cm.

5.6 ANALYSIS OF THE PHYSICAL AND ELECTROCHEMICAL CHARACTERISTICS OF THE ACTIVATED CARBON ELECTRODES
5.6.1 Porosity and surface area of the activated carbon electrodes

The ideal activated carbon for reversible electrochemical storage of hydrogen, should be porous and have a wide range of pore sizes including macropores (diameter >50 nm), mesopores (diameter from 2 – 50 nm), micropores (diameter from 0.7 to 2 nm) and ultramicropores (diameter < 0.7nm). It would be expected that activated carbon samples with higher BET surface area would have higher electrochemical hydrogen storage capacity. In the present project thirteen aC samples were fabricated from different precursors of carbon. Among the fabricated porous aC sample electrodes mesoporous carbon MC 1:7 KOH was found to have highest BET surface area of 1922 m²/g amongst all other samples, and highest micropore volume of 0.586 cm³/g. Another good performer in terms of BET surface area and micropore volume was mesoporous carbon MC 1:5 KOH.

5.6.2 Proton conductivity of the activated carbon electrodes soaked in sulphuric acid

The experimental values of proton conductivity of the composite aC_PTFE electrodes soaked in 1 mol dilute sulphuric acid were between 0.0043 and 0.096 S/cm at room conditions (Table 9). Except for the mesoporous carbon MC 1:7 KOH sample electrode, all the other aC electrodes had lower proton conductivity compared to nafion membrane. The proton conductivity for nafion 117 membrane has been reported to be 0.095 S/cm at full hydration (F. Lufrano et al. 2004). The value of the mesoporous carbon MC 1:7 KOH material at full hydration condition needs to be checked again in the future, before any conclusion because the sample was soaked in acid for more than 24 hours but not immersed in acid while actual testing.

The proton conductivity of the acid soaked aC electrodes increases with increase in pore volume because it is considered that higher pore volume offers more storage spaces within particles of carbon wherein acid could penetrate and conduct protons and hence provides higher proton conductivity. On the other hand the aC sample electrodes showing less proton conduction have got lower pore volume.
5.6.3 Electron conductivity of the activated carbon electrodes

The electron conductivity of the composite materials increases with decreased porosity of aC samples. The value of the electron conductivity ranges from 5.79 S/cm for graphitic carbon foam to 14.47 S/cm for MC 1:7 KOH electrodes. These values are depicted in Table 9.

The possible explanation of this behaviour might be that less porous aC offer close or tight packing of carbon particles that provide pathways for flow of electrons. The increase in porosity means that the distance between the carbon particles increases and the contact between the carbon particles is reduced.

5.6.4 Other applications for the fabricated activated carbon electrodes

The characterisation of a number of fabricated composite aC-PTFE materials has been described in this chapter, and many of these materials when soaked in acid 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; H. Yang et al. 2010; S. N. Patel et al. 2012; C. Y. Liu et al. 2012; Tortello et al. 2012).
6. DOUBLE LAYER CAPACITANCE AND REVERSIBLE HYDROGEN STORAGE CAPACITY OF ACTIVATED CARBON ELECTRODES

6.1 OVERVIEW

In this chapter, the double-layer capacitance and reversible hydrogen storage capacity of the aC electrodes with PTFE binder characterised in chapter 5 are measured when used with a liquid sulphuric acid electrolyte. The double-layer capacitance is formed by the interfaces between the surfaces of carbon particles and the sulphuric acid. Mobile hydronium ions within the sulphuric acid and conducting electrons within the carbon particles can both move under the influence of an electric field to produce regions near the interface of compensating excess positive or negative charge density. This capacitance can also contribute to the measured hydrogen storage potential of the aC electrodes by positively-charged hydronium ions being held electrostatically near the negatively-charged surfaces of pores within the aC particles. Additional storage of hydrogen occurs as some hydronium ions give up an H\(^+\) ion (a proton), which then forms a bond with a carbon atom in the pore surface actual bonds are formed between hydrogen.

6.2 THE CONCEPT OF DOUBLE-LAYER CAPACITANCE

6.2.1 Origins of the concept

A particular inter-facial region formed at any electrode immersed in an electrolyte solution is termed a double-layer (Zbigniew Stojek 2002). The double-layer has a significant effect on the electrochemical properties of such a layer. The double-layer can be viewed as a capacitor when an electric circuit is used to measure the current that flows at a particular working electrode. The concept of a double-layer of opposing charges existing at the surface of a metal
in contact with an electrolyte was introduced by Helmholtz in 1879 (H.L.F. von Helmholtz 1879). The first theoretical model assumed the presence of a compact layer of ions in contact with the charged metal surface (Zbigniew Stojek 2002). Another model presented by Gouy and Chapman, involves a diffuse double-layer in which the accumulated ions, due to the Boltzmann distribution, extend some distance from the solid surface. Stern (1924) further proposed that the electrified solid-liquid interface included both the rigid Helmholtz layer and the diffuse one of Gouy and Chapman. Specific adsorption of ions at the metal surface was pointed out by Graham in 1947 (D. C. Graham 1947), followed by further developments in which the solvent's role has been taken into account (Parsons 1954; J. Bockris 1963; Zbigniew Stojek 2002).

Although in the literature, many models for the double-layer have been published but there is no general model that can be used in all experimental situations. The main reason for this is the dependency of the double-layer structure and its capacity on several parameters such as: electrode material (carbons, metals, semiconductors, electrode porosity, the presence of layers of either oxides or polymeric films or other solid materials at the surface), type of solvent, type of supporting electrolyte, extent of specific adsorption of ions and molecules, and temperature (Zbigniew Stojek 2002).

### 6.2.2 Experimental setup to measure double-layer capacitance

In the present study, a split flat coin cell for battery R & D supplied by MTI was employed to measure the double-layer capacitance of all fabricated aC electrodes, as shown in Figure 34.
A split flat coin cell for battery R & D of 15 mm diameter.

This coin cell comprised two end plates or metal electrodes with attached terminal clips for electrical connections (Figure 35). One of the end plates had a cavity of 15 mm diameter to accommodate the electrodes to be tested. The two identical test electrodes needed to be separated by an electrical insulator.

The end plates of the split flat coin cell were fastened by four screws and wing nuts. The electrolyte used was 1 mol dilute sulphuric acid.
6.2.3 Double-layer capacitance of activated carbon electrodes

Cyclic voltammetry (CV) is a very effective tool in the field of electrochemistry that has been extensively used to calculate double-layer capacitance of supercapacitors, fuel cell and batteries in which the charged electrodes are commonly interspersed in an electrolyte solution (Hainan Wand and Laurent Pilon 2012). In such applications, only ions can access the electric double-layers formed at the electrode/electrolyte interfaces. The principle of CV involves imposing an electric potential at the electrode that varies with time linearly and periodically, and measuring the resulting current over time. Integration of the electric current with respect to time yields the amount of total accumulated charge at the surface of the electrode. Finally, the total charge divided by the potential is used to estimate the capacitance (Hainan Wand and Laurent Pilon 2012).

Pairs of electrodes were made from all the aC samples (as described in chapter 5) with PTFE binder using a similar procedure as mentioned in chapter 4, and with a size matching the cavity in the end plate of the split flat coin cell. Each pair of were electrically separated in the cell by porous filter paper. The electrolyte used to immerse these electrodes was 1 mol dilute sulphuric acid. The split flat coin cell was then closed and connected to the electrochemical workstation through terminals as shown in Figure 36.

![Figure 36. A schematic of the split flat coin cell connected to the electrochemical workstation for cyclic voltammetry](image)
The equivalent circuit associated with the capacitance measurement arrangement is shown in Figure 37. In the Figure, \( R_{e1} \) and \( R_{e2} \) represent the resistances of the end plates, \( R_e \) represents the resistance of the electrode, and \( R_p \) is the bulk resistance between its two faces, to proton transport. The electrochemical workstation was set to perform cyclic voltammetry or in other words, the linear sweep of potential (from 2 volts to -2 volts) with respect to time was applied and voltage was increased in equal incremental steps. The range of the potential sweep was selected based upon results of simple electrolysis test performed on the fabricated aC samples in a 3-electrode electrolytic cell. Platinum wire, Hg/HgO, and aC electrodes were used as counter, reference and working electrodes respectively. The results of the electrolysis test were in the form of voltage vs. current curves as shown in Figure 38.

![Figure 37. Equivalent circuit for capacitance measurement](image1)

![Figure 38. Voltage vs. current curve obtained from electrolysis of carbon sample aCP.](image2)
The point of gas formation was observed during electrolysis test, marked on the V-I curve, and the corresponding voltage was noted. This voltage was set as the maximum point for the voltage sweep in the cyclic voltammetry. The voltage scan rate for CV was set to 2mV/sec. The capacitance is considered as maximum and close to the capacitance under equilibrium conditions, if it is measured at low scan rate (Hainan Wand and Laurent Pilon 2012). The output in form of a voltammogram (a VI graph traced over a full time cycle) was obtained from the electrochemical workstation (Figure 39).

![Diagram of Cyclic Voltammogram](image)

**Figure 39.** Cyclic voltammogram for carbon-PTFE sample electrode aCP

The shape of the cyclic voltammogram can be used to analyse the electrochemical processes of charging and discharging capacitors (Hainan Wand and Laurent Pilon 2012). At the beginning of the cyclic voltammetry test, the current increases from zero potential during charging of the aC electrode up to max potential, followed by decrease in voltage due to which the current goes negative. A bulge (or hump) was observed in the voltammogram before the point of maximum voltage was reached that represented that some reaction was taking place as shown in Figure 39. The reason for this shape and its interpretation has been suggested differently in literature. For example, Pell and Conway et al, 2000, observed a similar hump in CV while using a low concentration electrolyte, which was absent while using a higher concentration...
electrolyte. The authors proposed it as an effect of low concentration and possible reason mentioned was the electrolyte starvation due to limited amount of ions at low concentrations (Hainan Wand and Laurent Pilon 2012). Moreover, this bulge was also connected to redox reaction at the electrode surface (Chmiola J. and Largeot C. et al. 2010).

In the present study, the peak current estimated from the voltammogram was used to calculate the double-layer capacitance per unit mass of carbon in the electrodes using equation 35 (A. Velikonja 2014).

\[ C = \frac{I_{\text{peak}}}{V_t \times M_c} \]  

Eq. 35

where,

- \( C \rightarrow \) capacitance in F/g
- \( I_{\text{peak}} \rightarrow \) peak current in mA (the highest identified value of current from Figure 39)
- \( V_t \rightarrow \) scan rate in mV/s
- \( M_c \rightarrow \) mass of carbon in grams

The values for double-layer capacitance per unit mass of carbon of all the fabricated aC-PTFE sample electrodes obtained from the experimental voltammograms and using this calculation method are presented in Table 11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak current (mA)</th>
<th>Scan rate (mV/s)</th>
<th>Mass of carbon powder (grams)</th>
<th>Total mass of electrode (grams)</th>
<th>Capacitance considering total mass of the electrode (F/g)</th>
<th>Capacitance considering mass of carbon powder (F/g)</th>
</tr>
</thead>
</table>

