Investigation of the Electrochemical Reactions Involved in All-Vanadium Redox Flow Cells

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presented by

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Summary

The rapidly growing demand for energy in the 21st century and the continuous exhaustion of traditional fossil fuels and their negative environmental impact has urged researchers to explore alternative clean energy sources. Wind and solar energy are promising candidates and global installed capacity is on the rise. The key issue however with these energy sources is unlike conventional power plants, wind and solar provide intermittent energy based on the time of day and climatic conditions. In order to overcome this issue a reliable form of energy storage capable of storing production surplus and coping with high demands is required. Energy storage has been around for a number of decades in some cases e.g. pumped hydro storage, however a market for a storage device tailored to this particular application is emerging. Batteries represent an excellent energy storage solution for renewable energy integration.

Among the different available battery technologies, redox flow batteries particularly the all-vanadium redox flow battery system have attracted a significant amount of attention as large-scale energy storage devices. These systems are based on reversible redox reactions where the active species are dissolved in a liquid electrolyte. They operate as energy storage and as power delivery devices. This PhD work is focused on optimising power density of a redox flow battery system to be used on a much smaller scale with an application in the computer industry. The REPCOOL project presents a new concept based on combined power delivery and cooling on a computer chip. While these are two very different applications, the underlying principles of a redox flow cell are the same and transferrable to both system scales.

Research conducted here focuses specifically on the kinetics of the electrochemical reactions occurring at the positive and negative electrode surfaces during discharge (power delivery) in the all-vanadium redox flow cell. The vanadium (V) reduction and vanadium (II) oxidation reactions were studied on different carbon electrodes. A systematic approach was adopted by first investigating these reactions separately on well-defined model carbon electrodes to gain a fundamental understanding of the system. Then, full-cell studies were conducted in a redox flow test cell using more complex commercial porous carbon electrodes. The transition from model carbon surfaces to porous carbon electrodes gave valuable insights into the dominating processes and key properties influencing electrode activity and stability. These findings could not have been identified directly from full-system studies owing to the complexity of the electrode
Summary

system as well as the myriad of different parameters influencing the performance in the full-system. Model studies revealed that surface oxygen groups introduced by different modification methods have a catalytic influence on the V(II) oxidation reaction, with more oxygen on the carbon surface corresponding to better activity. The V(V) reduction reaction however, was less sensitive to the presence of oxygen functional groups and influenced more by the structural properties of carbon. In this case, greater disorder and defects in the carbon structure correlated with higher electrode activity for V(V) reduction. These observations were in line with the full-cell studies where it was found that the V(II)/V(III) reaction was improved significantly on oxygen modified commercial electrodes, whereas the V(V) reduction reaction did not show any significant improvements on oxygen treated electrodes. The full-system studies also revealed the V(II)/V(III) reaction as the performance limiting reaction in the cell. Furthermore, through long-term durability tests in the full-cell it was found that the dominant losses in performance originated from the negative electrode where the V(II)/VIII) reaction takes place. Model electrode studies gave further insights into possible degradation mechanisms occurring at the negative electrode.

This work has provided a solid basis of understanding of key properties and processes influencing activity and stability of carbon electrodes used in the all-vanadium redox flow cell. The systematic approach adopted in this work using model electrodes and transitioning to full-cell commercial electrodes has allowed the decoupling of different properties influencing performance. The knowledge gained in this work will aid in the development of stable and active electrodes for both redox reactions and ultimately contribute to improved system performance and power density.
Zusammenfassung


Der Fokus der vorliegenden Forschungsarbeit liegt auf der Kinetik der elektrochemischen Reaktionen, welche an den Oberflächen der positiven und negativen Elektrode während der Entladung (Energieabgabe) einer reinen Vanadium Redox-Flow-Batterie stattfinden. Die Vanadium (V) Reduktionsreaktion, sowie die Vanadium (II) Oxidationsreaktion wurden, unter Verwendung einer systematischen Arbeitsweise, auf verschiedenen
Zusammenfassung


aktiver Elektroden für Redoxreaktionen erleichtern, und schlussendlich zur Verbesserung der Leistung und Energiedichte des Systems beitragen.
Acknowledgements

The present doctoral work was carried out at the Paul Scherrer Institut (PSI) between February 2014 and August 2017. This work would not have been possible without the help and support of certain colleagues, friends and family who I would like to acknowledge in the following paragraphs.

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# Declaration of self-citation

This PhD work is a cumulative doctoral thesis that contains three peer-reviewed published manuscripts and one submitted manuscript. The table below summarises the publications in the order in which they appear in the respective chapters in this thesis. The papers are numbered in chronological order in which they were written, P1 to P4.

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Publication</th>
<th>Paper number</th>
</tr>
</thead>
</table>

*These authors contributed equally to this work.*
The individual contributions of all co-authors is summarised here:

- **S.M. Taylor** carried out the experimental work, analysed data and wrote the manuscripts, P1-P4.
- **A. Pătru** supervised the work, assisted in experimental measurements and experimental design, contributed to analysis and interpretation of results, proof-read and edited manuscripts, P1-P4.
- **T. J. Schmidt** supervised work, discussed results and proof-read and edited manuscripts, P1 – P4.
- **O. Nibel** assisted in full-cell experimental measurements, discussed results, equally contributed to the writing of P3.
- **L. Gubler** discussed results, proof-read and edited manuscript, P3.
- **D. Perego** carried out measurements using the DEMS setup, contributed to discussion and analysis of results of P4.
- **E. Fabbri** carried out x-ray photoelectron spectroscopy measurements and discussed and contributed to results interpretation, P1-P4.
- **M. El Kazzi** carried out x-ray photoelectron spectroscopy measurements and discussed results P1.
- **D. Streich** assisted with Raman spectroscopy measurements and contributed to discussions of results of P1.
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Chapter 1. Introduction

This chapter covers a brief introduction to redox flow battery technologies typically used as large scale energy storage devices for renewable energy integration. This work however was carried out in the particular context of optimising a redox flow device for power delivery. Such a device could be used in the computer industry on a much smaller scale to combine power delivery and cooling on a computer chip. This concept forms the basis of the REPCOOL project which has the main aim of optimising power density of the redox flow cell device. The basic principles and key components of a redox flow cell as well as different redox chemistries are introduced. The all-vanadium redox flow battery (VRB) chemistry is the focus of the remainder of the chapter. State of the art electrode materials for VRBs and electrode activation treatments are reviewed. The progress on electrode development for the two redox reactions occurring in the VRB system is covered and current literature trends are discussed. Finally, critical gaps in understanding are identified and the scope of this PhD work is presented.
1. Introduction

1.1 Motivation

1.1.1 Renewable energy integration

The rapid and continuous exhaustion of fossil fuel resources has urged researchers to focus on renewable energy technologies to help reduce the carbon footprint of electricity generation. Renewable energy sources, particularly wind and solar energy are being deployed globally in larger numbers than ever before [1,2]. This rapid growth in renewables is being driven by a number of factors including the growing environmental concerns surrounding fossil fuels as well as implementation of dedicated policy initiatives and better access to financing. More importantly, technological advances are driving the costs of renewables down to values comparable to their traditional fossil fuel counterparts [1]. Thus, wind and solar energy are reaching a tipping point in cost competitiveness and availability. However, the challenge of their intermittent energy generation still needs to be addressed. Utilities are looking for solutions to address the problems of grid instability and poor reliability introduced by renewable power sources. Thus, successful integration of renewables on both the centralised and distributed level requires a viable and economic energy storage solution.

Electrical energy storage (EES) is not a new concept and has been around for several decades in some cases. EES has a number of applications ranging from power quality to peak shaving and load shifting as well as bulk power management. The categorisation of different EES technologies is typically based on the form in which the energy is stored. These different forms of energy include: mechanical energy (pumped hydroelectric storage (PHS), compressed air energy storage (CAES) and flywheels), electrochemical (conventional rechargeable batteries and flow batteries), electrical (capacitors, supercapacitors and superconducting magnetic energy storage (SMES), thermochemical (solar fuels), chemical (hydrogen storage coupled with fuel cells) and thermal energy storage (sensible heat storage and latent heat storage) [3]. Figure 1.1 illustrates some common EES technologies indicating their rated power (kW) on the x-axis and the duration of discharge (h) on the y-axis.
1. Introduction

![Figure 1.1 Comparison of discharge time and power rating for various EES technologies. (Reproduced from [4] with permission from EPRI).](image)

Pumped hydroelectric storage (PHS) is the oldest and most ubiquitous energy storage technology, accounting for 99% of the worldwide storage capacity [5]. Compressed air energy storage (CAES) has the second highest storage capacity worldwide, both these technologies are used for bulk power management but are severely restricted by locational constraints. Flywheels, supercapacitors and SMES have very short discharge times and are most commonly used for power quality and grid support applications. EES for load shifting presents an excellent application for a device which stores excess energy and releases it at times of greater demand, as is the case for wind and solar energy. Several of the EES technologies in Figure 1.1 are based on batteries. There are a number of desirable features of battery technologies including: pollution-free operation, flexible power and energy characteristics as well as long cycle life and low maintenance [5]. Battery technologies represent a promising storage technology for integration of renewable energies, mainly due to their modularity and scalability for use at distributed locations. Furthermore, metrics related to size and volume are much less critical for grid storage compared to transport applications [6]. However, high costs and a limited track record of safety and reliable operation have limited their widespread market penetration. It is predicted however, that like wind and solar energy, battery storage technologies will also reach a tipping point in cost and availability and ultimately become an economically viable storage solution for wind and solar energy. Redox flow batteries (RFBs) fall under the
battery category and have gained a significant amount of attention for the particular application of large-scale, stationary energy storage for wind and solar energy. Redox flow battery technologies will be the focus of the remainder of this chapter.

### 1.1.2 Redox flow batteries (RFBs)

A RFB is an electrochemical device capable of delivering energy but also capable of storing it, owing to the reversible nature of the electrochemical redox reactions involved in the system. RFBs were first developed by NASA during the energy crisis of the 1970’s [7]. Instead of storing the electrochemical reactants in the electrode itself (like metal/metal-alloy or intercalation electrodes), most flow battery systems utilise reversible redox species which are dissolved in an electrolyte and stored externally [6]. An attractive feature of RFB systems for stationary energy storage is the ability to decouple energy and power in one device. The power is dictated by the stack size or number of cells in the stack, while the energy or capacity is dictated by the size or number of storage tanks. This allows considerable design flexibility, for example the storage capacity can be increased relatively easily with minimal costs compared to the stack, which is typically the most expensive component [6]. Several different types of flow battery systems exist, classified either by the active redox species or by the solvent used (aqueous or non-aqueous). While the main application for this technology lies in large-scale stationary energy storage, RFBs can also be used as power delivery systems. One possible niche application for using this device as a power delivery system has emerged in the computer industry [8]. This idea forms the basis of the REPCOOL project under which this PhD work was carried out.

### 1.1.3 RFBs for electrochemical power delivery and cooling

Next generation computers require smaller system dimensions and higher power densities, which in turn makes the cooling of the system a critical issue. As a breakthrough solution to this issue, the combination of liquid cooling with electrochemical power delivery was proposed by the REPCOOL project (Redox flow electrochemistry for power delivery and cooling, Swiss national Science Foundation, Grant no. 147 661). The main goal was to radically improve and adapt miniaturized flow cell technology for microscale power delivery and cooling on a computer chip. This novel concept eliminates the conventional electrical supply network, liberating valuable communication space.

#### 1.1.3.1 Main challenge - power density

The key challenge of adapting existing flow cell technologies to this application, are the high power density requirements of the microprocessor. Figure 1.2 compares the power
densities of some typical RFB technologies to the power density demands of present-day microprocessors.

![Figure 1.2 Compilation of power requirements of high-performance microprocessors (per unit chip area) compared to power density of different redox flow cells (W cm$^{-2}$). Only single cells are considered, not cell stacks. The improvement required for on-chip electrochemical power delivery is indicated (Figure taken from REPCOOL project proposal [9]).](image)

The power density requirements for a microscale flow cell system which is enough to support microprocessor power demand lies between 10-100 W cm$^{-2}$. This is one to two orders of magnitude higher than the power density of the best redox flow systems to date. Thus, there is a considerable performance gap which needs to be bridged in order for this technology to be realised for this particular application. The improvement in power density can only be achieved if all key system components are optimised. This requires an interdisciplinary approach combing efforts from different fields of expertise. Table 1.1 summarises the project partners involved in the REPCOOL project and their specific areas of focus.
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Table 1.1 – REPCOOL project partners and respective fields of expertise.

<table>
<thead>
<tr>
<th>Institution</th>
<th>Function</th>
<th>Field of expertise</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBM Research Zürich</td>
<td>Device integration</td>
<td>Microtechnology and packaging</td>
</tr>
<tr>
<td>*Paul Scherrer Institut (PSI)</td>
<td>Advanced materials</td>
<td>Physical chemistry and material science</td>
</tr>
<tr>
<td>ETH Zürich</td>
<td>Transport analysis</td>
<td>Fluidics, transport phenomena and thermodynamics</td>
</tr>
<tr>
<td>University of Lugano</td>
<td>Computational electrochemistry</td>
<td>Atomistic and multiscale modelling</td>
</tr>
</tbody>
</table>

*The work at PSI was carried out by two PhD students: one working on electrode materials and electrochemical reaction kinetics (this work) and the other working on membrane development and optimisation.

The work carried out at PSI was focused on the advanced materials for the system which include the electrodes, electrolyte and membrane. This work however focuses only on the electrodes and electrolyte part of the system and addresses the fundamental aspects of the electrochemical reactions and electroactive materials. Figure 1.3 highlights the parameter space of the electrochemical system which was considered for the goal of optimising power density.
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Figure 1.3 Parameter space of the electrochemical system influencing power density. $P = \text{power density (W cm}^{-2}\text{)}, I = \text{current (A)}$ and $\Delta V = \text{cell voltage (V)}$.