102
<table>
<thead>
<tr>
<th>Material</th>
<th>aC</th>
<th>aCP</th>
<th>aCS</th>
<th>aC'N</th>
<th>aCK7.5</th>
<th>aCK2.5</th>
<th>aCK10</th>
<th>aCK10 1:1 KOH</th>
<th>aCK10 1:3 KOH</th>
<th>aCK10 1:5 KOH</th>
<th>aCK10 1:7 KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphitic carbon foam</td>
<td>102</td>
<td>2</td>
<td>1.8</td>
<td>2.0</td>
<td>25.5</td>
<td>28.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aCP</td>
<td>105</td>
<td>2</td>
<td>1.79</td>
<td>1.99</td>
<td>26.4</td>
<td>29.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexible carbon foam</td>
<td>115</td>
<td>2</td>
<td>1.8</td>
<td>1.98</td>
<td>29.0</td>
<td>31.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aCS</td>
<td>120</td>
<td>2</td>
<td>1.90</td>
<td>2.15</td>
<td>27.9</td>
<td>31.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon monoliths</td>
<td>130</td>
<td>2</td>
<td>1.95</td>
<td>2.15</td>
<td>30.2</td>
<td>33.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aC'N</td>
<td>160</td>
<td>2</td>
<td>1.95</td>
<td>2.15</td>
<td>37.2</td>
<td>41.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aCK7.5</td>
<td>420</td>
<td>2</td>
<td>1.99</td>
<td>2.19</td>
<td>95.9</td>
<td>105.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aCK2.5</td>
<td>470</td>
<td>2</td>
<td>1.98</td>
<td>2.18</td>
<td>107.8</td>
<td>118.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aCK10</td>
<td>570</td>
<td>2</td>
<td>2.05</td>
<td>2.25</td>
<td>126.7</td>
<td>139.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon 1:1 KOH</td>
<td>480</td>
<td>2</td>
<td>2.0</td>
<td>2.2</td>
<td>109.1</td>
<td>120.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon 1:3 KOH</td>
<td>680</td>
<td>2</td>
<td>2.0</td>
<td>2.23</td>
<td>152.5</td>
<td>167.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon 1:5 KOH</td>
<td>720</td>
<td>2</td>
<td>2.03</td>
<td>2.23</td>
<td>161.4</td>
<td>177.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon 1:7 KOH</td>
<td>765</td>
<td>2</td>
<td>2.02</td>
<td>2.22</td>
<td>172.3</td>
<td>189.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values of measured double-layer capacitance of all aC-PTFE electrodes with respect to their respective BET surface areas are compared with the earlier results of Vix Guterl et al. 2002, and found to be reasonably close as shown in Table 12. The ac samples from Vix Guterl et al. 2002, that had around the same BET area/TSA were sought and compared with the aC samples used in the present work.
Table 12. Table comparing the measured double-layer capacitance of all aC sample electrodes with Vix Guterl et al. 2000.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacitance considering mass of carbon powder in F/g</th>
<th>BET Surface area from N₂ isotherm adsorption in [m²/g]</th>
<th>Comparison with Vix Guterl et al. 2002</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphitic carbon foam</td>
<td>28.3</td>
<td>150</td>
<td>TSA* [m²/g]</td>
</tr>
<tr>
<td>aCP</td>
<td>29.3</td>
<td>208.9</td>
<td>Capacitance in F/g</td>
</tr>
<tr>
<td>Flexible carbon foam</td>
<td>31.9</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>aCS</td>
<td>31.6</td>
<td>381</td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon monoliths</td>
<td>33.3</td>
<td>619</td>
<td>630</td>
</tr>
<tr>
<td>aC‘N</td>
<td>41.0</td>
<td>673.9</td>
<td>713</td>
</tr>
<tr>
<td>aCK7.5</td>
<td>105.5</td>
<td>893.3</td>
<td>850</td>
</tr>
<tr>
<td>aCK2.5</td>
<td>118.7</td>
<td>919.2</td>
<td>850</td>
</tr>
<tr>
<td>aCK10</td>
<td>139.0</td>
<td>1012.5</td>
<td>1470</td>
</tr>
<tr>
<td>Mesoporous carbon 1:1 KOH</td>
<td>120.0</td>
<td>989</td>
<td>850</td>
</tr>
<tr>
<td>Mesoporous carbon 1:3 KOH</td>
<td>167.5</td>
<td>1271</td>
<td>1470</td>
</tr>
<tr>
<td>Mesoporous carbon 1:5 KOH</td>
<td>177.3</td>
<td>1658</td>
<td>1470</td>
</tr>
<tr>
<td>Mesoporous carbon 1:7 KOH</td>
<td>189.4</td>
<td>1922</td>
<td>2200</td>
</tr>
</tbody>
</table>

*TSA → total surface area.

The results obtained from cyclic voltammetry for double-layer capacitance are plotted against BET surface area of the sample electrodes in Figure 40. A generally monotonic relationship is evident with capacitance increasing with BET surface area, in line with similar behaviour cited
in the literature (Vix Guterl et al. 2000). Among all the fabricated electrodes, mesoporous carbon 1:7 KOH was the best performer in terms of double-layer capacitance at 189.4 F/g with the highest BET surface area of 1922 m$^2$/g.

![Graph showing relation between capacitance and surface area.](image)

Figure 40. Graph showing relation between capacitance and surface area. The sudden drop in curve is due to change in surface area of aC sample made from phenolic resin as compare to previous data points that corresponds aC samples from Victorian brown coal.

### 6.3 ELECTROCHEMICAL HYDROGEN STORAGE IN ACTIVATED CARBON

#### 6.3.1 Choice of acid electrolyte
Carbon materials have been researched extensively as energy storage media for electrical devices like supercapacitors (Blenda-Martinez MJ and Macia-Agullo JA et al. 2005, K. Jurewicz and Vix Guterl et al. 2004), because of their light weight, texture/structure diversity, high conductivity and easy availability. Electrochemical hydrogen storage by electrolysis of water is one of the potential electrochemical applications of carbon materials. This process consists of storage of electrical charge through electro-reduction of water and formation of weak chemical bonds between hydrogen and carbon (Levya-Garcia and F. Beguin et al. 2014). Various carbon materials such as carbon nano-tubes (CNT, activated carbon (aC), and others have been explored for this application. Porous activated carbons have been extensively studied for these applications due to more effective electrochemical hydrogen storage and greater reproducibility offered as compared to other forms of carbon (Levya-Garcia and F. Beguin et al. 2014).

The roles of porosity and other structural characteristics of carbons have been investigated in the literature leading to the conclusion that higher micropore volume (including micropores of size less than 2 nm and ultramicropores of size less than 0.7 nm) favours electrochemical hydrogen (H) storage (Levya-Garcia and F. Beguin et al. 2014). The existence of surface oxygen groups in the aC results in impregnation of active storage sites and therefore decreases the electrochemical hydrogen storage capacity of the aC. In the present study, we have chosen to use an acidic electrolyte (1 mol. dilute H₂SO₄) because the aC electrode was to be incorporated into a reversible fuel cell employing an acid-based PEM electrolyte

6.3.2 Experimental setup to measure electrochemical hydrogen storage capacity

6.3.2.1 Assembly of three-electrode electrolytic cell

The electrochemical hydrogen storage capacity of all the fabricated aC sample electrodes was measured by galvanostatic charging and discharging in a typical three-electrode electrolytic cell (Figure 41).
Figure 41. Three electrode-electrolytic cell used to measure the electrochemical hydrogen storage capacity of the aC electrodes.

The three-electrode electrolytic cell used in the present project was custom made on request of the author by Xi’an Yima Opto-electrical Technology Co. Ltd. located in China. The specifications of the three-electrode electrolytic cell are listed in Table 13.

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>3-electrode sealed electrolytic cell</td>
</tr>
<tr>
<td>Model</td>
<td>C001</td>
</tr>
<tr>
<td>Volume</td>
<td>250 ml</td>
</tr>
<tr>
<td>Diameter</td>
<td>60 mm</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Height</td>
<td>90 mm</td>
</tr>
<tr>
<td>Sealing</td>
<td>PTFE cover</td>
</tr>
<tr>
<td>Auxiliary/Counter electrode</td>
<td>Platinum wire of 0.8 mm diameter and 50 mm length</td>
</tr>
<tr>
<td>Reference electrode</td>
<td>Hg/HgO</td>
</tr>
<tr>
<td>Working electrode</td>
<td>Fabricated aC-PTFE electrodes</td>
</tr>
<tr>
<td>Gas collection</td>
<td>Glass tube housings on counter and working electrode</td>
</tr>
</tbody>
</table>

The working electrode holder supplied by the manufacturer is shown in Figure 42, and other two electrodes (counter and reference) in Figures 43 and 44. A detailed engineering drawing for the reference electrode is shown in Figure 45.

Figure 42. Working electrode holder for C001 electrolytic cell
Figure 43. Auxiliary/counter electrode (platinum wire) for C001 electrolytic cell

Figure 44. Reference electrode (Hg/HgO) for the C001 electrolytic cell
6.3.2.2 Preparation of liquid electrolyte

Dilute sulphuric acid was chosen as the acid electrolyte for the present project since it is a good proton conductor and readily available. Dilute sulphuric acid was prepared from 98% concentrated sulphuric acid according to the specifications listed in Table 14. It is hard to fully dissociate concentrated sulphuric acid into ions at room temperature and therefore it is considered as a poor electrolyte (M. Liler 1971). Hence, 1 mol dilute sulphuric acid was selected for the electrolyte in this research work, since it has relatively high proton conductivity (in the range of 10-5 – 10-2 S cm⁻¹ M. Rikukawa et al. 2000).
Table 14. Specifications of the concentrated sulphuric acid used to prepare an electrolyte

<table>
<thead>
<tr>
<th>Name</th>
<th>Sulphuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Concentration</td>
<td>98%</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>98.08</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Appearance form</td>
<td>Liquid</td>
</tr>
<tr>
<td>pH</td>
<td>1.2 at 5 g/l</td>
</tr>
<tr>
<td>Melting point/freezing point</td>
<td>3 °C</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>1.33 hPa at 145.8 °C</td>
</tr>
<tr>
<td>Vapour density</td>
<td>3.39 – (Air = 1.0)</td>
</tr>
<tr>
<td>Relative density</td>
<td>1.84 g/cm³</td>
</tr>
<tr>
<td>Molarity</td>
<td>18.4 M</td>
</tr>
<tr>
<td>Normality</td>
<td>36.8 N</td>
</tr>
<tr>
<td>Surface tension</td>
<td>55.1 mN/m at 20 °C</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

The first step in preparation of 1M dilute sulphuric acid from concentrated acid was to check the molarity of the concentrated acid. In the present project the molarity (number of moles contained in 1 litre of reagent) of the concentrated sulphuric acid was 18.4, as mentioned in Table 13. The volume of concentrated sulphuric acid required to prepare 1 litre of dilute sulphuric acid of 1M molarity was calculated from equation 36:

\[
\frac{1 \text{ ml}}{0.0184 \text{ moles}} = \frac{x \text{ ml}}{1 \text{ mole}}
\]

Eq. 36

where

x → is the required volume.

Solving for ‘x’ in equation 36 gave the value of 54.3 ml that was slowly added into distilled water to obtain 1 litre of 1 mol. dilute sulphuric acid solution.
The calculated amount of concentrated sulphuric acid (54.3 ml) was slowly added to distilled water, as mixing acid with water is an exothermic reaction evolving heat. For safety, 700 ml of distilled water was taken in a glass flask and the 54.3 ml of 98% concentrated sulphuric acid was poured into it. The flask was held in a water pool and continuously stirred to dissipate the heat evolved from the exothermic reaction. Since the density of the concentrated sulphuric acid is more than water, the acid mainly sank to the bottom of the flask where the reaction occurred without splashing due to changes in thermal conditions. The prepared 1 mol. dilute sulphuric acid was stored in a glass bottle with tight cork sealing. This dilute acid was then used to fill the electrolytic cell to act as electrolyte in the electrochemical experiments.

6.3.2.3 Assembly of three-electrode electrolytic cell with electrochemical workstation

Galvanostatic charging and discharging has been used as an important tool to measure electrochemical hydrogen storage capacity of various materials (K. Jurewicz et al. 2002, Vix Guterl et al. 2005, Garcia and F. Beguin et al. 2014). The experimental set up used in the present project to measure the electrochemical hydrogen storage capacity of all the fabricated aC-PTFE electrodes was based on the 3-electrode electrolytic cell (as mentioned in 6.3.1) employed in conjunction with a CH Instruments electrochemical workstation, as shown in Figure 46. The experimentation was done at School of Applied Sciences, RMIT University Melbourne.

Figure 46. Electrochemical workstation used to measure hydrogen storage capacity of the aC-PTFE electrodes at RMIT University Melbourne
The electrochemical cell was filled with 1 mol dilute sulphuric acid to the level such that working electrode (aC-PTFE), counter electrode (platinum wire) and reference electrode (Hg/HgO) were fully immersed. The gas outlets from the working and counter electrodes were connected to the graduated cylinders filled with water to collect the gas bubbling out of the water, as shown in Figure 47. The working electrode was connected to the negative terminal of the electrochemical workstation to attract the positive ions (H$_3$O$^+$) produced during slitting of water on the counter electrode connected to the positive terminal of the workstation; the reference electrode was connected to the neutral terminal. The schematic of the whole setup is shown in Figure 48. The graduated cylinders used for gas collection were fully sealed with parafilm from the top to avoid any gas escaping into atmosphere. The electrolytic cell was fully sealed with its threaded PTFE cover to avoid atmospheric contamination and escape of gases.

Figure 47. Graduated cylinders connected to working and counter electrodes of the 3-electrode electrolytic cell.
Figure 48. Schematic of experimental set-up to measure electrochemical hydrogen storage capacity of aC-PTFE electrode using galvanostatic charging and discharging

6.3.3 Hydrogen storage capacity of activated carbon electrodes

A preliminary test of simple electrolysis was run on all the fabricated aC electrodes with 1 mol dilute sulphuric acid as electrolyte to mark the voltage and current values on a VI curve where H\textsubscript{2} gas formation started (refer Figure 95). To suppress the hydrogen gas generation the charging current and voltage in galvanostatic charging were kept below than the marked values. The aC-PTFE sample electrodes were charged (galvanostatic charging or electrolyser mode) at a constant charging current of 150 mA until a sudden rise in H\textsubscript{2} gas generation was observed indicating that the storage has reached to its maximum capacity (total charging time recorded was of 18 hours). The E-mode operation was stopped thereafter. The water was split into hydrogen and oxygen ions on the counter electrode with the usual water electrolysis reaction as shown in eq. 37.

$$\text{H}_2\text{O} \rightarrow 2 \text{H}^+ + 0.5 \text{O}_2$$

Eq. 37
The oxygen gas liberated as the result of reaction at the counter electrode was collected in the graduated cylinder and the volume of gas was recorded. This amount was later used in the calculations to estimate the quantity of hydrogen electrochemically produced. The hydrogen gas formed at the working electrode was collected in another graduated cylinder and the volume was recorded.

After galvanostatic charging of the cell, the system was allowed to rest for 1 hour before switching to galvanostatic discharging. Thereafter, the electrolytic cell was set for galvanostatic discharging (Fuel cell mode) at constant discharge current of 80 mA in the first cycle, but the time for discharging was not fixed. Rather, the discharging ceased when the cell could not maintain the set discharge current. The time for discharging was recorded. In the second cycle, the electrolytic cell was charged again with the same charging current of 150 mA for 18 hours, but discharging current was set to 30 mA, which was quite low as compared to the discharging current in the first cycle. The process of galvanostatic charging and discharging of the electrolytic cell during both cycles was recorded in the form of potential versus time curves for all the electrodes. These curves are shown in Figures 49 to 61.

Figure 49. Galvanostatic charge-discharge curves for sample graphitic carbon foam in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1st cycle +80 mA, discharge–1st cycle +80 mA until electrochemical station removed the load, 2nd cycle +30 mA until open circuit potential.
Figure 50. Galvanostatic charge-discharge curves for sample aCP in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1\textsuperscript{st} cycle +80 mA, discharge–1\textsuperscript{st} cycle +80 mA until electrochemical station removed the load, 2\textsuperscript{nd} cycle +30 mA until open circuit potential.

Figure 51. Galvanostatic charge-discharge curves for sample flexible carbon foam in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1\textsuperscript{st} cycle +80 mA, discharge–1\textsuperscript{st} cycle +80 mA until electrochemical station removed the load, 2\textsuperscript{nd} cycle +30 mA until open circuit potential.
Figure 52. Galvanostatic charge-discharge curves for sample aCS in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1st cycle +80 mA, discharge–1st cycle +80 mA until electrochemical station removed the load, 2nd cycle +30 mA until open circuit potential.

Figure 53. Galvanostatic charge-discharge curves for sample mesoporous carbon monolith in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1st cycle +80 mA, discharge–1st cycle +80 mA until electrochemical station removed the load, 2nd cycle +30 mA until open circuit potential.
Figure 54. Galvanostatic charge-discharge curves for sample aCN in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1<sup>st</sup> cycle +80 mA, discharge–1<sup>st</sup> cycle +80 mA until electrochemical station removed the load, 2<sup>nd</sup> cycle +30 mA until open circuit potential.

Figure 55. Galvanostatic charge-discharge curves for sample aCK7.5 in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1<sup>st</sup> cycle +80 mA, discharge–1<sup>st</sup> cycle +80 mA until electrochemical station removed the load, 2<sup>nd</sup> cycle +30 mA until open circuit potential.
Figure 56. Galvanostatic charge-discharge curves for sample aCK2.5 in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1\textsuperscript{st} cycle +80 mA, discharge–1\textsuperscript{st} cycle +80 mA until electrochemical station removed the load, 2\textsuperscript{nd} cycle +30 mA until open circuit potential.

Figure 57. Galvanostatic charge-discharge curves for sample aCK10 in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1\textsuperscript{st} cycle +80 mA, discharge–1\textsuperscript{st} cycle +80 mA until electrochemical station removed the load, 2\textsuperscript{nd} cycle +30 mA until open circuit potential.
Figure 58. Galvanostatic charge-discharge curves for sample mesoporous carbon 1:1 KOH in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1st cycle +80 mA, discharge–1st cycle +80 mA until electrochemical station removed the load, 2nd cycle +30 mA until open circuit potential.

Figure 59. Galvanostatic charge-discharge curves for sample mesoporous carbon 1:3 KOH in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1st cycle +80 mA, discharge–1st cycle +80 mA until electrochemical station removed the load, 2nd cycle +30 mA until open circuit potential.
Figure 60. Galvanostatic charge-discharge curves for sample mesoporous carbon 1:5 KOH in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1st cycle +80 mA, discharge–1st cycle +80 mA until electrochemical station removed the load, 2nd cycle +30 mA until open circuit potential.

Figure 61. Galvanostatic charge-discharge curves for sample mesoporous carbon 1:7 KOH in 1 mol sulphuric acid. Charge-150 mA during 18 hours, discharge: 1st cycle +80 mA, discharge–1st cycle +80 mA until electrochemical station removed the load, 2nd cycle +30 mA until open circuit potential.
In the process of galvanostatic charging, hydrogen was stored electrochemically under the influence of the charging current (150 mA during 18 hours). The amount of hydrogen reversibly stored was assessed by subjecting the cell to the discharge current of 80 mA in first cycle and 30 mA in second cycle until the open circuit potential was reached. During galvanostatic discharge, the total charge flow was calculated using equation 38.

\[ Q_{\text{discharge}} = I \cdot t \]  \hspace{1cm} \text{Eq. 38}

Where,
I → current (A)
t → discharge time (s)

It should be noted that \( Q_{\text{discharge}} \) as indicated in equation 39, includes contribution from capacitive charge (capacitance of activated carbon) \( Q_{\text{cap}} \), and charge \( Q_H \) from electrochemically stored hydrogen.

\[ Q_{\text{discharge}} = Q_{\text{cap}} + Q_H \]  \hspace{1cm} \text{Eq. 39}

Mass of hydrogen released from the electrode was calculated by using equation 40.

\[ M = \frac{I \cdot t}{1000 \cdot F} \]  \hspace{1cm} \text{Eq. 40}

where,
M → mass of hydrogen generated in kg.
I → discharge current in mA
t → discharge time in sec.
F → Faraday’s constant (96485 C mol\(^{-1}\))

Hence, the amount of hydrogen (mass %) stored in activated carbon was calculated by applying equation 41.
\[
M \% = \frac{M}{M + M_C}
\]

where,

\(M\) → mass of hydrogen in kg

\(M_C\) → mass of activated carbon in kg

The hydrogen mass % stored in the aC-PTFE electrodes as measured and estimated in the discharge cycle are listed in Table 15 and provide a measure of the reversible hydrogen storage capacity of these electrodes.

<table>
<thead>
<tr>
<th>Name of the sample</th>
<th>No. of cycle</th>
<th>Galvanostatic discharge current [mA]</th>
<th>Time of Discharge [hrs]</th>
<th>Equivalent mass of hydrogen stored in carbon [mass %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphitic carbon foam</td>
<td>1</td>
<td>80</td>
<td>2.5</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>6</td>
<td>0.33</td>
</tr>
<tr>
<td>aC_P</td>
<td>1</td>
<td>80</td>
<td>3.25</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>8.5</td>
<td>0.46</td>
</tr>
<tr>
<td>Flexible carbon foam</td>
<td>1</td>
<td>80</td>
<td>3.5</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>9</td>
<td>0.49</td>
</tr>
<tr>
<td>aC_S</td>
<td>1</td>
<td>80</td>
<td>4</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>10</td>
<td>0.54</td>
</tr>
<tr>
<td>Mesoporous carbon monolith</td>
<td>1</td>
<td>80</td>
<td>7.25</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>18.75</td>
<td>1.01</td>
</tr>
<tr>
<td>aC_N</td>
<td>1</td>
<td>80</td>
<td>7.5</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>19</td>
<td>1.03</td>
</tr>
<tr>
<td>aC_K_7.5</td>
<td>1</td>
<td>80</td>
<td>8.5</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>21.5</td>
<td>1.16</td>
</tr>
<tr>
<td>aC_K_2.5</td>
<td>1</td>
<td>80</td>
<td>9</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>23</td>
<td>1.24</td>
</tr>
</tbody>
</table>
The calculated equivalent mass of hydrogen stored in activated carbon ranged from 0.36 % to 1.6 % in these experiments. The fabricated aC_PTFE sample named as mesoporous carbon 1:7 KOH showed the highest electrochemical hydrogen storage capacity at 1.6% during the first galvanostatic charge discharge cycle amongst all the fabricated aC_PTFE sample electrodes whereas graphitic carbon foam showed the lowest capacity. This hydrogen storage capacity is equivalent to that of the best-performing commercially available metal hydrides on a material basis.

All the tested aC_PTFE sample electrodes performed better in terms of reversible electrochemical hydrogen storage capacity in first cycle as compared to second cycle of galvanostatic charging and discharging. In the second cycle of testing, a percentage fall of electrochemical hydrogen storage capacity of the aC electrodes in the range of 1-2 % was observed. One possible explanation of such behaviour is that not all of the stored hydrogen move out of the electrodes during first cycle thereby limiting the storage sites for the second cycle of galvanostatic charging.

The measured amount of H$_2$ during charging was used to estimate the mass of hydrogen produced as gas. The total hydrogen production was calculated using Faraday’s law (Eq.40). The net hydrogen that was likely to have entered in the storage was estimated by subtracting the mass of H gas from the total H produced. The amount of hydrogen discharged was
calculated and found to be less than the amount of hydrogen that entered the storage. The hydrogen accounting was found to be consistent. These calculations are included as a spreadsheet in appendix of this thesis.

### 6.3.4 Contribution of double-layer capacitance in electrochemical hydrogen storage capacity of activated carbon electrodes

The mass % of stored hydrogen listed in Table 16 is the equivalent mass of hydrogen including hydrogen storage resulting from double-layer capacitance (with no charge transfer) and hydrogen storage from an electrochemical reaction (involving charge transfer). The amount of equivalent hydrogen stored to double-layer capacitance and due to electrochemical reaction is separately listed in Table 15 and shown in graphical form in Figure 62.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Equivalent hydrogen wt% stored due to capacitance wt %</th>
<th>Equivalent hydrogen wt% stored due to reaction wt %</th>
<th>Equivalent hydrogen obtained in discharging wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphitic carbon foam</td>
<td>0.03</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td>aCP</td>
<td>0.03</td>
<td>0.44</td>
<td>0.47</td>
</tr>
<tr>
<td>Flexible carbon foam</td>
<td>0.03</td>
<td>0.48</td>
<td>0.51</td>
</tr>
<tr>
<td>aCS</td>
<td>0.03</td>
<td>0.55</td>
<td>0.58</td>
</tr>
<tr>
<td>Mesoporous carbon monoliths</td>
<td>0.03</td>
<td>1.01</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>1.04</td>
<td>1.08</td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>aC(N)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aC(K7.5)</td>
<td>0.11</td>
<td>1.11</td>
<td>1.22</td>
</tr>
<tr>
<td>aC(K2.5)</td>
<td>0.12</td>
<td>1.17</td>
<td>1.29</td>
</tr>
<tr>
<td>aC(K10)</td>
<td>0.14</td>
<td>1.22</td>
<td>1.36</td>
</tr>
<tr>
<td>Mesoporous carbon 1:1 KOH</td>
<td>0.12</td>
<td>1.31</td>
<td>1.43</td>
</tr>
<tr>
<td>Mesoporous carbon 1:3 KOH</td>
<td>0.17</td>
<td>1.31</td>
<td>1.48</td>
</tr>
<tr>
<td>Mesoporous carbon 1:5 KOH</td>
<td>0.18</td>
<td>1.38</td>
<td>1.56</td>
</tr>
<tr>
<td>Mesoporous carbon 1:7 KOH</td>
<td>0.19</td>
<td>1.41</td>
<td>1.60</td>
</tr>
</tbody>
</table>

In Figure 62, the green bars represent the contribution of reaction between H and carbon in hydrogen storage capacity whereas, the grey portion of each bar represent the contribution from the double-layer capacitance. The aC samples with high surface area and pore volume were found to have more contribution in H storage capacity from double-layer effect compared to aC samples with relatively low surface area (refer Figure 62). Particularly, the double-layer capacitance contribution was found to be significant in the range of 1.0-1.59 wt % of the total hydrogen storage capacity, but remains an order of magnitude less than the contribution from an electrochemical reaction between the hydrogen and the carbon surface within pores. A rising trend of contribution from double-layer capacitance in electrochemical hydrogen storage capacity of aC samples was observed with increase in surface area.
Figure 62. Graphical representation of contribution of double-layer capacitance and electrochemical reaction in equivalent hydrogen mass % stored in aC-PTFE electrodes.
6.3.5 Volumetric energy densities of activated carbon electrodes

The amount of energy (hydrogen energy) stored per unit volume of the storage is termed volumetric energy density (VED). This parameter (i.e. VED) is an important basis for comparison between commercially-available energy storage devices. Therefore, the VEDs of all the fabricated activated carbon electrodes were calculated using the following equation:

\[
VED = \frac{m \times 39.7 \times \varepsilon}{V} \quad \text{Eq. 42}
\]

where,

m → mass of hydrogen stored electrochemically in the aC electrode in grams
\(\varepsilon\) → efficiency of cell (considered as 0.5 in the present work)
V → volume of the aC electrode in litre.