The redox couple selection and the accompanying supporting electrolyte dictate the maximum achievable cell voltage as well as the solubility limits of the active species. The kinetics of the redox reactions are dependent on the electrode surface properties; fast reaction kinetics will ultimately contribute to an overall improvement in power density. The kinetic aspects including reversibility of the redox reactions involved in the system is also addressed in this work. Even though operation as a power delivery device essentially means that the reversibility of the reactions is not critical, the present study includes this aspect as it is relevant to large-scale applications. These three aspects of the system are all inter-related and this parameter space for improving power density was kept in mind throughout this work. Furthermore, this strategy of improving power density by optimising different key properties is flexible to both large and small-scale applications. The knowledge gained in this work by electrochemical reaction kinetic studies is relevant and beneficial for both systems scales.

1.2 RFB basic principles

A RFB can operate as an energy storage device and as a power delivery device. Moreover, the basic operating principle of a RFB is valid for both small and large-scale systems. The following section covers the basic principles governing RFBs and their operation. The redox system chosen for the basis of this research, the all-vanadium redox flow cell, will be covered in detail in Section 1.3.
1. Introduction

1.2.1 **RFB operating principle and device architecture**

A typical RFB system is illustrated in Figure 1.4 and consists of two external reservoirs storing the electroactive species (e.g. metallic ions) dissolved in a supporting liquid electrolyte, two electrodes (positive and negative) a separator (typically a polymer ion exchange membrane) separating the two electrodes and electrolytes and a flow circulation system (e.g. peristaltic pumps). Membraneless RFB systems also exist mainly on the microfluidic scale, however this configuration is limited to low Reynolds number flowrates to avoid cross-mixing and additional design issues are imposed on the system [8,10]. The flow fields are found at either side of the cell, and are used to efficiently transport reactants and products to/from the electrode surfaces.

![Figure 1.4 – Schematic diagram of a typical redox flow battery system during discharge showing key system components and basic operating principle.](image)

When the RFB operates as a power delivery device (discharge phase), the electrolytes containing the electroactive species in different oxidation states are pumped through the cell. An oxidation reaction occurs at the negative electrode and a reduction reaction occurs at the positive electrode. The electrons produced at the negative electrode flow through the external circuit generating an electrical current. The electrolytes are continuously recirculated during operation until all available electroactive species are consumed (i.e. the electroactive species at the negative electrode are fully oxidised and the electroactive species at the positive electrode are fully reduced). At this point the system is considered to be fully discharged. The electrolytes can be recharged in the same device by
simply reversing the process. Operation in this way corresponds to an energy storage process, whereby the discharged electroactive species are charged by an external electrical energy source (i.e. wind or solar energy). In this case, electrical energy is supplied to the system and converted into chemical energy and stored as charged redox species in the electrolyte storage tanks. In order to charge and discharge the system continuously at constant efficiency, it is crucial that the redox reactions are electrochemically reversible. The forward and reverse redox reactions should therefore occur at relatively fast and similar rates (see section 2.1.1 for detailed explanation of electrochemical reversibility). The general reaction equations occurring during charge and discharge at the positive and negative electrodes can be written as follows:

**Negative electrode:**

\[
\begin{align*}
\text{charge:} & \quad A^{n+} + xe^- \rightarrow A^{(n-x)+} \\
\text{discharge:} & \quad A^{(n-x)+} \rightarrow A^{n+} + xe^- \\
\end{align*}
\]

\[ n > x \tag{1.1} \]

**Positive electrode:**

\[
\begin{align*}
\text{charge:} & \quad B^{(m-y)+} \rightarrow B^{m+} + ye^- \\
\text{discharge:} & \quad B^{m+} + ye^- \rightarrow B^{(m-y)+} \\
\end{align*}
\]

\[ m > x \tag{1.2} \]

### 1.2.2 RFB system components

A brief overview of the key system components and their respective functions is given here.

#### 1.2.2.1 Electrodes and membrane

The electrodes are a critical component of the RFB system, as they provide the surface on which the electrochemical reactions occur. The electrodes in most RFBs are not required to undergo physical changes such as phase change or insertion/disinsertion during operation, since the electrochemical reactions occur in the solution phase at the electrode-electrolyte interface [6]. An ideal electrode material should provide a high surface area, low electronic resistance, reasonable porosity, good mechanical and chemical stability, reasonable cost and high electrochemical activity [11]. Typical electrodes used in RFBs are divided into metallic and carbon-based materials. Metallic electrodes are less commonly used for this application, mainly due to issues of weight and particularly cost which make them unattractive for large-scale applications. On the other-hand, carbon materials are widely used electrodes in RFBS owing to their reasonable cost, high chemical stability and wide operating potential range. Section 1.3.2 covers an extensive review of different
carbon-based electrode materials and surface modification methods used to improve electrochemical activity.

The membrane acts as a physical barrier that prevents cross mixing of the positive and negative electrolytes during operation. It also allows ion transport of non-reaction ions (such as $\text{H}^+$ ions) to maintain electro-neutrality and electrolyte balance [5]. An ideal membrane should have a high ionic conductivity, low permeability of active species, good chemical stability and reasonable cost [11]. Typical separators used in RFBs are ion exchange membranes which are produced from polymeric materials. In aqueous environments, these membranes are designed to conduct positively charged ions (e.g. $\text{H}^+$ or $\text{Na}^+$) known as ‘cationic membranes’ or negatively charged ions (e.g. $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Cl}^-$) known as ‘anionic membranes’. Perfluorosulfonic acid (PFSA) membranes such as Nafion® 117 (Dupont, USA) are commonly used in RFBs due to their high conductivity and good chemical stability in the oxidising electrolytes [12]. The properties of the membrane can significantly affect the overall system performance [13].

1.2.2.2 Electrolyte

The energy density (Wh.L$^{-1}$) of the RFB system is influenced by the solubility of the redox species in the electrolyte. The supporting electrolytes are typically acid based in most aqueous systems and electrolyte requirements include reasonable conductivity, thermal stability and low viscosity [14]. Increasing the concentration of redox species and/or increasing the electrolyte volume, both increase the overall energy storage capacity of the RFB. A huge constraint to aqueous RFB system performance and energy density is the operational limitation imposed by the electrochemical stability window of water, equations 1.3 and 1.4.

$$2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad E^0 = 1.23\text{V}/\text{SHE} \quad (1.3)$$

$$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2 \quad E^0 = 0\text{V}/\text{SHE} \quad (1.4)$$

Aqueous electrolytes theoretically decompose at standard electrode potentials greater than 1.23 V/SHE by the oxygen evolution reaction (OER) and below 0 V/SHE, by the hydrogen evolution reaction (HER). These are thermodynamic values and the actual overpotentials for the HER and OER will be determined by the kinetics of the reaction at a given electrode surface. Nonetheless there is still a limitation to the operational window for aqueous RFB systems.

Organic based RFBs are emerging as feasible alternatives to their aqueous counterparts which use expensive metal ion active species. The use of organic redox species in aqueous
or non-aqueous systems is a promising approach to reducing the overall electrolyte cost in the system [15]. Furthermore, non-aqueous electrolytes are not limited by the electrochemical stability window of water and therefore allow wider operating potential windows compared to aqueous electrolytes. The electrochemical stability window of typical non-aqueous solvents such as acetonitrile and propylene carbonate can exceed 5 V [16]. In addition to this, many in-organic redox couples have been reported to have high solubility’s in both aqueous and non-aqueous electrolytes [17,18]. For example methyl-para benzoquinone has a solubility of up to 5 mol L⁻¹ in acetonitrile [19]. However, several challenges still need to be addressed for these systems to reach practical application stage [15]. This work will be focused exclusively on aqueous RFB systems.

1.2.3 Advantages and key challenges of RFBs

RFBs present a number of attractive properties for the particular application as large-scale energy storage devices. The independent power and energy sizing aspect allows significant design and locational flexibility. Minimal self-discharge occurs since both the positive and negative electrolytes are stored separately and relatively low maintenance is required for these systems. Furthermore, RFBs are capable of rapid response, allowing their application base to span from power quality to energy management services, Figure 1.1 [20]. Despite these apparent advantages, the power and energy densities of aqueous RFB systems are relatively low compared to other technologies [12]. Furthermore, these systems have also been limited to few field trials, making their reliability track record uncertain [5]. Current research in the field is geared towards designing lower-cost materials which allow higher energy and power densities. Advancements in the area of material research and optimisation requires an improved understanding of RFB fundamentals [7].

1.2.4 Aqueous RFB chemistries

Selection of positive and negative redox couples is typically based on the solubility of the active species in the supporting electrolyte and their corresponding standard redox potentials. The chosen redox couple combination should give a reasonable cell voltage for practical applications and high solubility of redox species is beneficial for attaining a high power density [11]. The REPCOOL project was primarily concerned with liquid cooling and power delivery therefore only liquid-liquid redox systems were considered in this work. Table 1.2 gives examples of some of the most common aqueous RFB chemistries investigated over the past 40 years, summarising the respective electrode reactions, electrode materials, electrolytes and standard cell potentials. Figure 1.5 illustrates the position of the different redox couples on the standard potential scale. It highlights how
the selection of positive and negative redox couples affects the achievable theoretical cell voltage and ultimately the available power density of the system ($P=I\Delta V$).

Figure 1.5. Position of different redox species on the standard potential scale.
Table 1.2 Examples of different redox couples for all-liquid RFB systems

<table>
<thead>
<tr>
<th>Redox couples</th>
<th>Electrode Reactions (V/SHE)</th>
<th>$E^{0}_{\text{OCV}}$ (V)</th>
<th>Electrodes (positive/negative)</th>
<th>Supporting Electrolyte ($M = \text{mol L}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Cr</td>
<td>$\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$</td>
<td>1.18</td>
<td>Carbon or graphite felt</td>
<td>1 M CrCl$_3$ in 3 M HCl</td>
</tr>
<tr>
<td></td>
<td>$E^0 = -0.41$ V</td>
<td></td>
<td>+Au-Pb/carbon or</td>
<td>1 M FeCl$_3$ in 3 M HCl</td>
</tr>
<tr>
<td></td>
<td>$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$</td>
<td>0.77 V</td>
<td>graphite felt</td>
<td></td>
</tr>
<tr>
<td>Poly-Sulphide/Br$_2$</td>
<td>$S_4^{2-} + 2e^- \rightarrow 2S_2^{2-}$</td>
<td>1.36</td>
<td>Co-graphite</td>
<td>1.3 M Na$_2$S$_4$/ 4 M NaBr</td>
</tr>
<tr>
<td></td>
<td>$E^0 = -0.27$ V</td>
<td></td>
<td>felt/graphite felt</td>
<td></td>
</tr>
<tr>
<td>V/Fe</td>
<td>$V^{3+} + e^- \rightarrow V^{2+}$</td>
<td>1.02</td>
<td>graphite felt/graphite felt</td>
<td>2 M FeCl$_3$ in 1.5 M HCl</td>
</tr>
<tr>
<td></td>
<td>$E^0 = -0.26$ V</td>
<td></td>
<td></td>
<td>2 M VCl$_3$ in 3 M HCl</td>
</tr>
<tr>
<td>V/Ce</td>
<td>$V^{3+} + e^- \rightarrow V^{2+}$</td>
<td>1.93</td>
<td>graphite/graphite</td>
<td>0.5 M V$^{3+}$ in 1 M H$_2$SO$_4$</td>
</tr>
<tr>
<td></td>
<td>$E^0 = -0.26$ V</td>
<td></td>
<td></td>
<td>0.5 M Ce$^{3+}$ in 1 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>V/Mn</td>
<td>$V^{3+} + e^- \rightarrow V^{2+}$</td>
<td>1.77</td>
<td>graphite/graphite</td>
<td>0.3 M V$^{3+}$ in 5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td></td>
<td>$E^0 = -0.26$ V</td>
<td></td>
<td></td>
<td>0.3 M Mn$^{3+}$ in 5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>All-vanadium</td>
<td>$V^{3+} + e^- \rightarrow V^{2+}$</td>
<td>1.26</td>
<td>graphite felt/graphite</td>
<td>2 M V in 5 M H$_2$SO$_4$ [21]</td>
</tr>
<tr>
<td></td>
<td>$E^0 = -0.26$ V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{VO}_2^{2+} + 2H^+ + e^- \rightarrow \text{VO}^{2+} + H_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E^0 = 1.0$ V</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*This table is an adaption of Table 2 in reference [12]. $E^0_{\text{OCV}}$ – standard redox potentials at open circuit voltage (OCV) measured in Volts (V) versus the Standard Hydrogen Electrode (SHE).

The RFB systems listed in Table 1.2 each have advantages and disadvantages associated with cost, safety and performance. The Fe/Cr was one of the first RFB systems to be developed by NASA in 1973 [22]. However, despite great efforts towards scale-up, the system suffered from a very low energy density due to cross contamination [12]. Furthermore, the sluggish kinetics of the Cr(II)/Cr(III) reaction meant a noble metal catalyst was required, which added to increased system costs [12]. Over the next few decades alternative redox couple combinations which could provide longer cycle life and high energy and power densities were investigated. The Bromine-polysulphide system was patented by Remick and extensively studied by Regenysys® technologies and a 1 MW pilot was installed in Wales, U.K. [12]. A key attribute of this system is the relative abundance.
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and high solubility of the electroactive species that comprise the electrolytes [7]. However technical challenges existed such as cross-contamination of electrolytes which lead to performance losses as well as environmental issues associated with the release of toxic gases, Br₂ and H₂S [12]. The all-vanadium redox flow battery (VRB) is one of the most well-established and technically mature systems to date, it exploits vanadium in four different oxidation states as the active species in the positive and negative electrolytes. The issue of species crossover is much less important in this system as the active species are all of the same element. This is a major advantage of this technology over other RFB chemistries. Different variations of the vanadium based systems using the V(II)/V(III) redox couple at the negative electrode have also been explored (e.g. V/Ce, V/Mn and V/Fe). Using either Ce(III)/Ce(IV) or Mn(II)/Mn(III) redox couples at the positive electrode allows higher theoretical cell voltages to be achieved. However, issues of low solubility of active species (e.g. cerium sulphate) as well as the negative effects of cross-contamination in all three systems present the main technical issues for these redox chemistries. The all-vanadium system presents an attractive solution to the issue of cross-contamination and shows a reasonable cell voltage and performance compared to other RFB chemistries, this system was investigated in this PhD work. The following sections cover a brief overview of the VRB technology focusing specifically on the electrochemical reactions and electrode materials used in this system.

1.3 The all-vanadium redox flow battery (VRB)

The all-vanadium redox flow battery concept was first suggested by Pissoort and was further developed in the 1980’s at the University of New South Wales (UNSW) Australia, by Maria Skyllas-Kazocos and co-workers [21]. The system referred to as the generation 1 (G1) VRB, was taken from the initial concept stage in 1984 to the development phase of several stationary and mobile applications during the late 1980s and 1990s [23–25]. The use of the same element in both half-cells eliminates the issue of cross contamination of ions across the membrane. This ultimately allows an extended electrolyte life compared to other RFB chemistries. Despite its numerous advantages, the G1 VRB is still limited by a relatively low energy density. Research efforts over the past few decades are still ongoing and have been focused on gaining a more fundamental understanding of the electrochemistry and operation principles of the system. Detailed understanding of material properties of main system components, specifically electrode, electrolytes and membranes is key to optimising and improving overall cell performance [25].
1.3.1 Vanadium redox reactions

Vanadium exists in solution in four different oxidation states: V(II), V(III), V(IV), V(V). The all-vanadium system employs the V(II)/V(III) redox couple at the negative electrode and the V(IV)/V(V) couple at the positive electrode. During discharge in the positive half-cell, V(V) ions are reduced to V(IV) ions. Protons are consumed in this reaction, therefore H\(^+\) ions must move through the membrane from the negative to the positive half-cell to maintain electrical neutrality of the electrolytes. During discharge in the negative half-cell, V(II) ions are oxidised to V(III) ions releasing one electron. The reverse reactions occur during charging. Equations 1.5 and 1.6 show the discharge (forward reaction) and charge (reverse reaction) processes occurring in the VRB system at the positive and negative electrodes respectively.

**Positive electrode:**

\[
VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \quad E^{0+} = 1.00 \text{ V vs. SHE} \tag{1.5}
\]

**Negative electrode:**

\[
V^{2+} \rightleftharpoons V^{3+} + e^- \quad E^{0-} = -0.26 \text{ V vs. SHE} \tag{1.6}
\]

1.3.1.1 Thermodynamic aspects

The standard half-cell potentials for each redox reaction is indicated and the difference between the positive standard half-cell potential \(E^{0+}\) and the negative standard half-cell potential \(E^{0-}\) yields the standard cell voltage for the redox system \(E_{cell}^{0}\):

\[
E_{cell}^{0} = E^{0+} - E^{0-} \tag{1.7}
\]

For the all-vanadium system the standard cell voltage is:

\[
E_{cell}^{0} = 1.00 - (-0.26) = 1.26 \text{ V} \tag{1.8}
\]

The Nernst equation relates the reversible electrode potential \(E_{rev}\) to the standard electrode potential \(E^{0}\) and the activities of the electroactive species [26]. The Nernst equation for a simple redox reaction where species A is oxidised to species B is shown in equation (1.9).
Nernst equation:

\[ xA \rightleftharpoons yB + e^- \]

\[ E_{rev} = E^0 + \frac{RT}{nF} \ln \left[ \frac{a_B^y}{a_A^x} \right] \]  

(1.9)

where: R is the universal gas constant (8.315 J K\(^{-1}\) mol\(^{-1}\)), F is the Faraday constant (96,485 A s mol\(^{-1}\)), T is temperature (K), n is the number of electrons, \( a_A \) and \( a_B \) are the activities of the active species raised to the power of their respective stoichiometric coefficients. For dilute concentrations, the activity and concentration of active species are equal [27].

The Nernst potentials of the positive and negative discharge reactions in equations (1.5) and (1.6) can be written as follows:

**Positive half-cell:**

\[ E_{rev}^+ = E^{0,+} + \ln \left( \frac{[VO_2^2^+][H^+]^2}{[VO^2^+]^2} \right) \]  

(1.10)

with liquid H\(_2\)O by definition having an activity of 1 and therefore does not appear in the equation.

**Negative half-cell:**

\[ E_{rev}^- = E^{0,-} + \ln \left( \frac{[V^{3^+}]}{[V^{2^+}]} \right) \]  

(1.11)

where: \( E_{rev}^+ \) and \( E_{rev}^- \) are the reversible half-cell potentials for the positive and negative half cells respectively and \( E^{0,+} \) and \( E^{0,-} \) are the standard cell potentials for the V(V)/V(IV) and V(II)/V(III) redox reactions respectively.

By combining the Nernst equations for the half-cell reactions, equations (1.10) and (1.11), the reversible cell voltage for the full cell is given by equation (1.12) and depends on the vanadium species and the proton concentrations respectively.

\[ E_{cell}^{rev} = E^{0,cell} + \frac{RT}{nF} \ln \left( \frac{[VO_2^2^+][H^+]^2[V^{3^+}]}{[VO^2^+]^2[V^{2^+}]} \right) \]  

(1.12)

where: [V] is the concentration (mol L\(^{-1}\)), \( E^{0,cell} \) is the standard cell voltage [21].
1.3.2 **Key VRB components**

The electrolyte, membrane and electrodes are the key materials in the VRB system. The requirements and important properties of these components will be discussed briefly, with the focus being placed on the electrode materials.

1.3.2.1 *Vanadium electrolyte*

In general, the concentration of vanadium species in the electrolyte determine the total electrolyte volume and energy density of the system, which is relatively low for VRBs between 30-50 Wh kg\(^{-1}\) [28]. The vanadium electrolytes are typically produced by electrolysis of V(IV) (prepared as VOSO\(_4\) dissolved in H\(_2\)SO\(_4\)) to form V(V) and V(II) solutions. An alternative way to prepare for example V(V) solution is directly from vanadium pentoxide (V\(_2\)O\(_5\)), however this is not a feasible route as the solubility of V\(_2\)O\(_5\) in sulphuric acid is relatively low (~0.3 mol L\(^{-1}\)) [29]. By electrolysis however, concentrations of up to 2 mol L\(^{-1}\) V(V) in can be achieved in 5 mol L\(^{-1}\) H\(_2\)SO\(_4\) [14,30]. Higher vanadium concentrations are desirable to achieve reasonable energy densities. It has been shown that the solubilities of V(II), V(III) and V(IV) species in H\(_2\)SO\(_4\) increase with increasing temperature and decreasing acid concentration [30]. The reduced solubility in high acid concentrations is a result of the common ion effect, as the V(II), V(III) and V(IV) ions precipitate as sulphate salts. Precipitation of V(II), V(III) and V(IV) species have been reported at temperatures below 10\(^{\circ}\)C [31]. V(V) however does not precipitate as a sulphate but undergoes thermal precipitation by an endothermic reaction to form V\(_2\)O\(_5\) at temperatures > 40\(^{\circ}\)C [14]. The maximum vanadium ion concentration is therefore set by the operating temperature of the VRB system which lies between 10-40\(^{\circ}\)C [30]. The preferred electrolyte composition for this temperature range is a total vanadium ion concentration between 1.6-2 M and a total sulphate concentration of 4-5 mol L\(^{-1}\) from the H\(_2\)SO\(_4\) supporting electrolyte. It is critical to stabilise the V(V) species against thermal precipitation, which means higher sulphate concentrations closer to 5 mol L\(^{-1}\) are desirable. However, for colder climates lower sulphate concentrations of 4 mol L\(^{-1}\) would be required to prevent precipitation of the V(II), V(III) and V(IV) ions. The solubilities of the vanadium species limit the practical concentration of VRBs and research in this area has been geared toward finding precipitation inhibitors which stabilise supersaturated solutions of high vanadium concentrations. Adding precipitation inhibitors is an effective method for stabilising both positive and negative vanadium electrolytes [14,30,32]. Mousa et al. found that ammonium phosphate, ammonium sulphate and sodium pentopolyphosphate are suitable to stabilise 2 mol L\(^{-1}\) V(II) and V(III) ions with high sulfuric acid concentration [33]. It was also demonstrated that 2 mol
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L$^1$ V(V) can be stabilised in 3 mol L$^{-1}$ H$_2$SO$_4$ at 40°C by adding 3% trishydroxymethyl aminomethane [34].

1.3.2.2 Ion exchange membrane

The ion exchange membrane is a critical component of the system as it prevents the positive and negative vanadium electrolytes from mixing and simultaneously allows the transfer of protons to maintain charge balance. The power density of the VRB system is limited by the resistance of the membrane. Improving ionic conductivity to reach values of 10$^{-3}$ to 10$^{-1}$ S cm$^{-1}$ will minimise ohmic losses and improve voltage and energy efficiency [11]. Use of thinner membranes reduces overall ionic resistance, however at the cost of mechanical stability. Research in this area is therefore focused on finding a compromise between thickness, ionic conductivity and stability. Furthermore, the membrane must display low permeation rates of active species to reduce self-discharge. Commercially available membranes such as Nafion®117 have been employed for the VRB system as they display good chemical stability in acidic environments [21]. However, these membranes have not been designed for this system and high costs and issues with water cross-over have posed limitations to their use. Researchers are therefore focused on addressing these critical issues and several novel synthesis approaches have resulted in significant advances in membranes for this application [11,35]. Researchers from the Paul Scherrer Institut, also working on the REPCOOL project, developed a novel membrane for the VRB system [35,36]. Nibel et al. designed a bifunctional ion-conducting membrane by radiation grafting with amidoxime moieties and sulfonic acid proton exchange sites. They reported a four-fold reduction in vanadium cross-over in the presence of amidoxime groups on the membrane and see negligible effects on membrane conductivity [35,36]. In more recent work, Nibel et al. presented a new design concept for an amphoteric ion-exchange membrane based on radiation grafting of vinylpyridine into an ethylene tetrafluoro-ethylene base film. Cationic and anionic exchange sites were introduced by a two-step functionalisation. These membranes were reported to have superior properties compared to the benchmark Nafion® 117 [37]. Moreover, the synthetic route was significantly simplified compared to their previous work.

1.3.3 Electrode materials

The electrodes are a key component of the system as they provide the active surface on which the electrochemical reactions occur. The acidic and strongly oxidative environment of a VRB limits the electrode material choice. In general, inert, high surface area graphite or other carbon-based materials are commonly used for VRB applications and have a number of attractive properties including stability over a wide pH range and reasonable
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cost [11,21]. The electrode material properties can affect the VRB performance in a number of ways [11]:

(i) Electrochemical activity - influences overpotential losses, particularly activation overpotential, which is directly related to voltage efficiency and power density.

(ii) Electrical resistance – contributes to ohmic losses during operation which can influence cell voltage and energy efficiency.

(iii) Chemical stability – in the acidic electrolyte will determine the lifetime of the system. Resistance to corrosion at high oxidising potentials at the positive electrode will also influence the electrode lifetime.

(iv) Porosity – will influence the pressure drop through the cell wand hence the pumping energy losses are affected by porosity, which ultimately influence the overall energy efficiency of the system.

It is therefore crucial to develop robust and reliable electrodes to reduce undesirable effects associated with these properties. Furthermore well designed electrodes with maximum surface area and activity characteristics will contribute to an overall cost reduction associated with stack size and production [22]. To this end, significant research has been carried out to understand and enhance the kinetics of the redox reactions by developing electrodes with excellent electrochemical properties [22]. In many cases a pre-treatment or surface modification is needed to improve wettability and electrode activity of carbon materials. As a consequence, research in this area has been focused on the development of different surface modification methods for carbon-based materials. Furthermore, researchers are attempting to gain a detailed fundamental understanding of the electrochemical processes occurring at the electrode surface to develop highly active and stable carbon electrodes for VRBs. An overview of the typical surface modification methods employed to improve carbon electrode activity is presented below and the current state of electrode research is discussed.

1.3.3.1 Carbon surface modification

A number of surface modification approaches have been explored in the literature and significant improvements in electrode activity have been reported [22,38]. Surface modification typically involves the introduction of different functional groups or metal ions onto the carbon surface. Nitrogen-doped carbons for example have been reported to exhibit enhanced activity compared to untreated carbon materials. Wu et al. proposed an ammonia treatment which successfully introduced nitrogen groups onto the carbon surface. These groups were suggested to facilitate the charge transfer between electrodes
and vanadium ions [39]. Furthermore, introduction of various metallic compounds by ion exchange methods have also been investigated. Impregnation of carbon felt with solutions containing Mn(II), Te(IV) and In(III) ions showed promising activity [40]. From the viewpoint of cost, non-precious metals such as Bi have also been incorporated onto a carbon felt surface by wet chemical methods. A marked increase in specific surface area (0.92 to 3.36 m$^2$ g$^{-1}$) and activity was observed [41]. Further progress was made by use of an electrodeposition method to incorporate Bi onto carbon surface. In this case the reversibility of the V(II)/V(III) reaction was improved by suppression of the hydrogen evolution also known to occur at the negative electrode [42]. However, the most widely used activation method for carbon electrodes involves an oxidation process which introduces different oxygen functional groups onto the carbon surface i.e. -C-OR groups (-C-OH and O-C-O), -C=O and -COOH groups [43]. The oxygen functional groups are thought to improve electrode activity and overall performance by (i) catalytic effects and (ii) improved hydrophilicity/wettability leading to increased active surface area (discussed in detail in section 1.3.2.2). The most commonly used oxidative surface treatments are summarised here.

(i) Thermal treatment

Early work by Sun and Skyllas-Kazacos showed that thermal treatment at 400°C for 30 h greatly improved electrochemical activity and performance of carbon felt [38]. This improvement was attributed to the reduced resistance, increased hydrophilicity of the carbon surface and the introduction of oxygen functional groups particularly -C-O and -C=O groups onto the surface. These groups were suggested to increase hydrophilicity and behave as active sites for the vanadium redox reactions. More recent studies by SGL carbon group, have optimised the thermal treatment process by reducing treatment time and increasing treatment temperature (air, 750°C, 5 mins) thus making it a more economically viable process [44].