The calculated VEDs of all aC electrodes were found to be in the range of 0.26 – 0.52 kWh\textsubscript{e}/litre, which is comparable with the commercially available MH-based hydrogen storage canister with VED of up to 0.8 kWh\textsubscript{e}/litre. The calculated VEDs of the aC electrodes are listed in Table 17.

Table 17. Volumetric energy densities of all aC electrodes

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of sample</th>
<th>Volume of electrode [litre]</th>
<th>Mass of hydrogen stored [grams]</th>
<th>Volumetric energy density [kWh\textsubscript{e}/litre]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Graphitic foam</td>
<td>0.00125</td>
<td>0.0167</td>
<td>0.26</td>
</tr>
<tr>
<td>2</td>
<td>aCP</td>
<td>0.00125</td>
<td>0.0175</td>
<td>0.27</td>
</tr>
<tr>
<td>3</td>
<td>Flexible carbon foam</td>
<td>0.00125</td>
<td>0.0179</td>
<td>0.28</td>
</tr>
<tr>
<td>4</td>
<td>aCS</td>
<td>0.00125</td>
<td>0.0184</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>Mesoporous carbon monolith</td>
<td>0.00125</td>
<td>0.0252</td>
<td>0.39</td>
</tr>
</tbody>
</table>
### 6.4 RELATIONSHIP BETWEEN HYDROGEN STORAGE CAPACITY AND CHARACTERISTICS OF ACTIVATED CARBON ELECTRODES

#### 6.4.1 Effect of surface area on electrochemical hydrogen storage capacity

From the analysis of all the experimental data it was observed that there was a monotonic relationship between the equivalent mass percent of hydrogen stored electrochemically in activated carbon and BET surface area of activated carbon. The mass % of hydrogen increased with increase in BET surface area and this behaviour is plotted in a graph along with experimental error bars as shown in Figure 63.
Figure 63. Graph showing the generally monotonic relationship between H mass % stored and surface area of activated carbon, especially as mass% increased.

### 6.4.2 Effect of pore volume on electrochemical hydrogen storage capacity

Similar to the BET surface area, pore volume also affected the hydrogen mass % stored electrochemically in aC-PTFE electrodes. The mass % hydrogen stored increased with increase in pore volume of activated carbon which is plotted in a graph along with experimental error bars as shown in Figure 64.
Figure 64. Graph showing monotonic relationship between H mass % stored and pore volume of activated carbon.

One of the possible explanations of such behaviour could be that increase in BET surface area and pore volume offers more storage sites for hydrogen within the activated carbon. The kinks around the middle of the curves in Figures 63 and 64 may be due to the different behaviour of electrodes made from brown coal and phenolic resin.

6.5 CONCLUSIONS

It is interesting to note here that, in a composite carbon – PTFE electrode of the kind being considered here, the proton conduction from the nafion boundary into the smaller pores is most likely to take place via hydronium movement or Groththus proton exchange through sulphuric acid and filling the pore volumes of the carbon. Furthermore, little is known at present about the structure of the connections between the sulphuric acid, PTFE and the surfaces of carbon particles. For example, how do the water-filled channels and micelles
within the nafion membrane link up with the surface planes of charged carbon atoms? These questions could be fruitful areas for further research.

All the sample aC electrodes showed promising results in terms of mass % of hydrogen electrochemically stored in them. Nine out of thirteen samples were able to store more than 1 mass% of hydrogen electrochemically, which is comparable with the gravimetric density of commercially-available MH based solid hydrogen cylinders requiring pressurized hydrogen gas input at pressures of 10 – 20 bar. These activated carbon hydrogen storages also promise to be much less expensive to produce than metal hydride systems employing rare earth metals.

The electrode made from mesoporous carbon 1:7 KOH made from phenolic resin showed the highest double-layer capacitance and reversible electrochemical hydrogen storage capacity amongst all the fabricated aC-PTFE sample electrodes. This sample also had the highest BET surface area and limiting micropore volume, potentially offering more storage sites for hydronium ions and hydrogen atoms neutralised by excess electrons on the carbon surfaces. Based on these results mesoporous carbon 1:7 KOH sample aC was selected to fabricate an electrode to be incorporated into proton flow battery to test its performance in electrolyser and fuel cell mode. This activity is discussed in the next chapter.
7. TESTING OF ACTIVATED CARBON ELECTRODES IN THE PROTON FLOW BATTERY

7.1 OVERVIEW

This chapter covers the experimental testing of four selected sample aC electrodes in a proton flow battery to assess its charge-discharge and reversible hydrogen storage performance. The aC sample electrode named as mesoporous carbon 1:7 KOH in chapter 4 was selected on the basis of its hydrogen storage capacity measured in the earlier experiments reported in chapter 6. The proton flow battery used in the present project was based on a modified proton exchange membrane unitised regenerative fuel cell, designed and manufactured drawing on the previously published work by S. Mohammadi (2013), J. Andrews and S. Mohammadi (2014), and Mohammad Javad Jazaeri, at RMIT University (J. Jazaeri 2013).

7.2 DESIGN AND CONSTRUCTION OF THE EXPERIMENTAL PEM UNITISED REGENERATIVE FUEL CELL

7.2.1 Overall schematic of a URFC

A URFC is a single unit capable of running in both electrolyser and fuel cell mode. In electrolyser mode, hydronium ions emerge from the membrane, and the protons they carry enter into storage to form weak chemical bonds with the storage material ideally without producing any hydrogen gas. In fuel cell mode, the stored protons come out of the storage material under the influence of an opposite electric potential. These protons then travel back as hydronium ions where they react with oxygen and electrons on the oxygen-side catalyst to reform water and generate electricity. Since in the URFC employed in the present research work
the input is water that is continuously split into protons that then flow through the system into the storage in electrolyser mode, the device has been termed ‘a proton flow battery’ (PFB). The designing and fabrication of the components of PFB are explained in the following subsections.

7.2.2 Material of the end-plates

End plates and bi-polar plates of a proton exchange membrane (PEM) unitised regenerative fuel cells (URFC) are usually made from metals such as titanium and stainless steel, or metallic alloys (P. J. Hamilton and B. Pollet 2010). The attributes of a good material for end plates are high electrical conductivity, high thermal conductivity, high resistance to chemical corrosion, high mechanical strength, low permeability for gases, and low mass (Yuan et al. 2005). Metallic plates mainly made from stainless steel are actively being used by researchers as end plates in URFCs because of ease of manufacturing, low cost, good mechanical properties, and high thermal and electrical conductivity (A. Kumar and Reddy 2003). Other commonly-used materials for URFC end plates include graphite, which is corrosion resistant, light weight and possesses suitable mechanical and thermal properties, but is expensive (C. Turan et al. 2011). However, graphite could be subject to chemical attack in the E-mode operation. Therefore in the present research, SS316 stainless steel was used to fabricate the end plates of the modified URFC used to construct a proton flow battery (PFB). The end plates were machined with flow channels and headers to accommodate the flow of oxygen through the proton flow battery on the oxygen side of the membrane, and allow removal of any hydrogen generated on the other side. Both end plates of the proton flow battery were of same length and breadth 72 x 84 mm, but different thicknesses. The oxygen-side end plate was 7 mm thick, while the hydrogen-side end plate was 9 mm thick to accommodate the activated carbon electrode (around 2 mm thick). The active area of the membrane electrode assembly and activated carbon electrode was 25 mm x 25 mm. The actual end plates are shown in Figures 65 and 66 and engineering drawings in Figures 67 and 68.
Figure 6.5. Actual oxygen side end plate of the proton flow battery.

Figure 6.6. Actual hydrogen side end plate of the proton flow battery.
Figure 67. Engineering drawing of oxygen side plate of the proton flow battery.
Figure 68. Engineering drawing of hydrogen side plate of the proton flow battery.
7.2.3 Design of the flow channels

Flow channels have an essential role to play in the performance of the proton exchange membrane URFC. Circulation of reactant gases, proper and even distribution of oxygen and hydrogen on the electrode, and water removal from the electrode are major services provided by the flow channels and flow headers (C. Turan et al. 2011). Most of the flow channels are made in the form of rectangular cross-section, but there are many other forms of cross section mentioned in the literature (see, for example, Feser J. P., Prasad A. K. et al. 2007). Some common cross-sectional patterns for flow channels are shown in Figure 69.

![Flow channel patterns](image)

Figure 69. Flow channel patterns for fuel cell: 1- parallel, 2-serpentine, 3-interdigitated, 4-parallel serpentine, and 5-pin-type (Feser J. P., Prasad A. K. et al. 2007).

The droplets of water produced during operation in fuel cell mode have the tendency to adhere to the flow channels and thus block them, particularly in the parallel flow field pattern. When the pressure of the reactant gases increases to the level to overcome the surface tension between the surface of flow channel and water droplet, the water droplets get detached (J. Larminie and A. Dicks 2003). However, reactant gases tend to flow through those channels which offer least resistance to the flow as the numbers and size of droplets are different in channels. Hence, the use of parallel flow pattern in fuel cell may reduce the uneven distribution of reactant gas within the fuel cell.
In the present research project, a parallel pattern was selected for flow channels within both the end plates of the proton flow battery. The reason for selection of this flow channel pattern was its better performance in gas distribution as reported in the literature (Ferng and Su 2007). All other flow patterns were reported to have shown poorer performance in terms of gas distribution (Ramos-Alvarado et al. 2012) and therefore parallel flow pattern was selected for this project. The location of the inlet and outlet ports is another important factor influencing the performance of parallel flow channels (Ferng and Su 2007). The location of inlet and outlet ports of the flow channels in the proton flow battery used in this research was designed to be at the centreline of the channels allowing the uniform distribution of gases in all the channels, unlike in Ferng and Su’s (2007) design where the inlet was in the upper-right and the outlet was in the bottom-left leading to poor distribution. The specifications of the cell are listed in Table 18.

Table 18. Specifications of the experimental cell.

<table>
<thead>
<tr>
<th></th>
<th>Oxygen end-plate</th>
<th>Hydrogen end-plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions (mm)</td>
<td>Cell area 72 ×84</td>
<td>72 ×84</td>
</tr>
<tr>
<td></td>
<td>Active area 25 ×25</td>
<td>25 ×25</td>
</tr>
<tr>
<td></td>
<td>Thickness 7</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Ribs width 1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Channel depth 1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>No. of channels 11</td>
<td>11</td>
</tr>
</tbody>
</table>

7.2.4 Gas diffusion layer (GDL)

The gas diffusion layers (GDL) on either side of the membrane electrode assembly (MEA) are vital elements of a URFC. GDLs for PEM fuel cells are usually made of a porous material possessing a dense bunch of carbon fibres woven together. The GDL provides an electrically conductive pathway between the catalyst layer of the MEA and the end plate (or bipolar plates) of the URFC. Other functions of the GDL in a URFC are to allow diffusion of the
reactant gases into and out from the active area of the cell, mechanical support to the MEA, and protection of the catalyst layer from corrosion and erosion caused by flows or other factors (Sehkyu Park, Jong-Won Lee et al. 2012).

In the previous research work at RMIT University, it was observed that carbon-based GDLs on the oxygen side of the URFC were attacked by the oxygen in E-mode operation, as shown in Figure 70. Therefore, in the present project the oxygen side was equipped with porous sintered titanium felt to act as GDL instead of woven carbon fabric. The titanium felt used is shown in Figure 71 and its specifications are listed in Table 19. The catalyst loading on the oxygen side was a mixture of 2 mg of iridium oxide and 2 mg of platinum black. No GDL was used on the hydrogen side in this project. Instead, 1 mol. sulphuric acid was used.

Protons in the form of hydronium ions emerge from the nafion membrane in E-mode and travel to the storage sites in carbon through the sulphuric acid. Any hydrogen gas, and all the oxygen gas, that were formed in E-mode, passed though the flow channels, headers, and were stored in cylinders.

![SEM image of the carbon-based GDL](image)

Figure 70. SEM image of the carbon-based GDL used in the previous research work at RMIT University on a reversible PEM fuel cell. The broken strands of the carbon fabric indicate oxygen attack on the GDL to form carbon dioxide, and hence carbon removal from the fabric.
Figure 71. Porous sintered titanium felt used as the GDL on the oxygen-side of the proton flow battery

Table 19. Specifications of the sintered titanium felt used as the oxygen-side GDL of the proton flow battery

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Make</td>
<td>Bekaert Germany</td>
</tr>
<tr>
<td>2</td>
<td>Product</td>
<td>Sintered titanium felt</td>
</tr>
<tr>
<td>3</td>
<td>Thickness</td>
<td>1 mm</td>
</tr>
<tr>
<td>4</td>
<td>Size</td>
<td>27 x 27 mm</td>
</tr>
<tr>
<td>5</td>
<td>Porosity</td>
<td>50 - 65 %</td>
</tr>
<tr>
<td>6</td>
<td>Fibre diameter</td>
<td>20 ( \mu )m</td>
</tr>
</tbody>
</table>

7.3 THE CONSTRUCTION OF THE EXPERIMENTAL PROTON FLOW BATTERY

7.3.1 Use of a modified URFC

For the present project a modified URFC with a solid carbon-based electrode was employed, as the experimental proton flow battery to test the feasibility of the concept. This novel device
was run in E-mode to split water, store hydrogen protons in the integrated aC storage electrode, and then supply these protons back in the FC-mode to reform water.

7.3.2 The structure of the proton flow battery

The experimental proton flow battery consists of many components similar to a normal URFC. The few modified components were:

1. Hydrogen side end plate (modified by machining flow channels and headers in plate)
2. Storage electrode – activated carbon electrode in this project
3. Gas diffusion layer – sintered titanium felt in this project

A schematic of the experimental proton flow battery including all components is shown in Figure 72. The detailed view A-A of the proton flow battery is shown in Figure 73.
Figure 72. Schematic diagram of the experimental proton flow battery. The orientation of the cell was rotated in the actual setup with the aC electrode at the bottom.
Figure 7.3. The detailed view of the proton flow battery, A-A, as defined in Figure 7.2. The aC electrode is in the horizontal position in the lower half of the cell to accommodate the acid.

7.3.3 The components of the cell

7.3.3.1 Membrane electrode assembly

The storage electrode on the H-side, the catalyst layer deposited on the membrane on the O-side, and an ELAT (woven carbon fabric) GDL on the O-side constitute the membrane-electrode-assembly (MEA) located at the centre of the cell (Figure 7.2). A silicon seal of 1 mm thickness with a cut-out to accommodate the ELAT GDL was used on the O-side to avoid any leakage from the cell. The aC storage electrode was located in a specially cut depression in the end plate on the H-side. The nafion was used directly as the seal on that side. The nafion membrane contained in the MEA plays the role of the proton conductor as it transfers the
proton from oxygen side to hydrogen side while the PFB is running in electrolyser mode (E-mode) and vice-versa when PFB is running in fuel cell mode (FC-mode).

The oxygen electrodes used in the present project comprised a catalyst layer deposited on a nafion membrane, as shown in Figure 74. The hydrogen electrode consisted of a storage electrode made of activated carbon soaked in sulphuric acid. It is to be noted that no catalyst layer was provided on the hydrogen side.

Figure 74. The catalyst layer loading (2.5 cm x 2.5 cm) on carbon cloth on the oxygen-side of the proton flow battery. The catalyst loading was 2 mg/cm$^2$ of IrRuO$_x$ and 2 mg/cm$^2$ of PtB.

7.3.3.2 Activated carbon electrode

The activated carbon electrode that was used in the experimental proton flow battery in the present research work was fabricated using the selected aC powder sample and the nafion binder. The measured amount of the selected activated carbon powder was mixed with nafion-117 solution. The mixture was stirred thoroughly at room temperature followed by mixing on a hot plate stirrer. Similar procedure of fabrication was employed as aC-PTFE electrodes. The details of fabrication of the composite aC-nafion electrode are given in subsections 43 and 4.3.2.
7.3.3.3 The end-plates and the flow channel

The oxygen-side end-plate of the PFB consisted of parallel flow channels to accommodate the gas flow generated in E-mode and input of water. The design of the oxygen-side end plate was similar to a normal URFC. On the other hand, the hydrogen-side end plate was different in that it had a depression of 2 mm depth with flow channels to accommodate activated carbon electrode, sulphuric acid and input/output of hydrogen gas in FC-mode. Both the end plates have provisions to join the pipes from the outlets to the gas collecting cylinders.

7.3.3.4 The sealing of the cell

The most commonly used material in fuel cells as a seal is silicone rubber. Silicone rubber seals offer ease of fabrication and low production cost, and hence are widely accepted as a sealing material in fuel cell technology. To ensure proper sealing of the fuel cell the thickness of sealing gasket should be a bit more than the electrode (Tan et al. 2007). Therefore, a silicone gasket of 1 mm ± 0.02 mm thickness was used around the active area of the PFB on the oxygen side to seal the edges (Figure 71). To avoid the leakage of gases from the edges, silicon rubber adhesive was applied along the edges of the PFB. Ample time was provided for silicon adhesive to dry completely. The PFB was tested for leakage before using it in actual experiments. For the leak test the PFB was dipped completely in water by blocking all the outlets, air blown from the inlet points, and hence any bubble formation in water observed. After ensuring that the assembled PFB was leak proof it was employed for actual experiments.

7.4 EXPERIMENTAL SETUP

7.4.1 Components of the setup

7.4.1.1 Hydrogen extraction cabinet
The proton flow battery experiments were conducted in an enclosed cabinet designed particularly for hydrogen-related experiments in the Sustainable Hydrogen Energy Laboratory (SHEL) at the Bundoora East campus of the RMIT University. The cabinet is equipped with an extraction fan and hydrogen gas sensors as shown in Figure 75.

Figure 75. Hydrogen extraction cabinet in the Sustainable Hydrogen Energy Laboratory at RMIT University (Jazaeri 2013).

7.4.1.2 DC power supply

While operating the experimental proton flow battery in electrolyser mode for splitting the water, the cell was supplied from an Instek DC power supply, as shown in Figure 76. The specifications of the equipment are listed in Table 20.
Table 20. Technical specifications of DC power supply used in the experiments

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Description</th>
<th>Value</th>
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<td>Model</td>
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<tr>
<td>4</td>
<td>No. of outputs</td>
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</tr>
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<td>Range of voltage supply</td>
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</tr>
<tr>
<td>6</td>
<td>Range of current supply</td>
<td>0 – 5 V</td>
</tr>
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<td>7</td>
<td>Voltage error range</td>
<td>± 0.005 V</td>
</tr>
<tr>
<td>8</td>
<td>Current error range</td>
<td>± 0.005 A</td>
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</tbody>
</table>

7.4.1.3 Gas collection cylinders

Two separate graduated measuring cylinders as shown in Figure 77 were employed in the experiments for collection of oxygen and hydrogen gases produced while operating the PFB in E-mode. The volume of the gases was recorded from these graduated cylinders to use in later calculations to estimate the amount of hydrogen produced by electrolysis of water. The same
cylinders were used while operating the PFB in FC-mode. The specifications of the gas collection cylinders are listed in Table 21.

![Graduated cylinder used for gas collection](image)

Figure 77. Graduated cylinder used for gas collection

<table>
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<td>Base dimensions</td>
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<td>6</td>
<td>Accuracy</td>
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### 7.4.2 Setting-up of the apparatus

The modified PEM URFC used as our experimental proton flow battery was tested for its performance in the experimental set-up shown in Figure 78. In the actual arrangement, the
orientation of the cell was rotated so its hydrogen side end plate was horizontal direction and facing downwards to accommodate the aC electrode and liquid acid.

![Diagram of proton flow battery experimental set-up]

Figure 78. The schematic of the proton flow battery experimental set-up.

A variable resistor was used for the electrical load in FC-mode, and two multimeters employed to measure current and voltage in both modes.

The proton flow battery was operated in E-mode followed by FC-mode with differences in the set-ups as shown in Figures 79 and 80.
Figure 79. The proton flow battery in E-mode set-up.

Figure 80. The proton flow battery in FC-mode set-up.
7.5 EXPERIMENTAL PROCEDURE

7.5.1 Electrolyser mode

When the proton flow battery (PFB) was run in E-mode (electrolyser mode), distilled water was supplied from the storage tank. The electric circuit corresponding to E-mode operation of the PFB is shown in Figure 81.

![Electric circuit corresponding to E-mode operation of the PFB.](image)

The cell was charged in E-mode and then discharged in FC-mode for a total of nine cycles separately using the same electrode. For the first four cycles the cell was charged at constant current of 50 mA for the first four cycles with the applied voltage gradually increased over time to keep the charging current constant. Thereafter, the cell was charged at constant voltage of 1.6 V for the next five cycles. In E-mode water was split continuously into hydrogen on the oxygen side electrode, some of which entered the storage on the hydrogen side after passing through the membrane in the form of hydronium. Oxygen was liberated as a gas from the oxygen-side electrode and was collected in a graduated cylinder. The theoretical oxygen gas production was calculated from Faraday's law using equation 43.
\[ M_o = \frac{I \times t}{4F \times 1000} \times \frac{R \times T}{P} \]

where,

\( M_o \rightarrow \) mass of oxygen generated in Kg.

\( I \rightarrow \) current in amperes.

\( t \rightarrow \) time in seconds.

\( F \rightarrow \) faraday’s constant = 96485 J per volt gram equivalent.

\( R \rightarrow \) gas constant = 8.314 J/mol.K

\( T \rightarrow \) ambient temperature in Kelvin

\( P \rightarrow \) atmospheric pressure in kilo Pascals.

The PFB was charged in E-mode continuously until the rate of hydrogen gas production and corresponding current value increased rapidly, suggesting that the storage electrode had been fully filled with hydrogen. The charging operation was stopped thereafter. Over the entire duration of charging, the corresponding current, voltage and volume of the gas generation were recorded with respect to time.

The mass of hydrogen gas generated was subtracted from the total mass of hydrogen generation calculated from Faraday’s law to estimate the amount of hydrogen entering the storage electrode. The total mass of hydrogen generated was calculated from equation 44.

\[ M_H = \frac{I \times t}{F \times 1000} \]  

Eq. 44
where,

\[ M_H \rightarrow \text{mass of hydrogen generated in Kg.} \]

\[ I \rightarrow \text{current in amperes.} \]

\[ t \rightarrow \text{time in seconds.} \]

\[ F \rightarrow \text{Faraday’s constant} = 96485 \text{ J per volt gram equivalent.} \]

The mass of hydrogen that entered the storage was divided by the mass of carbon powder in the electrode to get the stored wt % of hydrogen in the activated carbon medium.

### 7.5.2 Fuel cell mode

After the E-mode operation, the PFB was allowed to rest for 30 minutes and thereafter set to run in FC-mode. The gas connections on the hydrogen electrode side were disconnected from the hydrogen gas tank to make sure that there was no other source of hydrogen other than that stored in the aC electrode for FC-mode operation. The oxygen side was purged and supplied with oxygen gas from the tank where it was previously collected during the E-mode operation. The electric circuit corresponding to FC-mode operation of the PFB is shown in Figure 82.