(ii) Chemical treatment

Chemical treatment is another method used to functionalise carbon materials with oxygen. It was shown that treatment of carbon felt with concentrated Nitric acid (HNO$_3$), sulphuric acid (H$_2$SO$_4$) or a mixture of the two acids resulted in a significant increase in surface oxygen groups and improved VRB performance [45]. Additionally, chemical treatment resulted in a lower resistance of the carbon felt which was found to be a function of acid concentration and treatment time. Other researchers investigated the effects of acid treatment combined with heat treatment [46]. They found that the
combination of the two treatments increased the fraction of -COOH functional groups which were thought to be responsible for the dramatic improvement in performance. Furthermore, Li et al. carried out chemical treatment using a mixed acid solution of nitric (HNO₃) and phosphoric acid (H₃PO₄) in a 3:1 ratio. This method introduced abundant -OH groups onto the carbon surface and significantly improved electrode activity [47].

(iii) Electrochemical oxidation

Electrochemical oxidation involves oxidation of the carbon surface by holding the potential at oxidising potentials in an acidic solution, typically H₂SO₄. Li et al. reported an increase in surface area and activity after oxidation [45]. XPS revealed that the O/C ratio increased significantly with -COOH being the predominant functional group on the surface after treatment. Moreover, electrochemical oxidation has been seen to erode the carbon surface, resulting in an increased surface area and significant structural changes. This observation has been made in numerous studies involving electrochemical oxidation of carbon materials [48–50].

These three methods of oxidation are vastly different in their approach, and it is very difficult to quantify and compare the observed improvements which result from these treatments. This is mainly because vastly different materials and treatment conditions are used. Furthermore, several new strategies have been proposed, which aim to maximise oxygen functionalisation of the carbon surface. Kim et al. found that a combination of corona discharge and hydrogen peroxide (H₂O₂) treatment introduced a very high concentration of oxygen groups onto carbon felt. This modification method was argued to be more time and cost effective compared to the traditional treatment methods [51]. Dixon et al. treated carbon felt electrodes by oxygen plasma treatment and reported enhanced redox kinetics of the vanadium reactions in the system.

This work is focused exclusively on the effects of oxygen treatment on carbon electrode activity for the vanadium redox reactions. Research in this area is on the rise, with many studies concentrating on gaining a more fundamental understanding of how surface oxygen groups influence the electrochemical reactions occurring at the electrode surface. A review of the current state of research on this topic will be given.

1.3.3.2 Current state of carbon electrode research

There are limited fundamental, mechanistic studies on the vanadium redox reactions in the literature showing the catalytic effects of these groups, as a lot of attention has been paid to the applied side of this technology [52]. Nonetheless, a few reaction mechanisms
involving different oxygen groups have been reported [22,47]. It is typically suggested that both reactions occur via an inner-sphere reaction mechanism involving oxygen groups. However contradictions have arisen over recent years regarding this point [38,52–54]. In an inner-sphere reaction, there is a strong interaction between the reactant/product and the electrode surface. The reactants, intermediates or products are often adsorbed on the surface of the electrode [55]. Whereas in an outer-sphere reaction, the electron transfer between the active species and electrode occurs without any bonding between them, the electron is tunnelled from one to the other, typically across a solvation layer [55]. Inner and outer-sphere reactions can often be distinguished experimentally by assessing the sensitivity of the reaction to the nature of the electrode material. An outer-sphere reaction does not depend significantly on the type and nature of electrode material [6], whereas inner sphere reactions depend strongly on the nature of the electrode material. Over recent years, there have been reports that contradict the idea of an inner-sphere reaction mechanism for the V(V)/V(IV) redox couple. Wu et al. and Yamamura et al. referred to the V(V)/V(IV) reaction as a ‘slow outer-sphere’ reaction [56,57]. Gattrell et al. proposed a multi-step chemical and electrochemical mechanism involving an electron transfer and two proton transfers, which do not involve the electrode surface [54]. Furthermore, some authors have suggested that the V(V)/V(IV) reaction is not influenced by surface functional groups at all [58]. Other studies report that functional groups may even impede the reaction kinetics [53,59–61]. These conflicting findings in the literature may be related to the nature and composition of the electrode surfaces used in the different studies making it very difficult to compare results across a broad array of different types of carbon electrodes and treatment methods [53]. The V(V)/V(IV) reaction has received a considerable amount of attention and was thought to be the limiting reaction in the system [38]. This was due mainly to the nature of the complex oxo-vanadium species as well as the additional H+ and H2O species involved in the reaction, equation (1.5). However, it has been shown by a growing number of authors that this reaction in fact has faster reaction kinetics compared to the V(II)/V(III) reaction which takes place at the negative electrode [59,62]. This finding is not intuitive, considering the more complex reaction species involved in the V(V)/V(IV) reaction, equation (1.5), compared to the simple V(II)/V(III) ions present for the negative electrode reaction, equation (1.6). Early work by McCreery et al. on oxidised glassy carbon electrodes, showed that like the Fe(II)/Fe(III) reaction, the V(II)/V(III) redox reaction is ‘surface sensitive’, and more specifically ‘oxide sensitive’. This suggests an inner-sphere reaction via a bridging mechanism involving surface oxides [63]. Recent work has supported this hypothesis, it has been proposed that a transition from an outer to inner-sphere mechanism occurs on
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an non-oxidised to an oxidised carbon surface and further that the V(II)/V(III) reaction may be the limiting reaction in the system [53,58,64–66].

In addition to the catalytic effects and mechanisms involving surface oxygen groups, other properties such as carbon microstructure have also been suggested to play a role in improving kinetics for the vanadium reactions. Surface structure and surface preparation is known to drastically affect the electrode activity of carbon materials [67]. Surface modification by introduction of oxygen groups can lead to changes in the carbon structure in the form of defect sites and disorder [68,69]. Researchers have generally agreed that graphite edge sites are more active than basal planes toward electron transfer [53,70–73] and the graphitic nature of carbon has been correlated with activity for the V(V)/V(IV) reaction [74]. Furthermore, the starting precursor used to make carbon felt electrodes has been shown to influence the resulting electrochemical properties of the material. Carbon felt can be produced from a number of precursors including rayon, pitch and polyacrylonitrile (PAN). In an early study by Zhong et al. the physical, chemical and electrochemical properties of rayon and PAN based graphite felts were compared [75]. PAN-based felts exhibited superior conductivity compared to rayon-based felts. However, rayon-based felts interacted more easily with oxygen particularly forming C=O groups, whereas PAN-based felts were more resistant to oxidation. This was thought to be related to the microcrystalline structures of the two materials. Thus, the properties of the starting carbon material such as microstructure, have a significant effect on how the surface reacts to a given activation treatment. Additionally, the activation treatment itself may induce structural changes which cannot be ignored when considering reasons for improved activity.

Finally, another factor to consider is the increased hydrophilicity or wettability of the carbon surface as a result of the presence of surface oxygen groups [52,60,76–78]. This can lead to an increased wetted electrode surface area and affect the apparent electrode kinetics [79]. It is clear from these numerous studies that in general, oxidation of carbon materials results in improved activity and performance. The actual mechanisms responsible for this improvement however, remain unclear. This is part of an ongoing debate in the literature in this field. Separating the effects of these different properties on electrode activity is a key challenge which needs to be addressed. The key properties which have gained the most attention and need to be considered are:

(i) The catalytic role of oxygen groups
(ii) Carbon microstructure
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(iii) Hydrophilicity/wettability

These different properties are all related and therefore great care must be taken to decouple the effects of each property on the observed electrode activity. A further contributing factor to the complexity of the VRB reactions on carbon electrodes is that carbon itself is a complex material. There are several different types of carbons and the same pre-treatment of even the same carbon materials can yield different surface species which significantly impacts electrochemical activity [7]. Furthermore, the stability of these electrode materials under real operating conditions must be considered. An improved understanding of the fundamental kinetics of these reactions and insights into degradation and stability would allow the development of stable, high performance electrodes for this application and ultimately improve power density and performance.

1.4 Scope of this work

The goal of this work is to gain a deeper understanding of the electrochemical kinetics of the two redox reactions occurring in the all-vanadium system at carbon-based electrodes. This work covers a detailed kinetic study of the vanadium (V) reduction reaction and vanadium (II) oxidation reaction occurring at the positive and negative electrodes respectively (discharge reactions). In an attempt to simplify the complex commercial porous electrodes used in the full cell, the two reactions were first studied at well-defined, model carbon electrode surfaces. In this way, valuable insights into different properties affecting activity and stability could be investigated. The model electrode surfaces were treated by different oxidative methods and correlations between surface chemistry (oxygen groups) and carbon microstructure are discussed. Chapter 3 covers the results of the model electrode study for the V(V) reduction reaction at different oxidised carbon surfaces. Chapter 4 covers a similar study for the V(II) oxidation reaction. Furthermore, the stability of different types of carbon materials oxidised by the same method was investigated for the V(II)/V(III) reaction. The influence of the hydrogen evolution reaction was considered and the effect of the type of carbon on the observed stability was studied. Finally, chapter 5 presents full-cell characterisation of commercially relevant carbon materials, namely carbon felt and carbon paper. The performance and cycling stability of the pristine and thermally oxidised materials was investigated. Parallels between the model carbon electrode system and the porous carbon electrodes are discussed. Valuable insights into the role of different carbon properties on full-cell performance are identified. Chapter 6 summarises the key findings and main conclusions of this research. An outlook section identifies areas requiring further investigations and provides suggestions for possible avenues of research.
Chapter 2. Experimental methods and techniques

This chapter covers the experimental methods and characterisation techniques used in this PhD work. It starts with the electrochemical characterisation section which is split into two parts, ex-situ, half-cell characterisation and in-situ, full-cell characterisation. The half-cell characterisation section describes the typical electrochemical techniques and the three-electrode electrochemical cell setup used. The full-cell characterisation section details the key components of the redox flow cell system used to study performance of different electrode materials. The typical full-cell performance assessment techniques are described. Electrode materials and treatment methods are then summarised, followed by the physicochemical methods used to characterise the properties of the electrode materials. This chapter serves as a collective summary of all methods and techniques used throughout this work, and more detailed information regarding experimental conditions can be found in the experimental parts of chapters 3, 4 and 5.
2. Experimental methods and techniques

2.1 Half-cell electrochemical characterisation

To access kinetic parameters associated with the catalytic performance of the electrodes, two typical electrochemical techniques were used namely: cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

2.1.1 Cyclic voltammetry

Cyclic voltammetry is a classic electrochemical technique used to study different phenomena occurring at the electrode-electrolyte interface (e.g. charge transfer in oxidation-reduction processes, adsorption and diffusion). In a typical cyclic voltammetry measurement, a linear variable, potential, is applied to an electrode known as the working electrode (WE). The potential is varied with time between two fixed potential limits ($E_1$ – lower potential limit and $E_2$ – upper potential limit) as seen in Figure 2.1 (a). The potential at the WE at a given time, $t$, is defined by:

$$E(t) = E_1 \pm vt$$  \hspace{1cm} (2.1)

where: $E(t)$ is the potential of the WE at time $t$, $E_1$ is the initial starting potential, $v$ is the potential scan rate (mV s$^{-1}$) and $t$ is time (s).

The resulting potential versus current curves are known as cyclic voltammograms (CVs). The shape of the CVs gives valuable information about the reaction under investigation. Figure 2.1 (b) is an example of a typical CV for a reversible redox reaction occurring at an electrode surface.
2. Experimental methods and techniques

Figure 2.1 - (a) triangular waveform of applied potential versus time for a single potential sweep from E1 to E2 and back to E1. (b) Typical cyclic voltammogram showing peak current \(i_{p,a}/i_{p,c}\) and peak potential \((E_{p,a}/E_{p,c})\) for 50:50 solution of 0.1 mol L\(^{-1}\) ferri/ferrocyanide in 1 mol L\(^{-1}\) KCl at a glassy carbon electrode.

The CV in Figure 2.1 (b) was measured for the ferri/ferrocyanide ([FeCN\(_6\)]\(^3-\)/[FeCN\(_6\)]\(^4-\)) redox couple, which is a typical example of a fast, one electron transfer redox process with no side reactions. As the potential is scanned positively from \(E_1\) to \(E_2\), an oxidation reaction occurs producing the anodic current peak with peak intensity \(i_{p,a}\). On the negative, reverse scan from \(E_2\) to \(E_1\), a reduction reaction occurs producing the cathodic current peak, with intensity \(i_{p,c}\). The Randles-Sevcik equation can be used to describe the relationship between the peak current \((i_{p,a}\) or \(i_{p,c}\)) and the scan rate [80]:

\[
i_p = 0.4463nF \cdot \left(\frac{nF}{RT}\right)^{1/2} AD^{1/2}C^{1/2} \nu^{1/2}
\]

where: \(i_p\) = peak current (A); \(n\) = number electrons; \(A\) = electrode area (m\(^2\)); \(D\) = diffusion coefficient (m\(^2\) s\(^{-1}\)); \(C\) = concentration of active species (mol L\(^{-1}\)) and \(\nu\) = scan rate (V s\(^{-1}\)), for a solution at 25°C, \(F\) is the Faraday constant (96 485 A s mol\(^{-1}\)), \(T\) is temperature (K).