![Electric circuit corresponding to FC-mode operation of the PFB.](image)

Figure 82. Electric circuit corresponding to FC-mode operation of the PFB.
The oxygen-side electrode was then fed with oxygen gas previously produced in E-mode and collected in the storage cylinder. The PFB while operating in FC-mode was connected to an electronic load to draw the current. The consumption of the oxygen gas from the graduated storage cylinder was clearly observed. The cell was allowed to discharge at a constant current of 30 mA for the first four cycles. For the next five cycles the cell was first discharged at a constant current of 30 mA followed by further discharging at a current of 10 mA. The amount of hydrogen discharge in kilograms was calculated from equation 44 (based on Faraday’s law). The hydrogen wt% liberated in FC-mode was estimated by dividing the total amount of hydrogen discharged by the mass of activated carbon powder in the aC electrode.

### 7.6 EXPERIMENTAL RESULTS AND DISCUSSION

#### 7.6.1 Charging results

The V-I curve in E-mode for the PFB with an integrated aC electrode was first measured using the Electrochemical Measurement System with small increments in applied voltage from zero to 2.9 V (Figure 83). The usual VI curve for a PEM electrolyser was obtained, with a cut-in voltage of around 1.6 V consistent with water splitting on the oxygen-side, and a maximum current density of 0.08 mA/cm$^2$. The latter was relatively low compared to a dedicated PEM electrolyser, but in the PFB the hydrogen is entering the carbon-based storage directly.

The PFB was then charged at a constant current of 50 mA over an 18 hour period. The cell was operated in E-mode initially at a relatively low voltage to minimise hydrogen gas formation and maximise the amount of hydrogen entering the aC storage directly. However, to maintain the steady current of 50 mA, the applied voltage had to be increased steadily and continuously over the 18 hour period, as shown in Figure 84. The graphs of voltage and current versus time corresponding to the performance of the PFB in E-mode are shown in Figures 84 and 85 respectively.
Figure 83. V-I curve for E-mode operation of the PFB recorded separately from the voltage vs. time and current vs. time curves. The cell was charged for 18 hours before the rate of hydrogen gas production increased leading to rise in current.
Figure 84. Voltage characteristics over time of the proton flow battery in E-mode. The cell was charged at constant current of 50 mA over 18 hours. The operation was stopped after 18 hours due to a sudden increase in the rate of hydrogen gas production.
Figure 85. Current characteristics over time of the proton flow battery in E-mode. It took some time for the current to reach 50 mA. The operation was stopped after 18 hours after a sudden rise in current due to increased rate of hydrogen gas production.
The cumulative volumes of oxygen gas and hydrogen gas generation over time were recorded in E-mode operation of the PFB, and are shown in Figure 86 and 87 respectively. After around 18 hours of charging time, the rate of hydrogen gas evolution increased rapidly (Figure 86), in association with a significant rise in current (Figure 85). By this time, however, the applied voltage had reached a high value of nearly 2.9 V (Figure 88).

Figure 86. Cumulative volume of hydrogen gas generated over time in E-mode.

The oxygen gas production rate appeared to decrease after around 13 hours, but then picked up again (Figure 87). However, the rate of oxygen gas production did not show a sudden increase after 17 hours, as was observed for hydrogen.
Figure 87. Cumulative volume of oxygen gas generated over time in E-mode.
The volume of hydrogen liberated as gas in E-mode increased with increase in applied voltage as shown in Figure 86. The sudden rise in the curve clearly indicates the additional or enhanced reaction for hydrogen gas evolution once voltage reaches the value of around 2.4 V. This voltage might therefore be a threshold voltage for hydrogen bonding to certain types of carbon site within the pores of the aC or on particle surfaces.

Figure 88. Volume of hydrogen gas generated with increase in voltage in E-mode.

A summary of the results for the charging part of the cycle 1 is presented in Table 20. Here the expected total mass of hydrogen evolved for the total charge flow during charging, calculated using Faraday's law and assuming no losses, is also given. It was assumed that the mass of hydrogen entering the storage electrode is given by the difference between this total calculated mass of hydrogen evolution, and the mass of the hydrogen gas actually collected. On this basis, the cumulative hydrogen stored in the electrode, and the corresponding cumulative
hydrogen gas collected, by time of charging in cycle 1 are plotted in Figure 89. It can be seen that the mass of hydrogen entering storage was always much greater than that of the hydrogen gas evolved, with both initially increasing linearly with time for the first 10 to 11 hours. From around 11 to 18 hours, the rates of hydrogen entering storage and hydrogen gas evolution both increased. After around 17 hours of charging, the rate of hydrogen entering storage tended to zero, while the rate of hydrogen gas evolution increased steeply. The latter was also associated with an increase in current.

On the basis of the assumptions made, the amount of hydrogen that entered the activated carbon storage electrode in cycle 1 was a highly credibility Table 1.36 wt%. However, the total volume of oxygen gas collected (38 cm$^3$) in cycle 1 was less than a fifth of that expected on the basis of Faraday’s law (202 cm$^3$) and the assumption that the only electrochemical reaction taking place was splitting of water into oxygen and hydrogen. Possible explanations of this anomaly will be discussed later in section 7.7, after reporting on the discharging experimental results.
For next five cycles the PFB was charged at constant voltage and current dropped with time. However, in calculation of amount of hydrogen stored using Faraday's law, a constant current of 50 mA was considered so as to compare with other cycles. So the constant current was used but, for shorter duration to formulate the above mentioned comparison amongst all cycles.

It is to be noted that, at the end of each charge part of a cycle, the PFB was discharged under the conditions described in subsections 7.5.2 and 7.6.3 of this thesis. Then the next cycle was started with charging again similar to the previous cycle.
Table 22 presents the measured volumes, and corresponding calculated masses, of hydrogen gas and oxygen gas actually evolved in E mode in each cycle (nine in total) compared to the total masses of hydrogen and oxygen that would be expected to be released on the basis of Faraday’s law. The calculations are again based on the assumption that all the hydrogen produced by water splitting in charge mode either entered the aC storage or formed hydrogen gas that was collected.

The hydrogen stored in the carbon electrode calculated from the experimental results declined from 1.36 wt% after charging in cycle 1 to 1.15% wt % in cycle 9. The percentage of H produced that entered the storage stayed reasonably constant over all the cycles (between 81 and 86%). The measured volume of hydrogen gas collected declined in line with the total charging time, as would be expected. But the measured volume of oxygen collected stayed relatively constant at around 40 cm$^3$ even though the total charge time decreased in the later cycles.

The large disparity between the actual oxygen gas collected and that expected on the basis of Faraday’s law that was observed in cycle 1 remained in all the subsequent cycles, a point that will be returned to after covering the discharge results.
Table 22. Performance of the PFB with an integrated solid carbon-based electrode (mesoporous carbon 1:7 KOH) in E-mode.

<table>
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<tr>
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<td>38 ± 5</td>
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<td>18</td>
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<td>15</td>
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<td>53 ± 5</td>
<td>0.0000044</td>
<td>0.00002358</td>
<td>84.3</td>
<td>1.15 ± 0.02</td>
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<td>9</td>
<td>50</td>
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<td>41 ± 5</td>
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Focussing on cycle 1, it is noteworthy that the total volume of oxygen gas collected (38 cm$^3$) is less than a fifth of that expected on the basis of Faraday’s law (202 cm$^3$) and the assumption that the only electrochemical reaction taking place is splitting of water into oxygen and hydrogen. Similar differences are evident in the subsequent cycles. Possible explanations of this anomaly will be discussed later in section 7.7, after reporting on the discharging experimental results.

7.6.2 Discharging results

The V-I curve for the PFB operating in FC mode was recorded and displayed by the electrochemical measurement system on a visual display unit. The displayed curve is shown in Figure 90. The curve is typical of a PEM fuel cell though the voltage falls off with current relatively quickly. The maximum current was 75 mA, active area of MEA was 5 cm$^2$, so the maximum current density was 15 mA/cm$^2$.

Figure 90. V-I curve for FC-mode operation of the PFB measured separately from voltage vs. time and current vs. time curves.
In FC-mode after the E-mode part of each cycle, the cell was connected to an electronic load set to draw the constant current of 30 mA from the PFB and the voltage dropped with respect to time. When the voltage dropped to a value just insufficient to the supply the required current, the operation stopped. The cell was then subjected to a much lower constant current of 10 mA. The time of discharge was recorded and the consumption of oxygen gas from the collection cylinder was observed. The voltage and current characteristics over time of the PFB operating in FC-mode are shown in Figures 91 and 92 respectively.

Figure 91. Voltage characteristics over time of the proton flow battery in FC-mode, for current profile shown in Figure 90.
In FC-mode there was no external source of hydrogen supplied to the cell. The only source of hydrogen was that stored electrochemically in the aC electrode in E-mode operation. The cumulative amount of hydrogen discharged from the PFB running in the FC-mode over time in cycle 1 is shown in Figure 93, calculated from the total charge flow.
Figure 93. Graph showing the cumulative amount of hydrogen discharged over time from the PFB.

A summary of the results for the discharging part of the cycle 1 is presented in Table 23. Assuming all the electrochemical current that flowed in FC-mode arose from hydrogen being released from the aC storage, and then passing through the nafion membrane as hydronium to recombine with oxygen on the other electrode to form water, the amount of hydrogen discharged in cycle 1 was 1.09 wt% of the carbon in the aC storage electrode. This compares with the estimated 1.36% stored in the electrode during charge mode.
In cycle 1, the amount of required oxygen consumption calculated from the integrated charge flow (current x time) using Faraday’s law was 133 cm\(^3\). However, the total amount of oxygen gas collected in the charging part of cycle 1 was only 38 cm\(^3\). As in charge mode, here is again a major difference in discharge mode between the actual measured oxygen consumption during discharging. Possible explanations of this anomaly will be discussed along with the similar one in charge mode in section 7.7.

The aC sample electrode (made from mesoporous carbon 1:7 KOH) employed in the proton flow battery in the present research work, was charged and discharged for nine consecutive cycles to check the reversibility of the electrochemical storage process. A summary of all the results obtained is provided in Table 23. Again, assuming all the electrochemical current that flowed in FC-mode arose from hydrogen being released from the aC storage, the amount of hydrogen stored declined slightly with repeated cycling from the 1.09 wt% recorded for cycle 1 to 0.97% in cycle 9.

A comparison between wt% of hydrogen stored in the aC electrode calculated after charging, and wt% of hydrogen released during discharging, is provided in Table 24 for all nine cycles. The amount of hydrogen stored during charging but not released during discharge fell from 0.27 wt% in cycle 1 to 0.18 wt% in cycle 9. These differences are likely to be an indicator of the partial irreversibility of the charging process.

The large disparity between the required oxygen consumption in FC mode calculated using Faraday’s law (and the same assumptions about the electrochemical reactions taking place as stated earlier), and the observed consumption of the oxygen gas collected in E-mode was evident in all cycles. The ratio of expected to actual oxygen gas consumption varied from 3.5 in cycle 1 to 2.9 in cycle 9.
Table 23. Performance of the PFB with an integrated solid carbon-based electrode (mesoporous carbon 1:7 KOH) in FC-mode.

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<th>Cycle No.</th>
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<th>Discharging time [hr]</th>
<th>Mass of hydrogen released during discharging [Kg]</th>
<th>Mass % of hydrogen stored in electrode</th>
<th>Mass % of hydrogen for each constant current stored in carbon</th>
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<td>10</td>
<td>3.5</td>
<td>0.000001306</td>
<td>0.06</td>
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<td>0.97</td>
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</tbody>
</table>
Table 24. Calculated wt % of hydrogen entering and discharging from the proton flow battery with an integrated aC electrode.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Calculated wt % of hydrogen in the aC electrode after charging [wt%]</th>
<th>Calculated wt % of hydrogen in the aC electrode that has been discharged [wt%]</th>
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</thead>
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</tr>
<tr>
<td>9</td>
<td>1.15</td>
<td>0.97</td>
</tr>
</tbody>
</table>

7.6.3 Discussion

A notable feature during the charge part of each of the cycles was the rapid rise in hydrogen gas generation that occurred after around 18 hours of charging (cycles 1 to 5). Two possible hypotheses may be advanced to explain this feature.

The first hypothesis is that after such a long period of charging most of the storage sites for hydrogen atoms on the inner surfaces of the activated carbon particles may have been filled. The peaking of hydrogen entering storage indicated by Figure 89, which shows the relative amounts of hydrogen entering storage and forming hydrogen gas, would appear to support this hypothesis. More hydronium ions may then cluster on the surfaces of macro pores of the aC and on outer surfaces of the aC particles. Since these surfaces will also be negatively charged due to excess electrons, the reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ may thus be encouraged and take place at a faster rate.
The second hypothesis is that after 18 hours of charging the applied voltage has had to be increased substantially (to around 2.8 V) to maintain the preset constant charging current of 50 mA. Figure 86 strongly indicates that after this voltage is reached the rate of hydrogen production increased at a much faster rate. Hence it may be that certain sites on the surfaces of the activated carbon particles, or within the macropores of the aC, require a certain potential difference compared to the acid electrolyte potential before they become fully active in catalysing the hydrogen gas evolution reaction.

It is also possible that both hypotheses have some foundation, since the larger increase in voltage required for maintaining a constant charging current after 18 hours may be due to the lower-energy hydrogen storage sites having been largely filled by that time, so that gas formation requiring a higher over potential is necessary to maintain the preset current.

The calculated wt% of hydrogen that entered the storage dropped in the range of 1 – 2 % with every cycle, although this drop was not very significant and stabilised after few cycles. A possible reason for this drop in wt% of hydrogen stored reversibly is that not all of the hydrogen got discharged in every cycle, resulting in some hydrogen being irreversibly stored and less free sites available after repeated cycling.

It should be noted that the electrochemical hydrogen storage in aC, as calculated in E-mode, and the amounts discharged in FC-mode, were based on the assumption that the only electrochemical reactions taking place in E-mode was water splitting into oxygen and hydrogen on the O-side electrode, and hydronium entering the aC electrode and being neutralised by electrons, plus hydroniums combining with electrons to form hydrogen gas, on the H-side electrode.

However, the disparities between oxygen collection in E-mode and oxygen consumption in FC mode, compared to the corresponding expected volumes calculated using Faraday’s law on the basis of the integrated charge flows, may indicate that other electrochemical reactions to those assumed in the foregoing calculations were also taking place.
Possible explanations of these disparities in oxygen production and consumption are the following.

- The experimental cell may have had some leakage on the oxygen-side gas connections, piping and collection systems. Such leaks would have reduced the volume of oxygen gas collected in E-mode, and allowed oxygen from the air to drive the reaction in FC-mode. However, testing of both H and O-sides of the cell prior to the experiment, and subsequent testing of the same cell after the experiment, showed no detectable leaks.

- Some of the oxygen evolved on the O-side electrode in E-mode may have reacted with the Pt catalyst, and/or the sintered Ti GDL, to form an oxide layer. Then in FC mode this reaction was reversed allowing the released oxygen to combine with hydronium ions to form water once again. Further testing of the O-side materials by SEM and XDS would need to be performed after E-mode operations to detect the presence of surface oxides to provide evidence of this oxidation reaction.

- Hydronium ions from the dissociated dilute sulphuric acid soaking the aC H-side electrode may enter the electrode and be stored directly, rather than being sourced from water dissociation on the oxygen-side electrode and transit via the nafion membrane to the hydrogen side. This removal of H\(^+\) ions from the acid would need to be accompanied by movement (by diffusion and electrical conduction) of bisulphate ions (HSO\(_4\)\(^-\)) through the nafion membrane in the reverse direction to the oxygen side. There these anions would need to react with the Pt catalyst and/or the sintered Ti GDL. This whole process would need to take place in the reverse direction in FC mode. There is experimental evidence that bisulphate ions can diffuse through nafion (Q. Huang et al. 2003). However, a preliminary calculation suggests that there are insufficient hydronium ions in the dilute sulphuric acid soaking the aC electrode in the experimental proton flow battery used here (by at least an order of magnitude) to account for the disparity in evolved oxygen found in these experiments. Further calculations, and associated experiments, will need to be performed to investigate whether this alternative electrochemical reaction is taking place to any significant
extent. In any case, the potential for bisulphate ions to move through nafion and out of the aC electrode indicates that dilute sulphuric acid may not be a suitable proton conductor in this application.

Further experiments of the kinds outlined here are thus necessary to find out the real causes of the disparities observed in the present experiments between oxygen production in E-mode and consumption in FC mode and corresponding calculated oxygen gas volumes using Faraday’s law and the measured total charge flow.

7.7 CONCLUSION

This chapter has given a detailed report on the experiments carried out to test the performance of the proton flow battery with an integrated activated carbon electrode. The selected sample activated carbon – mesoporous carbon 1:7 KOH – was used to fabricate the solid electrode with nafion-117 binder. Dilute sulphuric acid of 1 mol concentration was used to act as the transportation medium for the hydronium ions emerging from the membrane while operating the PFB in E-mode.

On the basis of the assumptions stated in the previous section, the wt% hydrogen stored in the aC electrode during E-mode and released again reversibly during FC mode was at maximum around 1.1 wt% of the carbon content of the electrode. This is a good result for a first trial on a non-optimised PFB and aC electrode system. Importantly a reversible electrochemical hydrogen storage capacity of more than 1 wt% is comparable with the gravimetric density of commercially-available MH based solid hydrogen cylinders requiring pressurized hydrogen gas input at pressures of 10 – 20 bar, and also lithium-ion and lithium-polymer batteries.

While the experiments that have been conducted in this thesis have indicated the likely attractive potential of aC electrodes in a PFB to act as reversible hydrogen stores, the anomalies in the results obtained for oxygen production and consumption need to be explained.
by the conduct of additional experiments before it can be stated with confidence that the PFB design tested here does work effectively as planned. Unfortunately these further experiments have been beyond the scope, resources and timelines of the present thesis.

There are many other areas that require further research to achieve higher energy densities and to rectify the problems encounter in the present project. The use of other proton conductors such as protic ionic liquids and proton conducting gels, the problem of bisulphate ions reacting with platinum catalyst and titanium GDL could be avoided. Further, the use of air-tight fittings for connections could fix the gas leakages if any. To achieve the optimum working of the proton flow battery with an integrated aC-based storage, further research work is required on optimization of the structural properties (including porosity, and pore size distribution) of carbon employed.
8. CONCLUSIONS AND RECOMMENDATIONS

8.1 OVERVIEW

This chapter presents answers to the research questions set for the present project based on the experimental data collected and the analysis of the experimental results obtained. Other key findings emerging from the research work are described. Recommendations for further research to resolve outstanding questions and move towards a practical functioning proton flow battery are made in the last part of the chapter.

8.2 RESPONSES TO THE RESEARCH QUESTIONS

8.2.1 How can the proton conductivity of an activated carbon electrode be maximised?

Proton conductivity is a very important property of a hydrogen storage electrode of the type developed in this project for a proton flow battery since it determines the flow rate of protons to and from storage sites within the pores of the aC. In the previous research work in this field at RMIT University, nafion-117 was used as a solid proton-conducting medium binding together metal alloy particles within the hydrogen storage electrode (Andrews and S. Mohammadi, 2014). A composite MH-nafion electrode of this kind was used with the hydrogen being stored as a metal hydride and the nafion conducting protons to and from the metal alloy particles. When this composite MH-nafion electrode was tested in the proton flow battery it performed well in charge mode, but poorly in discharge mode. In follow-up work at RMIT, Mohammad Javad Jazaeri (2014) fabricated composite aC-nafion electrodes, and found that these had acceptable dual proton and electron conductivities. However, when this composite aC-nafion electrode was tested in the proton flow battery, no detectable signs of reversible hydrogen storage were observed. The explanation offered was that the nafion was
unable to penetrate into the smaller spores of the aC considered to be the primary storage sites for hydrogen, so that the nafion could not conduct protons all the way to these sites.

The present study has therefore investigated using a liquid proton conducting medium, namely a dilute acid, that is capable of penetrating into the smallest and deepest pores of activated carbon in the range of ultra-micro porosity (pore size <0.7 nm). In particular, 1 mol. dilute sulphuric acid has been used as the liquid proton conducting medium in the present project by soaking aC electrodes in this acid.

The proton resistance of all the fabricated aC samples soaked in sulphuric acid has been measured using EIS and their corresponding proton conductivities calculated. The proton conductivities of aC samples made from Victorian brown coal were found to be in the range of 0.0083 – 0.03 S/cm, whereas aC samples made from phenolic resin had proton conductivities in the range of 0.005 – 0.096 S/cm at room conditions. On the other hand, the electron conductivities of aC samples from brown coal were much higher, in the range of 8.4 – 11.9 S/cm, while those of aC samples from phenolic resin were in the range of 5.7 – 14.4 S/cm. The details of measurement of proton and electron conductivity were described under sections 5.5.5 and 5.5.6 in chapter 5 of this thesis.

From the analysis of the results, it was found as expected that activated carbon electrodes with higher porosity (both within aC particles and between particles) yield higher proton conductivity (as shown in Figure 94), because more dilute sulphuric acid is available for the proton conduction. However, the higher the porosity the lower the bulk electron conductivity of the electrodes was found to be.
In the future design of hydrogen storage electrodes for a proton flow battery it will therefore be important to find the optimal balance between the bulk proton and electron conductivities. Generally electron conductivity is much higher by 150 orders of magnitude, so the first priority will be to ensure that the proton conductivity is sufficient, without having too much negative impact on electron conductivity. Further work is also needed to investigate the relative impacts on proton flow battery performance of porosity within the aC particles and porosity due to the spaces between particles as they are fabricated using a PTFE or nafion binder. The comparative performance of electrodes made using PTFE and nafion binder material also merits further study.

Another important material property that is required to achieve high proton conductivity within activated carbon particles is ‘tortuosity’, that is, a measure of the extent to which the pores are ‘twisted’, and hence the number of bends in a connected path through the material.
In order to obtain higher proton conductivity, straight connecting paths between the pores of aC are needed, which is possible with aC having low tortuosity. On the other hand, high tortuosity is associated with high surface but non-straight pathway connection between pores. Therefore, for higher proton conductivity activated carbon with low tortuosity is required. On the other hand, higher tortuosity may assist protons in forming bonds with carbon atoms on the pore surfaces due to the slower movement of hydronium ions through pores.

8.2.2 What structure and composition of a carbon-based solid electrode in a reversible PEM fuel cell yield the best performance in terms of sustained hydrogen charge capacity, rates of charge and discharge, and gravimetric and volumetric energy densities?

Activated carbon samples made from Victorian Brown Coal (five samples) and phenolic resin (seven samples) were employed in the present study and their physical and electrochemical properties were measured. These activated carbon samples had different structural properties in terms of surface area, pore volume, and range of porosity. Solid electrodes were fabricated using the mentioned aC samples and PTFE binder. The proton conductivity of the fabricated electrodes soaked in sulphuric acid was measured using EIS, double-layer capacitance using cyclic voltammetry, and reversible electrochemical hydrogen storage capacity using galvanostatic charging-discharging methods. The best performing aC sample electrode in terms of double-layer capacitance (189.4 F/g), and electrochemical hydrogen storage capacity (1.6 mass %), was mesoporous carbon 1:7 KOH, which also had the highest pore volume (0.586 cm³/g), pore surface area (1922 m²/g), and bulk proton conductivity (0.0965 S/cm).

This form of aC was used to fabricate a solid electrode for the proton flow battery using nafion-117 binder. The proton flow battery with integrated aC electrode was tested for its feasible running and gravimetric and volumetric energy densities were calculated.

Analysis of the results revealed that more hydrogen entered the storage with high charging current applied for a long time. The mass % of hydrogen stored in the carbon in the electrode generally increased with increase in BET surface area for those samples with a larger measured storage capacity. This relationship was not evident for the particular forms of aC.
that exhibited lower mass% H capacities. As would be expected from the relationship for BET surface area, the hydrogen mass % stored electrochemically in the aC electrodes also generally increased with limiting pore volume, for the samples with higher storage capacities.

A possible explanation of the observed increase in hydrogen storage capacity with BET surface area and limiting micropore volume is that as the latter parameters increase there will be more storage sites for formation of weak C-H bonds on the inner surfaces of the pores. The lack of dependence of storage capacity on BET surface area for the samples with low total storage capacity indicate that other factors such as presence of surface groups and surface morphology may be more influential in these forms of aC, which came from different precursors of carbon.

From the graphs shown in Figures 62 and 63, it is clear that in order to achieve higher gravimetric and volumetric energy densities, activated carbons with large BET surface areas and high limiting micropore volume are required. However, the optimum distribution of these pore sizes in order to maximise the electrochemical hydrogen storage capacity of such activated carbons is still an area where further research is required. Larger surface areas do increase the storage sites within the particles of activated carbon for electrochemical storage of hydrogen but at the same time a low tortuosity is required for higher proton conductivity to allow the hydronium ions or hydrogen protons to flow into the deepest pores of aC.