In the present work cyclic voltammetry was used to assess the so-called reversibility of the electrochemical reactions of interest in the VRB system. The anodic and cathodic peak currents \((i_{p,a}/i_{p,c})\) and the potentials at which the peak currents occur \((E_{p,a}/E_{p,c})\) are typical features of a cyclic voltammogram used to gain information regarding the reversibility of the redox system. Electrochemical reversibility is related to the rate of electron transfer...
between the electrode and the redox species in solution. If the electron transfer between the electrode surface and solution redox species is fast, the system is termed reversible or electrochemically reversible. An reversible redox system fulfils the following criteria [81]:

(i) The peak-to-peak separation ($\Delta E_p = E_{p,a} - E_{p,c}$) is small, corresponding to a value for an $n$ electron process of:

$$\Delta E_p = 2.218 \frac{RT}{nF} \approx \frac{59 mV}{n} \text{ (at 298K)}$$

(ii) The ratio of anodic and cathodic peak currents is equal to 1:

$$\left| \frac{i_{p,a}}{i_{p,c}} \right| = 1$$

(iii) The peak current is proportional to the square root of the scan rate according to the Randles-Sevcik equation (2.2).

$$i_{p,a/c} \propto \nu^{1/2}$$

(iv) The position of the potentials ($E_{p,a}/E_{p,c}$) at which the peak currents occur does not vary with scan rate, Figure 2.2.

\[ \text{Figure 2.2 - Cyclic voltammograms for a reversible redox system at various scan rates.} \]

In reality however, these criteria are rarely fulfilled and as not all redox systems display ideal reversible behaviour. Reactions with intermediate or slow electron transfer between electrode and redox species in solution are known as quasi-reversible or irreversible. The different rates of electron transfer give rise to different voltammetric profiles observable in a CV, Figure 2.3.
Figure 2.3 - Cyclic voltammograms for (a) reversible, (b) quasi-reversible and (c) irreversible redox reactions.

The CV for the reversible case, Figure 2.3 (a), is characterised by well-developed anodic and cathodic peaks with a peak-to-peak separation $\Delta E_p = \frac{59}{n}$ mV. As the system transitions from reversible, Figure 2.3 (a), to irreversible Figure 2.3 (c), the shape of the CV changes. The peaks become less well developed and the $\Delta E_p$ peaks becomes very large. Nicholson made use of these differences in $\Delta E_p$ observable by cyclic voltammetry, to develop a relationship between the standard rate constant for electron transfer ($k_s$) and the peak-to-peak separation $\Delta E_p$ [82]. This relationship is shown in equation (2.6):

$$\psi = k_s [\pi D n v F / R T]^{-1/2}$$

(2.6)

where: $\psi$ is the dimensionless kinetic parameter and is tabulated at a fixed temperature for a one step, one electron transfer process as a function of $\Delta E_p$ (Tabulated values of $\Delta E_p$ with $\psi$ can be found in the work by Nicholson [82]), $k_s$ is the standard rate constant for electron transfer (cm s$^{-1}$), $D$ is the diffusion coefficient of active species (cm$^2$ s$^{-1}$), $n$ is the number of electrons, $v$ is the scan rate (V s$^{-1}$), $T$ is temperature (K), $R$ is the universal gas constant (8.315 J K$^{-1}$ mol$^{-1}$), $F$ is the Faraday constant (96 485 A s mol$^{-1}$).

The $\Delta E_p$ values determined by cyclic voltammetry at a fixed scan rate can be used to estimate $\psi$ and the standard rate constant ($k_s$) can be determined by equation (2.6). As an approximation a redox reaction could be classified into the following reversibility regimes in terms of $\Delta E_p$: 


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- **Reversible:** $\Delta E_p = \frac{59}{n} \text{ mV}$
- **Quasi-reversible:** $59 < \Delta E_p < 210 \text{ mV}$
- **Irreversible:** $\Delta E_p > 210 \text{ mV}$

These approximations were used as a guideline in this work to evaluate the reversibility of the vanadium (V) reduction and vanadium (II) oxidation reactions at different electrode surfaces.

2.1.2 **Electrochemical impedance spectroscopy**

Another technique used in this work to study the processes occurring at the electrode/electrolyte interface was electrochemical impedance spectroscopy. EIS measurements are carried out using an ac perturbation over a range of frequencies. In direct current (dc) theory, where frequency is zero, resistance is defined by Ohm’s Law:

$$R(\Omega) = \frac{E}{I} \quad (2.7)$$

where: R is resistance (Ω), E is potential in (V) and I is current in (A).

In this case only resistors impede the flow of current. In alternating current (ac) theory where frequency is non-zero, ‘impedance’ is the ac equivalent of resistance. In addition to resistors, capacitors and inductors also impede the flow of current in an ac circuit. Therefore, the total impedance is the combined opposition of resistors, capacitors and inductors to the flow of electrons. The analogous equation is the impedance (Z) given by equation (2.8):

$$Z(\omega) = \frac{E(t)}{I(t)} \quad (2.8)$$

where: Z is the impedance (Ω), E is potential (V) and I is current in (A).

Impedance is usually measured by applying an ac potential to an electrochemical cell and measuring the current response as a function of frequency. Small amplitude excitation signals are used (5 to 10 mV) which cause only minimal perturbation of the system and thus reduce errors caused by the technique. The frequency limit is generally limited to $1 \times 10^2$ to $5 \times 10^4$ Hz [83]. If a sinusoidal potential excitation is applied to the system, the response will be a sinusoidal current signal of the same frequency but shifted in phase. The potential excitation signal as a function of time has the form:

$$E(t) = E_0 \sin(\omega t) \quad (2.9)$$
where: \( E(t) \) is the instantaneous potential at time \( t \) (V), \( E_0 \) is the maximum amplitude (V), \( \omega \) is the radial frequency (Hz) and \( t \) is time (s).

The current response to this perturbation is described by equation (2.10):

\[
I(t) = I_0 \sin(\omega t + \theta)
\]  
(2.10)

where: \( I(t) \) is the instantaneous current at time \( t \) (A), \( I_0 \) is the maximum amplitude (A), \( \omega \) is the radial frequency (Hz) and \( t \) is time (s) and \( \theta \) is the phase shift (radians).

Substituting equations (2.9) and (2.10) into equation (2.8), the impedance \( (Z) \) takes the following form:

\[
Z(\omega) = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \theta)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \theta)}
\]  
(2.11)

The impedance can be expressed as a vector in terms of a magnitude \( (Z_0) \) and phase shift \( (\theta) \). Another form of representation which is often more convenient for numerical analysis is the complex number notation. A complex number is made up of a real and imaginary component which can be expressed as a single number, \( z \):

\[
z = a + bj = e^{j\theta}
\]  
(2.12)

where: \( j = \sqrt{-1} \), \( a= \) real part of \( z \) and \( b= \) imaginary part of \( z \).

Euler’s formula is used to convert equation (2.11) to complex form

**Euler’s formula:** \( e^{j\theta} = \cos\theta + jsin\theta \)  
(2.13)

Thus the impedance in equation (2.11) can be expressed by a complex function as a sum of its ‘real’ and ‘imaginary’ parts:

\[
Z(\omega) = \frac{E(t)}{I(t)} = \frac{E_0 e^{j\omega t}}{I_0 e^{j(\omega t - \theta)}} = Z_0 e^{j\theta} = Z_0 (\cos\theta + jsin\theta) = Z' + Z''j
\]  
(2.14)

where: \( Z' = \) real part of \( Z \) and \( Z'' = \) imaginary part of \( Z \).

**Electrical circuit elements**

EIS data is typically analysed by fitting the data to an equivalent electrical circuit model. The different electrical circuit elements and their corresponding symbols used to model EIS data in this work are summarised in Table 2.1.
2. Experimental methods and techniques

Table 2.1 - Equivalent circuit elements and corresponding circuit symbols.

<table>
<thead>
<tr>
<th>Circuit element</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>![Resistor Symbol]</td>
</tr>
<tr>
<td>Capacitor</td>
<td>![Capacitor Symbol]</td>
</tr>
<tr>
<td>Warburg</td>
<td>![Warburg Symbol]</td>
</tr>
</tbody>
</table>

In an electrochemical system several phenomena can impede the flow of electrons including: the rate of electron transfer at the electrode surface and diffusion processes. The system can be modelled by a number of different circuit elements. An electrochemical system consisting of (i) a double layer capacitance (C<sub>DL</sub>), (ii) an electron transfer resistance (R<sub>ct</sub>) and (iii) uncompensated electrolyte resistance (R<sub>s</sub>) is illustrated in Figure 2.4. The so-called Randles circuit is typically used to model the electrochemical impedance of an interface involving these three phenomena.
Figure 2.4 Illustration of the electrode/electrolyte interface in a simple electrochemical system showing the corresponding electrical circuit elements which model (i) a capacitor (CDL) which models the double layer capacitance at the interface, (ii) a resistor which models the charge transfer resistance of the electron transfer process occurring at the electrode surface ($R_{ct}$) and (iii) the uncompensated solution resistance between the working and reference electrode ($R_s$).

**Data representation – Nyquist plot**

One common form of impedance data representation is the Nyquist plot or complex impedance plot. In this form, the imaginary impedance component ($Z'$) is plotted against the real impedance component ($Z''$) at each excitation frequency. Figure 2.5 (a) illustrates a simple Nyquist plot for a system without mass transport resistance.
2. Experimental methods and techniques

Figure 2.5 Nyquist impedance plots for (a) a system without mass transport resistance indicating the kinetically controlled region and (b) an equivalent circuit with mass transfer resistance showing the Warburg impedance element and corresponding linear feature at low frequencies in the ‘diffusion controlled region. $R_s$ is the solution resistance, $C_{DL}$ is the double layer capacitance and $R_{ct}$ is the charge transfer resistance (see Figure 2.4).

Figure 2.5 (a) is typical of an electrochemical process limited entirely by charge transfer resistance ($R_{ct}$) and solution resistance ($R_s$). In the high frequency region (left side of the plot) the impedance of the cell is almost entirely created by the solution resistance ($R_s$). The x-intercept in this case corresponds to the value of the solution resistance ($R_s$) in the cell. In the low frequency region (right side of plot), the intercept is equal to the sum of the solution resistance and the charge transfer resistance ($R_s + R_{ct}$). The diameter of the semi-circle is therefore the total resistance due to charge transfer ($R_{ct}$). In the ideal case, the semi-circle is perfectly centred on the x-axis (a perfect geometric semi-circle). In reality, the circle is not always perfectly centred and may be shifted by a so-called ‘depression angle’. This rotation in the complex plane can be accounted for by using different mathematical models. The most frequently used model in this case is the constant phase element (CPE). Equation (2.15) gives the relationship between the CPE ($Q$) and capacitance ($C$).

$$C = Q\omega^{(a-1)}$$ (2.15)

where: $a$ is a dimensionless parameter $0 < a < 1$, $a=1$ corresponds to an ideal capacitor, $Q$ is a constant with units mF.s$^{(a-1)}$, $\omega$ is the frequency (Hz) corresponding to the apex of the Nyquist plot.

The CPE is often used in place of the ideal capacitor as it accounts for non-idealities in the system including surface inhomogeneities such as surface roughness and impurities.
Another mathematical model used in EIS was developed by Warburg to account for resistance to mass transfer in the system. The Warburg element typically exhibits a 45° phase shift which is halfway between that of a resistor (0° phase shift) and a capacitor (90° phase shift). Figure 2.5 (b) shows a Nyquist plot which includes mass transport resistance. There are two distinct regions in the Nyquist plot, a semicircle at high frequency whose radius depends on the charge transfer resistance \((R_{ct})\) and a sloped line in the low frequency region associated with the Warburg impedance \((W)\).

There are several advantages to using the Nyquist representation, specifically the visual aspect which makes it easy to see the effects of ohmic resistance by reading off the x-axis. Furthermore, the general shape of the plot also gives an idea of the dominant processes occurring in the system. Another form of data representation not used in this work is the Bode plot which plots the impedance with the logarithm of frequency on the x-axis and both the absolute values of impedance \((|Z| = Z_0)\) and the phase shift \((\theta)\) on the y-axis. Unlike the Nyquist representation the Bode plot shows frequency information. The Nyquist representation of EIS data was used in this work.

### 2.1.3 Electrochemical cell setup and measurement conditions

The cyclic voltammetry and EIS measurements for the reactions in this work were carried out in a typical three-electrode configuration coupled with a Biologic SP-300 potentiostat. This setup employs a counter electrode (CE), a reference electrode (RE) and a working electrode (WE) combined in a glass cell with two side compartments. The counter electrode was separated from the main compartment containing the WE by a glass frit. This was necessary so products formed at the counter electrode did not mix with the bulk solution in the main compartment. A schematic of the electrochemical cell is shown in Figure 2.6.
2. Experimental methods and techniques

Figure 2.6 - Typical three-electrode setup used in this work showing working electrode (WE), reference electrode (RE) and counter electrode (CE).

In the three-electrode setup, the WE is the electrode of interest on which a given electrochemical reaction is being studied. The RE monitors the potential of the working electrode and does not allow any current to pass through it. It is generally placed in close proximity to the WE surface. The CE completes the circuit path of current flow in the electrochemical system. A Hg/HgSO$_4$ (C3 Prozess - und Analysentechnik GmbH) RE and a platinum mesh CE were employed for all measurements in this work. The WEs studied here were carbon based materials, for example glassy carbon or edge and basal plane pyrolytic graphite disk electrode modified by different treatment methods (details of electrodes and treatment methods can be found in section 2.4). All potentials are reported versus the reversible hydrogen electrode (RHE). The above setup was used to study the kinetics and reversibility of the two discharge reactions occurring in the VRB system:

$$V^{2+} \rightarrow V^{3+} + e^- \quad (2.16)$$

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \quad (2.17)$$

Prior to each experiment, the electrolyte was de-aerated by bubbling with argon for 20 min. The argon atmosphere was maintained in the electrochemical cell during measurements. All cyclic voltammograms were corrected for ohmic resistance during data analysis by subtracting the corresponding solution resistance ($R_s$) measured by EIS. Detailed experimental procedures for the model electrode studies can be found in chapter 3 and chapter 4.
2. Experimental methods and techniques

2.2 Differential electrochemical mass spectrometry (DEMS)

2.2.1 Principle of operation

DEMS is an analytical technique that combines electrochemical half-cell experiments with mass spectrometry. By this method it is possible for in-situ detection of gaseous electrochemical reaction intermediates or products. In a typical electrochemical experiment (e.g. CV) only a total faradaic current is measured. This faradaic current may however be made up of a number of different currents coming from different electrochemical reactions occurring at the same time in the system. If one of the reactions produces a gaseous product, this can be detected by the mass spectrometer and ultimately the contributions of the different reactions to the total faradaic current can be determined. This is the case for the V(II)/V(III) reaction which occurs at the negative electrode in the VRB. The V(III) reduction reaction occurs at potentials below the standard potential for hydrogen evolution which is a parasitic reaction in the VRB. Thus these two reactions can occur at the same time in the system [86].

\[ 2H^+ + 2e^- \rightleftharpoons H_2 \quad E^0 = 0 \text{ V vs. SHE} \quad (2.18) \]

\[ V^{3+} + e^- \rightleftharpoons V^{2+} \quad E^0 = -0.26 \text{ V vs. SHE} \quad (2.19) \]

Using DEMS it was possible to separate the contributions of the two reactions to the overall faradaic current and calculate the faradaic efficiency (FE). The faradaic efficiency for V(III) reduction is defined as follows:

\[ FE \ (V(III)/V(II)) = \frac{I^F_{V(III)/V(II)}}{I^F_{Total}} \quad (2.20) \]

\[ I^F_{Total} = I^F_{V(III)/V(II)} + I^F_{HER} \quad (2.21) \]

where: \( I^F_{V(III)/V(II)} \) is the faradaic current originating from the V(III) reduction reaction, \( I^F_{HER} \) is the faradaic current from the hydrogen evolution reaction and \( I^F_{Total} \) is the total measured faradaic current.

The components of the DEMS setup used in this work are highlighted in Figure 2.7. The three main components include: the electrochemical half-cell, the PTFE membrane and the vacuum system linked to the quadrupole mass spectrometer (QMS).
2. Experimental methods and techniques

![Figure 2.7 - DEMS setup showing the main system components.](image)

The electrochemical half-cell contains the WE on which the electrochemical reaction takes place. The reactants flow to the electrode surface and the products of the reaction are then transported to the membrane interface. The membrane interface consists of a PTFE membrane separating the liquid reactants from the vacuum system required for the QMS. The membrane allows dissolved gaseous species to pass through it, evaporating into the vacuum system. The gaseous species are then transported to the mass spectrometer and observed online by monitoring the relevant mass ion currents. The DEMS was used to determine the faradaic efficiencies of V(III) reduction at oxidised edge and basal plane electrodes by determining the amount of hydrogen gas produced during the reaction (see section 4.2).
2.3 Full-cell characterisation

2.3.1 Redox flow cell setup

A commercial redox flow test system (Model 857, Scribner®) was used for all full-cell measurements in this work. An overall view of the system is depicted in Figure 2.8 (a). The main components of the system are: the electrochemical cell, two peristaltic pumps to supply electrolyte to each side of the cell and two electrolyte storage reservoirs. The components of the cell itself are shown in Figure 2.8 (b), the cell consists of two electrodes (in this case commercially available carbon felt) separated by a polymer-based ion exchange membrane (Nafion®117), two graphite triple serpentine flow fields for optimal electrolyte distribution, two polytetrafluoroethylene (PTFE) frames used as spacers between the electrodes and flow fields and two copper plate current collectors. All these components are fixed between two end plates with fixed liquid connections where the electrolytes enter the cell.

![Figure 2.8](image-url) (a) Scribner® Redox flow cell test system (b) key cell components.
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2.3.2 **Polarisation curve analysis**

Polarisation curves are an analytical technique commonly used in the field of fuel cells to gain information related to overall system performance [87]. This analysis can also be applied to flow cells. Figure 2.9 (a) shows typical charge and discharge polarisation curves obtained in a VRB system.

![Polarisation curves](image)

**Figure 2.9** – (a) charge and discharge full-cell polarisation curves for a VRB system (b) discharge polarisation curve showing the overpotential contributions from the positive and negative half-cell reactions to the total overpotential.

The total overpotential losses are indicated by the shaded regions in Figure 2.9 (a) and are made up of activation, ohmic and concentration overpotentials. In this work the primary goal was understanding and separating the overpotential contributions of the V(V) reduction reaction and V(II) oxidation reaction to the total overpotential measured for the full-cell. In order to do this a reference electrode was required in the system. A Hg/Hg$_2$SO$_4$ reference electrode (C3 Prozess - und Analysentechnik GmbH) was connected to the cell in an 'edge-type' configuration in which an extension of the Nafion®117 membrane was placed in contact with the reference electrode [88–90]. The junction region was kept hydrated with a 2 mol L$^{-1}$ H$_2$SO$_4$ solution. Figure 2.9 (b) illustrates a typical polarisation curve measured for a VRB in which the overpotential contributions of the positive and negative half-cell reactions are shown. The difference between the potential measured at a given current density ($j$) for the positive and negative half-cell reactions is equal to the overall cell voltage at current density, $j$ as indicated in Figure 2.9 (b) where:
\[ E_{\text{Full-cell}}(j) = E_{\text{positive}}(j) - E_{\text{negative}}(j) \] (2.22)

where: \( E_{\text{Full-cell}}(j) \) is the cell voltage at current density \( j \), \( E_{\text{positive}}(j) \) is the positive half-cell potential at current density \( j \) and \( E_{\text{negative}}(j) \) is the negative half-cell potential at current density \( j \).

It is clear from Figure 2.9 (b) that minimising overpotential losses from both positive and negative half-cells will result in a greater available cell voltage for the system and ultimately a greater power density \( (P= I.\Delta V) \). This polarisation curve analysis was used in chapter 5 to identify the limiting half-cell reaction in the VRB system. It was also used to study the influence of heat treatment of commercial carbon materials on overall cell performance and decouple the overpotential contributions of the positive and negative half-cell reactions.

### 2.3.1 Measurement conditions

**Polarisation curve measurements**

The polarisation curve analysis described previously was used to evaluate the overall performance of the system under realistic operating conditions. Since a possible application of the VRB is as a power delivery device, the cell performance was evaluated in discharge mode. In the Scribner\textsuperscript{®} test system, the electrolyte containing the active species is pumped through the cell where the reactions take place. The spent or used electrolytes that exit the cell from the positive and negative sides are then recirculated back to the electrolyte storage tanks. From here the electrolytes are fed back into the cell and the system operates with a continuous recirculation of electrolytes during operation.

In this mode of operation, the state of charge (SoC) of the electrolyte is continuously changing and is not at 100% during the polarisation measurements. To guarantee a 100% SoC of reactant throughout the measurement and eliminate any possible influences of changing SoC, a so-called ‘single pass’ method was used. In this single pass method, fully charged electrolytes enter and pass through the cell without being recirculated. The discharged electrolytes are collected externally in two separate containers as illustrated in Figure 2.10. This method allows higher measurement accuracy as the effects of changing state of charge which occur upon recirculation are eliminated.
2. Experimental methods and techniques

Figure 2.10 - Redox flow cell setup for single pass polarisation curve measurement.

Discharge polarisation curves were recorded galvanostatically with freshly charged electrolytes (100% SoC) at an electrolyte flow rate of 30 mL min\(^{-1}\). Data points were measured at different current densities ranging from 0 to 260 mA cm\(^{-2}\) holding for 20 seconds at each point. The current limit of this system was 280 mA cm\(^{-2}\) which is why the measured polarisation curves do not enter the mass transport limited region. However, since this work was primarily focused on the activation region and the kinetic effects of electrode modification, this was not an issue.

**Electrolyte preparation**

V(IV) solution was prepared by dissolving 1 mol L\(^{-1}\) VOSO\(_4\)\(\cdot\)nH\(_2\)O (Alfa Aesar 99.9%, where \(n = 3\) determined by thermogravimetric analysis) in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) (Sigma Aldrich 99.999%). Vanadium solutions in other oxidation states i.e. V(II) and V(V) were prepared by electrolysis of the as prepared V(IV) solution in the Scribner\(^{\circledR}\) redox flow cell test system. To achieve this, a double volume of V(IV) solution was needed at the positive side where V(IV) is oxidised to V(V), in order to balance the electrons required at the negative side to reduce V(IV)→V(III)→V(II). The solutions were considered to be fully charged (100% SoC) when the current density reached a value of 2 mA cm\(^{-2}\). To attain greater precision in electrolyte preparation, a commercially available 1.6 mol L\(^{-1}\) vanadium electrolyte solution supplied by OXKEM\(^{\circledR}\) (50:50, V(III): V(IV) in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\)) was employed to produce the V(V) and V(II) solutions. In this case equal volumes of
2. Experimental methods and techniques

OXKEM® electrolyte could be used at either side of the cell and the same electrolysis process was carried out to produce V(V) and V(II). Experimental sections in each chapter contain details of which electrolyte was used in the given study.

**Stability measurements**

Long-term electrode durability tests were carried out by extended charge/discharge cycling at constant current densities ranging from of 40 mA cm$^{-2}$ to higher values of 100 and 120 mA cm$^{-2}$ at 30°C, at a flow rate of 30 mL min$^{-1}$. The upper and lower cell voltage cut-off limits were set to 1.7 V and 0.8 V respectively. Coulombic efficiency (CEff), voltage efficiency (VEff) and energy efficiency (EEff) were calculated from the 2nd cycle [91]. The CEff efficiency is the ratio of the cells discharge capacity ($Q_{dis}$) divided by the charge capacity ($Q_{ch}$), in constant current (I) mode CEff can be described by ratio of the discharge time ($t_{dis}$) divided by the charge time ($t_{ch}$), equation (2.23).

$$CEff = \frac{Q_{dis}}{Q_{ch}} \times 100\% = \frac{I t_{dis}}{I t_{ch}} \times 100\% = \frac{t_{dis}}{t_{ch}} \times 100\% \quad (2.23)$$

The VEff is described by the cells mean discharge voltage ($V_{dis}$) divided by the cells mean charge voltage ($V_{ch}$) in equation (2.24). The EEff is the product of the CEff and VEff and is an indicator of the energy loss during the charge/discharge process, equation (2.25).

$$VEff = \frac{V_{dis}}{V_{ch}} \times 100\% \quad (2.24)$$

$$EEff = VEff \times CEff \quad (2.25)$$

2.4 Electrode treatment methods

2.4.1 Model carbon electrodes

Half-cell studies carried out in the three-electrode setup employed model electrodes to study the V(V) reduction and V(II) oxidation reaction kinetics. The electrodes were carbon based disk inserts compatible with the standard E4 series rotating disk electrode (RDE) tips from Pine Instruments Co. Three types of model electrodes were used in this work:
2. Experimental methods and techniques

(i) **Glassy carbon (GC)** (Sigradur®, pyrolysed at 1000°C, 5 mm outer diameter x 4 mm thickness, mirror polished).

(ii) **Basal plane pyrolytic graphite** (Pine Research®, 5.0 mm outer diameter, including 1 mm epoxy shroud).

(iii) **Edge plane pyrolytic graphite** (Pine Research®, 5.0 mm outer diameter, including 1 mm epoxy shroud).

Five different surface treatment methods were used to study the influence of surface modification on reaction kinetics of the two discharge reactions. The treatment methods can be separated into three categories: oxidative, non-oxidative and mixed treatment as depicted in Figure 2.11.

![Figure 2.11 - Categories of surface modification: oxidative, non-oxidative and mixed treatments.](image)
2. Experimental methods and techniques

(i) **Thermal oxidation**: was carried out at 400 °C in a tube furnace under O\textsubscript{2} atmosphere for 1 h, O\textsubscript{2} flow rate of 30 mL min\textsuperscript{-1} [38].

(ii) **Acid treatment**: was carried out in a 3:1 concentrated H\textsubscript{2}SO\textsubscript{4}/HNO\textsubscript{3} (Sigma Aldrich 99.999%) solution at 60 °C for 30 min.

(iii) **Electrochemical oxidation**: carried out in 2 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} solution, by potential holding at 2.2 V/RHE for 5 min followed by another potential holding at 0.1 V/RHE for 30 s, at a rotation rate of 1000 rpm to dislodge bubbles from the surface [49].

(iv) **Surface roughening**: Mechanical surface modification was carried out by manual polishing on an abrasive sandpaper surface (3M\textsuperscript{TM} sandpaper, Grit size-600).

(v) **Mixed treatment**: was a combination of mechanical surface roughening followed by electrochemical oxidation.

Glassy carbon electrode studies detailed in Chapters 3 employed all five treatment methods to study V(V) reduction reaction kinetics. In chapter 4 a similar study was carried out for the V(II) oxidation reaction, however in this study thermal oxidation which was found to have very little effect on the glassy carbon surface, was omitted. The edge and basal plane pyrolytic graphite electrode studies employed only the electrochemical oxidation to modify the electrode surfaces (chapter 4). Further details can be found in the experimental sections of the respective chapters.

2.4.2 Porous carbon electrodes

Full-cell studies performed in the Scribner\textsuperscript{®} redox flow cell test system were carried out using a number of commercially available PAN (polyacrylonitrile) based porous carbon electrode materials.

(i) SGL 39 AA carbon papers (thickness ~ 280 μm)

(ii) SGL 10 AA carbon papers (thickness ~ 360 μm)

(iii) Toray carbon papers (TGP-H-120) (thickness ~ 370 μm)

(iv) SGL SIGRACELL\textsuperscript{®} GFD4.6 EA carbon felt (thickness ~ 4300 μm)

The performance of the untreated and thermally treated materials were investigated and the thickness of the electrode materials was adjusted accordingly for comparison purposes (chapter 5). All electrode materials were treated by the same thermal oxidation method depicted in Figure 2.12.
2. Experimental methods and techniques

Figure 2.12 - Conditions for thermal oxidation of commercial carbon electrode materials.

The SGL 39 AA carbon papers and SGL SIGRACELL® GFD4.6 EA carbon felt were selected for further performance and stability investigations (chapter 5).