Measurements were made of the contributions of the two sources contributing to the reversible electrochemical storage of hydrogen in aC: - the chemical reaction between hydrogen ions and carbon particles; and the double-layer capacitance formed by the interfaces between the surfaces of the carbon particles and the dilute sulphuric acid used as a proton conducting medium. The double-layer capacitance is formed since mobile protons within the acid and conducting electrons within the carbon particles can both move under the influence of an electric field to produce regions near the interface of compensating excess positive or negative charge density. The measured contribution of double-layer capacitance to the reversible electrochemical storage capacity of the sample aC electrodes is shown in Figure 61. It was found that double-layer capacitance contributed between 6-12 % of the equivalent
electrochemical hydrogen storage in of the aC electrodes. The rest of the hydrogen storage – that is, 88-94 % of the total equivalent mass % stored – resulted from the electrochemical reaction between hydrogen and activated carbon.

8.2.3 To what extent can hydrogen gas formation in such a hydrogen storage electrode be suppressed?

The aim of the present study was to investigate the electrochemical storage of hydrogen in activated carbons, so it was important to minimise hydrogen gas formation. Further, activated carbon is known to be a poor catalyst for hydrogen gas formation as compared to the metal hydride used in previous research study at RMIT University. Hence in the galvanostatic charge-discharge experiments to measure the reversible hydrogen storage capacity of the various sample aC electrodes, a preliminary test of simple electrolysis was run on all the fabricated aC electrodes with 1 mol dilute sulphuric acid as electrolyte (section 6.3.2 of chapter 6 of this thesis). For all the aC electrodes separate VI curves were recorded and the points where the hydrogen gas formation started were marked on these curves. The cut-in voltage and voltage where the hydrogen gas formation starts were recorded. The typical V-I curve for the sample aCP is shown in Figure 38, showing the starting point for hydrogen gas formation. The V-I curves for all aC electrodes are shown on the same axes Figure 95.
The analysis of these curves revealed that the hydrogen gas formation could be avoided if the cell voltage in the PFB experiments was kept lower than the voltage marked on the V-I curve as the starting point of gas formation (Figure 38).

In summary, then the careful selection of the maximum charging voltage applied was the primary means used to suppress hydrogen gas formation, and hence maximise the amount of hydrogen entering the solid Ac electrode directly and being stored there electrochemically.

While operating the proton flow battery, the total cell voltage in E-mode (or charging mode) was kept within the permissible window available between the cut-in voltage and voltage of gas formation that was previously marked on V-I curves (Figures 38 and 95). However, the threshold voltage for hydrogen evolution may have been slightly different for the PFB than in
the preliminary experiments, so that in the PFB experiments some hydrogen gas was generally still generated.

The other difficulty encountered was that operating at a relatively low cell voltage to avoid hydrogen gas evolution led to slow charging rates. Hence the cell had to be charged for a very long time to ensure that the storage electrode was completely filled up with hydrogen. Nevertheless, after charging for a long time hydrogen gas formation generally increased leading to an increase in current. It is hypothesised that this point may have corresponded to the time at which the aC storage had become substantially filled with hydrogen. Further research will be necessary to prove this hypothesis.

8.2.4 Can a reversible fuel cell with integrated solid-state carbon-based hydrogen storage soaked in acid provide an energy storage that has superior gravimetric and volumetric energy densities, roundtrip energy efficiency, and lifecycle cost than compressed gas hydrogen storage, metal hydrides with gaseous charging and discharging, and the best performing lithium ion or polymer batteries?

This study has so far shown the experimental measurements of the reversible electrochemical hydrogen storage capacity of various aC samples. The electrodes were fabricated from different aC samples using PTFE binder and tested for their electrochemical hydrogen storage capacity by galvanostatic charging discharging. The electrodes were immersed in 1 mol dilute sulphuric acid contained in three electrode electrolytic cell and tested. The gravimetric energy density of stored hydrogen in electrodes was calculated and found to be in the range of 0.36 – 1.60 wt %, whereas the volumetric energy density was found to be in the range of 0.26 – 0.52 kWh/litre. The calculated volumetric density of aC electrode was comparable with commercially available MH canister with a typical volumetric energy density of 0.8 kWh/litre (Kazuhiko Mukai et al. 2014).

The best performing aC sample was used to make the integrated hydrogen storage electrode for the proton flow battery. While operating the PFB in E-mode or charging mode we have
managed to store 1.37 mass % of hydrogen into the storage electrochemically. In FC-mode of the PFB the best gravimetric density achieved during discharging was 1.09 mass %.

The results were compared with the previous research studies on reversible electrochemical storage of hydrogen at RMIT University. With the MH-nafion composite electrode only 0.62 wt% was stored in the storage in E-mode operation of the proton flow battery, whereas, the best gravimetric density achieved in FC-mode was 0.065 wt% (S. Mohammadi 2013). With the composite aC-nafion electrode as an integrated storage for the proton flow battery, the gravimetric densities achieved in E-mode and FC-mode was 1.5 wt % and 0.002 wt% respectively.

The latest results for reversible hydrogen storage are thus much better than for the MH-nafion electrode used in the first PFB (Andrews and S. Mohammadi 2014). These results are also obviously superior to those achieved with the PFB with a composite aC-nafion electrode tested by Jazaeri (2014), which showed no hydrogen storage potential. The gravimetric density of 1.09 mass% in FC-mode or discharge mode of the PFB is highly comparable with the gravimetric density of around 1wt% for commercially-available MH based solid hydrogen cylinders requiring pressurized hydrogen gas input at pressures of 10 – 20 bar. These activated carbon hydrogen storages promise to be much less expensive to produce than metal hydride systems. Further the gravimetric and volumetric energy densities achieved are highly comparable with commercially available lithium ion or polymer batteries.

The highest achieved volumetric energy density of the tested aC electrodes in the presented work was 0.52 kWh\textsubscript{e}/litre, which is less than that of MH-based hydrogen storage canisters available commercially, at around 0.8 kWh\textsubscript{e}/litre. So clearly this is an area that requires more research work to enhance this energy density. However, the highest volumetric energy density of an aC electrode achieved here is still well above that of most Li-ion batteries, in the range 0.2 – 0.5 kWh\textsubscript{e}/litre.
It has not been possible within the time lines and resources of the present project to measure the round-trip efficiency and life-cycle cost for a proton flow battery. Hence this topic requires further research investigation.

8.3 KEY FINDINGS

This thesis has contributed experimental and improved scientific understanding in the field of reversible electrochemical storage of hydrogen in a solid carbon-based material in acid electrolytes, and the technical feasibility of a proton flow battery incorporating such an electrode. The present study has also made a step forward towards the feasible working of the proton flow battery.

In addition to the answers to the research questions summarised in the preceding section, further key findings that have emerged from this thesis are the following:

1. It is technically feasible to design and construct a working proton flow battery with an integrated activated carbon electrode using a liquid proton conductor within the electrode to provide a bridge for proton conduction to-and-from nafion membrane to the storage.

2. Some aC samples used in this project were made from Victorian brown coal and achieved a reasonably attractive hydrogen storage capacities of more than 1 mass%, which is comparable with commercially available MH cylinders, lithium ion and lithium polymer batteries. Within this thesis, it has not been possible to optimize the performance of aC made from Victorian brown coal for this application. This is clearly a promising area requiring further work.

3. Other aC samples investigated in this thesis were obtained from CIC Energigune, Spain made from phenolic resin and activated by adding different ratio of potassium
hydroxide (KOH). The aC samples differed from each other in structural properties due to difference in the ratio of KOH added during activation. Five out of seven samples showed gravimetric densities for hydrogen storage of more than 1 mass%. The best performer in terms of proton conductivity, double-layer capacitance, and reversible electrochemical storage capacity was the aC sample, mesoporous carbon 1:7 KOH. This sample was found to have a reversible hydrogen storage capacity of 1.6 mass% (based on the carbon content on the electrode).

4. The mass % of hydrogen stored generally increased with increase in BET surface area of the aC particles used to fabricate the electrodes.

5. The contribution of double-layer capacitance to the equivalent mass of hydrogen stored in the electrodes was around 6 – 12 % of the total, with electrochemical storage involving charge transfer and an actual reaction between carbon and hydrogen accounting for the remaining 88 – 94%.

6. A small drop (of around 1-2 %) in wt% of hydrogen stored electrochemically in the aC electrodes with every cycle was found, but this fall declined to a very low level after a few cycles. A possible reason for this drop in wt% of hydrogen stored reversibly is that not all of the hydrogen was discharged in every cycle, resulting in some hydrogen being irreversibly stored and less free sites available after repeated cycling.

7. In the proton flow battery experiments, some disparities were observed between oxygen collection in E-mode and oxygen consumption in FC mode, compared to the corresponding expected volumes calculated using Faraday’s law on the basis of the integrated charge flows over time. These disparities may indicate that other electrochemical reactions to those assumed in the calculations were also taking place. To prove the feasibility of a PFB with an integrated aC electrode, it will be necessary to repeat and extend the experiments conducted in the present thesis with additional
precautions taken to ensure all gas is fully collected, and greater precision in all measurements of volumetric gas production and consumption.

8. It has been shown that it is possible to get a reasonable amount of hydrogen in and out from the porous activated carbon storage electrode soaked in dilute sulphuric acid in an electrolytic cell with a liquid acid electrolyte, and a proton flow battery system. So far, apart from the selection of the best-performing storage electrode among the limited range of aC samples tested in the present thesis, no further optimisation of the performance of these electrodes and the PFBs that used them has so far been performed.

8.4 RECOMMENDATIONS

The following recommendations are made on the basis of the research conducted for this thesis:

Further investigation needs to be conducted into the relationship between characteristics of the aC material used to make hydrogen storage electrodes—such as porosity, pore sizes and structure, pore size distribution between ultramicropores, micropores, mesopores, and macropores, and ultramicropores— and reversible hydrogen storage capacity.

It is interesting to note here that, in a composite carbon – PTFE electrode of the kind being considered here, the proton conduction from the nafion boundary into the smaller pores is most likely to take place via hydronium movement or Grotthus proton exchange through sulphuric acid and filling the pore volumes of the carbon. Furthermore, little is known at present about the structure of the connections between the sulphuric acid, PTFE and the surfaces of carbon particles. For example, how do the water-filled channels and micelles within the nafion membrane link up with the surface planes of charged carbon atoms? These questions could be fruitful areas for further research.
While the experiments that have been conducted in this thesis have indicated the likely attractive potential of aC electrodes in a PFB to act as reversible hydrogen stores, the anomalies in the results obtained for oxygen production and consumption need to be explained by the conduct of additional experiments before it can be stated with confidence that the PFB design tested here does work effectively as planned. Unfortunately these further experiments have been beyond the scope, resources and timelines of the present thesis.

There are many other areas that require further research to achieve higher energy densities and to rectify the problems encounter in the present project. The use of other proton conductors such as protic ionic liquids and proton conducting gels, the problem of bisulphate ions reacting with platinum catalyst and titanium GDL could be avoided. Further, the use of air-tight fittings for connections could fix the gas leakages if any. To achieve the optimum working of the proton flow battery with an integrated aC-based storage, further research work is required on optimization of the structural properties (including porosity, and pore size distribution) of carbon employed.

We do need further research on structures of carbon and precursors. It may depend on what surface chemistry and what precursors could yield the better results of electrochemical storage of hydrogen in carbon. We need to look in other proton conducting mediums like protic ionic liquid, proton conducting gels and oils that may give better results.

We have made some progress in understanding of relation between voltage and gas production. We have learned at high potentials the rate of gas production is higher. We need to look in this in detail. We need to test the effect of corrosion from acid on aC for long runs. Different concentrations of acid needed to be tested. Another variable is whether nafton is required as binder or do nafton provides another pathway for proton to flow through the proton flow battery.
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**APPENDIX**

Table 25. Mass of hydrogen generated and stored in the storage in the experiments conducted in chapter 6 with activated carbon electrodes immersed in a 1M dilute sulphuric acid electrolyte.

<table>
<thead>
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<th>Sr. No.</th>
<th>Name of sample</th>
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<th>Mass of total H produced calculated from Faradays Law (H1) [kg]</th>
<th>Volume of H2 gas generated during charging [m³]</th>
<th>Mass of H2 gas generated during charging (H2) [kg]</th>
<th>Net H that is likely to have entered in storage (H1-H2) [kg]</th>
<th>Mass of H discharged [kg]</th>
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