2.4.3 Carbon material properties

Carbon is a versatile element which can form many different structures. Properties of carbon materials can be broadly separated into (i) bulk properties which originate from the interior structure and (ii) surface properties which derive from surface chemistry and surface terminations [68]. The relationship between surface and bulk structure are of particular interest in electrochemistry, as they affect electrode kinetics and the interaction of molecules in solution with the electrode surface. A brief overview of the carbon materials used in this work will be given here, with an emphasis on their different structural properties.

(i) Graphite

Graphite is a crystalline allotrope of carbon with a layered, planar structure. Each layer consists of a number of hexagonal carbon rings with an inter-atomic distance between C-C atoms of 1.42 Å [92]. These individual layers are known as graphene. The graphene layers are stacked on top of each with an interlayer distance of 3.354 Å to form the highly ordered graphite structure illustrated in Figure 2.13 [92].
The carbon atoms within each graphite layer are sp$^2$ hybridised. The electronic configuration of carbon is 1$s^2$ 2$s^2$ 2$p^2$; in sp$^2$ hybridisation the 2$s$ orbital is mixed with two of the three available 2$p$ orbitals, forming a total of three sp$^2$ orbitals with one remaining p-orbital. Within each graphite layer, the three sp$^2$-hybrid orbitals are aligned in-plane and form three strong σ bonds with neighbouring carbon atoms. The remaining 2$p$-orbital overlaps with neighbouring 2$p$ orbitals from another carbon atom forming a π bond. The π bond is perpendicular to the graphene plane. This creates a delocalised π bonding system within each layer in which electrons can move around freely. Bonding between layers is via weak van der Waals forces, which allow layers to slide easily past each other.

Pyrolytic graphite is a highly ordered form of graphite. The pyrolytic graphite electrodes used in this work were supplied by Pine Research and were prepared by chemical vapour deposition [93]. The edge and basal orientations are illustrated in Figure 2.14 and are formed when a piece of pyrolytic graphite is cleaved either along the edge or basal plane.

**Figure 2.13** – Structure of (a) graphene and (b) graphite.

**Figure 2.14** – Edge and basal plane orientation of pyrolytic graphite.
The edge and basal planes differ significantly in their structural and electrochemical properties. The basal plane surface consists of 2-dimensional, flat graphite layers of sp² bonded carbons [94]. The edge orientation can contain a variety of different defect and step sites as well as oxygen terminations [94,95]. Edge sites have been reported to be more active to electron transfer, adsorption and chemical modification than the basal plane [68]. These two surfaces form a good basis for studying and understanding the electrochemistry of more complex carbon materials, as was done in this work (chapter 4).

(ii) Glassy carbon

Glassy carbon is an important variant of the graphite structure and was also used as a model carbon electrode surface in this work. It is made by thermal degradation of organic polymers, often polyacrylonitrile, in inert atmospheres at temperatures between 1000-3000°C [68]. The resulting carbon has a glass-like appearance and is typically very hard and brittle [96]. The disordered nature of glassy carbon makes structural characterisation rather difficult [68], however its structure is generally described as a network of randomly intertwined graphitic ribbons as can be seen in Figure 2.15.

![Figure 2.15 – Proposed structure of glassy carbon showing ribbon-like features (Reproduced from [97] with permission).](image)

(iii) Carbon felt and carbon papers

The commercial carbon electrodes used in this work are porous, carbon fibre-based fabrics such as carbon felts or carbon papers supplied by SGL Carbon Group. The detailed synthesis steps for both materials is not well-described by the company however there are a few basic details which are known. Carbon felt is manufactured by a pyrolysis process using a starting precursor such as polyacrylonitrile (PAN) [98]. A raw felt is produced which is then carbonised and graphitised [98]. The carbon papers used in this work are typically used as gas diffusion layers for fuel cell applications. The carbon fibres
in this case are made from PAN or cellulose starting precursors. The fibres are processed to a carbon fibre web using a wet-laying technology and undergo a series of carbonisation steps. In some cases a polymeric binder is added for mechanical stability [99]. SEM images showing the carbon fibre structure of both carbon felt and carbon papers used in this work are shown in Figure 2.16.

![SEM images of carbon felt and carbon paper](image)

**Figure 2.16** – SEM images of (a) SGL SIGRACEIL® GFD4.6 EA carbon felt and (b) SGL 39 AA carbon papers.

### 2.5 Physicochemical electrode characterisation

After the different oxidative and non-oxidative treatments described in section 2.4, it was important to investigate the changes in surface chemistry (oxygen functional groups) and structure of the carbon surfaces. These properties could have an influence on the electrochemistry and activity of the electrodes. In order to characterise the surface chemistry and structural properties of the carbon materials x-ray photo electron spectroscopy (XPS) Raman spectroscopy were used respectively. These techniques are described in detail in the following sections.

#### 2.5.1 X-ray photoelectron spectroscopy

XPS is a quantitative, surface sensitive technique used to analyse the chemical composition of a given sample. This is a high vacuum technique in which the surface of the sample is irradiated with an x-ray beam (typically Al-Kα, \( hv = 1486.6 \) eV or Mg-Kα, \( hv = 1253.6 \) eV). An x-ray photon hits the sample surface and transfers energy to a core-level electron in the sample. This core-level electron is then emitted with a kinetic energy (KE) dependent on the energy of the incoming x-ray (hv) and the binding energy (BE) of the atomic orbital from which it originates. This is the basis of the so-called photo-electric effect:
2. Experimental methods and techniques

\[ KE = hf - BE - \Phi_{spectrometer} \]  

(2.26)

where: KE is the kinetic energy of the emitted electron (eV), \( h \) is Planck’s constant \((6.636 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1})\), \( \nu \) is the frequency of the x-ray source (Hz), BE is the electron binding energy (eV), \( \Phi_{spectrometer} \) is the spectrometer work function.

The detector records the KE of the emitted electrons and the BE is calculated from equation (2.26). A typical XPS spectra plots the BE on the x-axis versus intensity on the y-axis. Each element produces a unique set of XPS peaks at characteristic binding energy values that directly identify the element that exists on the surface or of the material being analysed. Different binding energies correspond to the different core atomic orbitals in the atom of the element (1s, 2s, 2p, 3s etc.). the intensity of the peaks is related to the concentration of the element within a sampled region. In this work the relative amounts of oxygen to carbon were of interest and the O/C ratio was determined using this technique. Furthermore, the exact binding energy of an electron depends not only on the core level from which it is emitted but also on (i) the oxidation state of the atom and (ii) the local chemical environment. Any changes in (i) or (ii) result in small shifts in peak position in the spectrum known as ‘chemical shifts’. This idea forms the basis of the identification of different functional groups on the surface of a given sample.

In this work XPS was used to determine the surface oxygen to carbon ratio (O/C) and identify the different types of oxygen functional groups on the electrode surfaces. The measurements were performed using a VGESCALAB 220iXL spectrometer (Thermo Fischer Scientific) equipped with an Al-K\(\alpha\) monochromatic source (spot size: 500 mm; power: 150W) and a magnetic lens system. The base pressure of the system was 1 x 10^{-9} mbar and the electron emission angle was 90°. Survey spectra were initially recorded at low resolution, and subsequently high resolution spectra of the C1s and O1s peaks were collected to determine the surface oxygen to carbon ratio (O/C ratio) of the electrode samples. The different oxygen groups were identified by deconvolution of the carbon C1s peak using the appropriate chemical shifts values found in the literature, see Table 2.2 [43,100]. An example of the deconvolution of the carbon C1s spectra for an electrochemically oxidised basal plane pyrolytic graphite electrode sample used in this work is illustrated in Figure 2.17.
2. Experimental methods and techniques

Table 2.2 Peak assignment for deconvolution of the carbon C1s peak.

<table>
<thead>
<tr>
<th>Peak position (eV)</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>284.1</td>
<td>C-C</td>
</tr>
<tr>
<td>284.9</td>
<td>C-H</td>
</tr>
<tr>
<td>285.96</td>
<td>C-OR (including C-OH and O-C-O)</td>
</tr>
<tr>
<td>288.2</td>
<td>C=O</td>
</tr>
<tr>
<td>290.4</td>
<td>COOH</td>
</tr>
<tr>
<td>291.61</td>
<td>Shakeup satellite contributions</td>
</tr>
</tbody>
</table>

Figure 2.17 - Deconvolution of C1s spectra for an electrochemically oxidised glassy carbon sample.

2.5.2 Raman spectroscopy

Raman spectroscopy provides information about molecular vibrations that can be used for sample identification. This technique is based on the inelastic scattering (Raman scattering) of monochromatic light of a laser (typically in the visible, near infra-red or ultra violet range). The sample is illuminated with a laser beam and incident photons interact with the sample. Elastically scattered light with the same wavelength as the incident beam is filtered out (Rayleigh scattering). The inelastically scattered light which is typically very weak, is dispersed onto a detector. The energy of the inelastically photons can be either shifted up or down relative to the incident beam. This shift in energy is accounted for by the change in vibrational or rotational energy of the molecules in the sample. The Raman
2. Experimental methods and techniques

shift is reported in terms of wavenumbers (cm\(^{-1}\)) and is used to denote this shift in energy relative to the incident beam:

\[
\text{Raman shift (cm}^{-1}\text{)} = \left( \frac{1}{\lambda_0} - \frac{1}{\lambda_{\text{scattered}}} \right)
\]  

(2.27)

where: \(\lambda_0\) is the excitation wavelength and \(\lambda_{\text{scattered}}\) is the wavelength of the scattered light.

The vibrational frequencies are unique to a molecule's chemical bonds and symmetry and can therefore be used as a fingerprint to identify different molecules and structures. A typical Raman spectrum is a plot of the Raman shift or wavenumber on the x-axis versus the intensity on the y-axis. Raman spectroscopy is most sensitive to highly symmetric covalent bonds with little or no dipole moment \([101]\). As such it is a very useful tool for characterising carbon materials. There are a wide variety of different carbon materials and they are all similar from a molecular perspective being made up of C-C bonds. However, the orientation of these bonds varies in different materials. Every peak or 'band' in the Raman spectrum corresponds to a specific vibrational frequency of a bond within the molecule. There are two main signals of interest in the first order Raman spectrum of a carbon material, the D-band and G-band shown in Figure 2.18.

![Raman spectrum of edge-plane pyrolytic graphite from this work.](image)

The D-band occurs at \(\sim 1360\text{ cm}^{-1}\) and is a breathing mode of \(A_{1g}\) symmetry; this mode is forbidden in pure graphite and only becomes active in the presence of disorder. It therefore gives an indication of the defect concentration or “disorder” in the carbon material. The G-band occurring at \(\sim 1580-1600\) cm\(^{-1}\) relates to graphitic or “ordered”
domains in the carbon structure. It arises from the in-plane stretching of C-C bonds of sp² carbon systems (E₂g symmetry) [101–103]. The small peak at 1620 cm⁻¹, referred to as the D2-band is typically observed as a shoulder of the G-band peak and also accounts for structural disorder [104]. In general, the I_D/I_G intensity ratio can be used as a descriptor to assess the degree of amorphisation or graphitisation of a carbon material [105]. Raman spectroscopy was used to probe the near surface microstructure of the carbon materials studied in this work. For example, a graphene sheet, which only contains sp² bonded carbons exhibits only a sharp G-band peak and no D band [68]. Glassy carbon on the other hand which contains both graphitic and disordered domains in its structure exhibits distinct G and D band peaks in its Raman spectrum as well as relatively broad peaks related to disorder. In graphitic materials more disordered than GC, the D and G bands broaden further and begin to merge [102]. These different features were kept in mind when analysing Raman spectra of the different carbon materials in this work.

2.5.3 Ultra violet visible (UV-vis) spectroscopy

UV-vis absorbance spectroscopy measures the attenuation of a beam of light (in the UV-range) as it passes through a sample. The Beer-Lambert Law describes the relationship between the absorbance and concentration of the absorbing species, equation (2.28) [106].

\[ A = \varepsilon LC \]  

(2.28)

where: A is the absorbance, \( \varepsilon \) is the molar absorptivity, a physical constant of the substance (L mol⁻¹ cm⁻¹), L is the path length through the cell (where L= 1 cm) and C is the concentration (mol L⁻¹).

UV-vis was used to confirm the concentration of vanadium ions after charging the solutions in the Scribner® test system. A calibration curve for vanadium (V) solutions was determined by preparing a number of standard solutions of V(V) of known concentrations by dissolving vanadium pentoxide (V₂O₅) in 2 mol L⁻¹ H₂SO₄. The absorbance spectra were then measured as shown in Figure 2.19 (a). The absorption wavelength of V(V) occurs at 390 nm [106], at this wavelength the absorbance of each solution was determined and a plot of absorbance versus concentration was attained, Figure 2.19 (b).
2. Experimental methods and techniques

Figure 2.19 – (a) Absorbance spectra of different standard vanadium V(V) solutions in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) and (b) calibration curve of standard V(V) solutions showing absorbance as a function of concentration.

Due to sensitivity limitations of the instrument, the V(V) solutions obtained after charging in the Scribner\(^\text{"®}\) test cell were diluted by a factor of 10 before measuring their absorbance by UV-vis spectroscopy. Once the absorbance of the V(V) solutions of unknown concentration was measured, the concentration was determined using the calibration curve in Figure 2.19 (b). The values obtained were then multiplied by 10 to attain the actual concentration of V(V) ions in the undiluted solutions taken from the Scribner\(^\text{"®}\) cell after charging. The poor stability of V(II) solutions in air made it difficult to accurately measure absorbance of V(II) ions by UV-vis. Therefore it was assumed that the concentration of V(II) ions was the same as the concentration of V(V) ions at the end of the charging process.
Chapter 3. Positive electrode – V(V)/V(IV) redox couple

This chapter covers a detailed half-cell study of the vanadium (V) reduction reaction at model carbon electrodes. The electrodes were modified by oxidative and non-oxidative methods. The influence of oxygen content and different types of oxygen functional groups on activity was investigated. The influence of changes in carbon structure observable by Raman spectroscopy was also explored. Correlations between activity, oxygen content and carbon structural properties are discussed.

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3. Positive electrode – V(V)/(IV) redox couple

3.1 Abstract

This paper provides valuable insights into the kinetics of the vanadium (V) reduction reaction occurring at a glassy carbon (GC) model electrode surface treated by different oxidative and mechanical methods. Oxidative treatments were applied by thermal, acid and electrochemical means. Mechanical polishing on an abrasive sandpaper surface was used to prepare a rough GC electrode, this surface was also further electrochemically oxidised. The resulting surfaces were studied by x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Activity is defined in terms of peak potential separation (ΔE_p) and this descriptor was verified by EIS. No correlation between activity and oxygen to carbon ratio (O/C) or any specific oxygen functional group was found in this study. Raman spectroscopy revealed significant structural changes for GC electrodes treated by electrochemical oxidation and abrasive polishing. A correlation between structural disorder in GC and improvements in activity was observed. However, a limit of structural disorder exists, beyond which no substantial improvements in activity can be achieved.

3.2 Introduction

Redox flow battery (RFB) technologies have risen to prominence as a potential energy storage device for excess energy from renewable sources [12]. The all-vanadium system is one of the most well-researched technologies in the field. There are numerous full-size systems in operation around the world and research efforts into this technology are on the rise with several niche applications emerging [8,22,88]. Research is focused primarily on reducing overall material and component costs and improving system performance [23]. The design and optimisation of the carbon electrode materials has gained significant attention in this field over the past few years. Researchers have focused on improving electron transfer kinetics of the respective redox reactions by modifying the carbon electrode surface properties [11,38,51,54]. Improvements in electrode activity have been attributed to the presence of surface oxygen functional groups thought to serve as active sites, facilitating the electron transfer step. However, more recent studies have refuted the role of oxygen functionalities as electro-active sites. These studies suggest that there may be other factors affecting activity including surface wettability, carbon microstructure, roughness and surface area effects [72,74,78,107]. Correlations between carbon structure and sp² carbon content have been related to improvements in activity [74]. It has been shown by several authors that edge-sites are more active than basal sites for both V(II) oxidation and V(V) reduction [72,108,109]. These studies on different carbon surfaces have indicated that the kinetics of the vanadium redox reactions depend strongly on the
type of carbon used and on the preparation of the electrode surface itself [60,107]. While oxygen functionalities could play a role in improving wetting properties of the electrode surface, their role as electroactive sites remains unclear. The vast array of literature detailing kinetic studies on different carbon materials employing differing experimental conditions makes it difficult to compare and draw concrete conclusions on this topic. It is critical to gain a better understanding of the reaction kinetics of both the redox reactions involved in the system if the system is to be fully optimised.

It is the purpose of this study to systematically investigate the role of oxygen functional groups and carbon microstructure, on the activity for the V(V) reduction reaction. A model glassy carbon electrode surface was used in this study. The effects of oxygen functionalisation by three well-known oxygen treatment methods, on the activity of V(V) reduction was investigated. Mechanical polishing on an abrasive surface was used to prepare a rough GC electrode, this surface was also further electrochemically oxidised. Electrode activity was determined by cyclic voltammetry in terms of potential peak separation ($\Delta E_p$). EIS measurements were performed to validate the $\Delta E_p$ activity descriptor. Surface oxygen to carbon ratios (O/C) were determined by XPS and structural changes were probed by Raman spectroscopy. Correlations between activity, oxygen to carbon ratio (O/C) and carbon microstructure of the different GC surfaces in this study are discussed.

3.3 Experimental

3.3.1 Electrolyte preparation

The V(V) electrolyte was prepared by dissolving 1 mol L$^{-1}$ VOSO$_4$$\cdot$nH$_2$O (Alfa Aesar 99.9%, where n=3 determined by thermogravimetric analysis) in 2 mol L$^{-1}$ H$_2$SO$_4$ (Sigma Aldrich 99.999%). A commercial redox flow cell system (Scribner®) with a cell active area of 25 cm$^2$, carbon paper electrodes (Sigracet® GDL 39AA, Ion Power inc.) and a Nafion®117 membrane was used to charge the 1 mol L$^{-1}$ VOSO$_4$$\cdot$nH$_2$O solution to V(II) (negative electrode) and V(V) (positive electrode). The solutions were considered to be fully charged when the current density reached a value of 2 mA cm$^{-2}$. The concentration of the V(V) solution was determined by UV-visible spectroscopy (Metrohm® UV-visible spectrometer) to be 0.9 mol L$^{-1}$.

3.3.2 Electrode materials and treatment methods

Glassy carbon (GC) disk electrodes were purchased from Hochtemperaturwerkstoffe GmbH (Sigradur®, pyrolysed at 1000°C, 5 mm OD x 4 mm thickness, mirror polished).
All disk inserts were compatible with the standard E4 series RDE tips from Pine Instruments Co. The GC electrodes were treated by different oxidative and mechanical methods to produce six GC electrode samples including the pristine GC sample. Oxidative treatments were carried out following three standard oxidative treatment methods: (i) electrochemical oxidation in 2 mol L⁻¹ H₂SO₄ solution, by potential holding at 2.2 V/RHE for 5 minutes followed by another potential holding at 0.1 V/RHE for 30 seconds, while rotating at 1000 rpm [49] (ii) heat treatment at 400°C in a tube furnace under O₂ atmosphere for 1 hour [78] (O₂ flow rate 30 mL min⁻¹), (iii) acid treatment in a 3:1 concentrated H₂SO₄/HNO₃ (Sigma Aldrich 99.999%) solution at 60°C for 30 minutes [58]. Mechanical surface modification was carried out by manual polishing on an abrasive sandpaper surface (3M™ sandpaper, Grit size-600) to produce a rough GC surface. A second rough GC electrode was prepared and further electrochemically oxidised following the same method described previously. Two electrode samples were prepared by each treatment method, one electrode sample was characterised electrochemically and the other electrode sample was characterised by x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy without seeing any V(V) electrolyte. The nomenclature used throughout the text for the differently treated GC electrodes is summarised in Table 3.1.

Table 3.1 - Electrode sample names and corresponding nomenclature.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine glassy carbon</td>
<td>GC-P</td>
</tr>
<tr>
<td>Heat treated glassy carbon</td>
<td>GC-H</td>
</tr>
<tr>
<td>Acid treated glassy carbon</td>
<td>GC-A</td>
</tr>
<tr>
<td>Electrochemically oxidised glassy carbon</td>
<td>GC-EC</td>
</tr>
<tr>
<td>Rough glassy carbon</td>
<td>GC-R</td>
</tr>
<tr>
<td>Rough glassy carbon followed by electrochemical oxidation (mixed treatment)</td>
<td>GC-R+EC</td>
</tr>
</tbody>
</table>

3.3.3 Physical Characterisation

3.3.3.1 X-ray photoelectron spectroscopy (XPS)

The surface oxygen to carbon ratio (O/C) and the type of oxygen functional groups were investigated by XPS. The measurements were performed using a VG ESCALAB 220iXL spectrometer (Thermo Fischer Scientific) equipped with an Al-Kα monochromatic source (spot size: 500 μm; power: 150 W) and a magnetic lens system. The base pressure of the system was typically 1x10⁻⁹ mbar and the electron emission angle was 90°. A Shirley type background subtraction was applied and all curves were fitted according to a
Gaussian-Lorentzian function. Survey spectra were initially recorded at low resolution, and subsequently high resolution spectra of the C1s and O1s peaks were collected to determine the surface oxygen to carbon ratio (O/C ratio) for all electrode samples. Deconvolution of the C1s core level spectra was carried out fitting the following peaks: 284.1 eV, 284.9 eV, 285.96 eV, 288.2 eV, 290.4 eV and 291.61 eV which arise from C-C, C-H, C-OR (including C-OH and O-C-O), C=O, COOH and shakeup satellite contributions respectively [43,100] (see supplementary material Figure 3.7 for deconvolution of the C1s peak for each electrode).

3.3.3.2 Raman Spectroscopy
A Raman microscope (Labram HR800 Horiba-Jobin Yvon, Japan) with a He-Ne laser (632.8 nm) and a 50x objective (ULWDMS Plan 50, NA = 0.55, Olympus, Japan) was used to investigate the near-to-surface region of the GC electrodes in this study. The measurements were performed with a grating of 600 line/mm and a laser power of 20 mW. First order Raman spectra were recorded in the range 1000 to 2000 cm⁻¹.

3.3.4 Electrochemical characterisation
All experiments were carried out in a standard three-electrode setup using a platinum-mesh counter electrode and an Hg/Hg₂SO₄ reference electrode (Gamry instruments Inc.) at room temperature. The cyclic voltammograms (CVs) as well as electrochemical impedance spectroscopy (EIS) were recorded using a Biologic SP-300 potentiostat. Before each experiment, the electrolyte was de-aerated by bubbling with argon for 20 minutes. The argon atmosphere was maintained in the electrochemical cell during measurements. CVs of all electrodes were measured firstly in 2 mol L⁻¹ H₂SO₄ at 50 mV s⁻¹ between 0.05 and 1.0 V/RHE at a scan rate of 50 mV s⁻¹ (see Figure 3.8 in supplementary material). CVs were then recorded in 0.9 mol L⁻¹ V(V) 2 mol L⁻¹ H₂SO₄ electrolyte solution, scanning from 1.7 V/RHE to 0.5 V/RHE at 50 mV s⁻¹ recording the third scan. A fresh V(V) solution was used before each CV measurement. All CVs were corrected for ohmic resistance, with a typical resistance of 3 ohms being measured for all CVs measured in vanadium (V) solution. All CV data is reported against the reversible hydrogen electrode scale (RHE). Impedance spectra were recorded with a voltage amplitude of 10 mV in the frequency range of 1 MHz - 50 mHz in potentiostatic mode at ~10 mV overpotential for the V(V) reduction reaction. The experimental data were fitted to the equivalent electrical circuit by a randomize-simplex procedure using Z Fit EC Lab® software.
3.4 Results and Discussion

3.4.1 Surface and structural characterisation

3.4.1.1 XPS analysis

The results from the XPS analysis are summarised in Figure 3.1 showing the surface oxygen to carbon ratio of all the GC electrode samples in Figure 3.1 (a) and the contribution of each oxygen species to the total oxygen content in Figure 3.1 (b).

![Figure 3.1](image)

**Figure 3.1** - (a) Surface oxygen to carbon ratios (O/C) and (b) % contribution of each surface oxygen group to the total surface oxygen for pristine glassy carbon (GC-P), heat treated glassy carbon (GC-H), rough glassy carbon (GC-R), electrochemically oxidised glassy carbon (GC-EC), acid treated glassy carbon (GC-A) and rough glassy carbon followed by electrochemical oxidation (mixed treatment) (GC-R+EC).

No oxygen was introduced onto the surface of the heat treated GC electrode (GC-H) which showed a similar O/C ratio to the GC-P. A small amount of oxygen was introduced onto the GC-R after mechanical polishing. The surface O/C ratio increased the most for the GC-A, GC-EC and GC-R+EC electrodes after treatment, with the mixed treatment (GC-R+EC) showing the highest O/C ratio out of all the GC samples. Figure 3.1 (b) shows that the relative amounts of carbonyl (C=O) and carboxyl (COOH) groups increased in all samples after treatment except for the GC-R. The effect of surface oxygen groups on electrochemical activity for V(V) reduction will be discussed in the following sections.
3. Positive electrode – V(V)/V(IV) redox couple

3.4.1.2 Raman spectroscopy

Glassy carbon is a partially graphitised form of carbon suggested to have a turbostratic structure (i.e. layers of graphite-type microcrystallite regions connected by disordered regions) [102]. There are two main signals of interest in the first order Raman spectra of the carbon materials investigated here, namely the D-band and G-band. The D-band occurs at around 1360 cm$^{-1}$ and is associated with the defect concentration or “disorder” in the carbon material. The G-band occurring at ~1580-1600 cm$^{-1}$ relates to graphitic or “ordered” domains in the carbon structure [102,103]. In general, the $I_D/I_G$ intensity ratio is used as a descriptor to assess the degree of amorphisation or graphitisation of a carbon material [105]. In the case of transitions from nanocrystalline graphite towards amorphous carbons, a decrease in $I_D/I_G$ intensity ratio has been observed previously [103,110]. For amorphous carbons, D-band broadening is correlated with disorder in the carbon structure and is related to different distributions of clusters with different ring orders other than six [102,111,112]. Raman spectroscopy was used to probe any changes in the near surface microstructure of GC after the different treatment methods. Distinct G- and D-band peaks can be identified in the first order Raman spectra of all the GC electrodes shown in Figure 3.2. The D-band shows a higher peak intensity compared to the G-band in all samples ($I_D/I_G > 1$), this observation is in line with several literature studies on glassy carbon [43,68,113]. All $I_D/I_G$ intensity ratios (in terms of peak intensities) are summarised in Table 3.2 together with the corresponding FWHM as an indicator for peak width.
3. Positive electrode – V(V)/(IV) redox couple

**Figure 3.2** - Raman spectra of (a) GC-P, GC-H and GC-A (b) GC-R, GC-EC and GC-R+EC normalised to the G-band intensity maxima.

**Table 3.2** - I_D/I_G peak intensity ratios and peak widths (full width at half maximum, FWHM /cm^{-1}) from the Raman spectra of all GC sample electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>I_D/I_G</th>
<th>FWHM D-band / cm^{-1}</th>
<th>FWHM G-band / cm^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-P</td>
<td>2.21</td>
<td>60.3</td>
<td>67.2</td>
</tr>
<tr>
<td>GC-H</td>
<td>2.23</td>
<td>57.2</td>
<td>66.3</td>
</tr>
<tr>
<td>GC-A</td>
<td>1.96</td>
<td>66.1</td>
<td>67.5</td>
</tr>
<tr>
<td>GC-R</td>
<td>1.87</td>
<td>85.4</td>
<td>85.2</td>
</tr>
<tr>
<td>GC-EC</td>
<td>1.32</td>
<td>101</td>
<td>71.0</td>
</tr>
<tr>
<td>GC-R+EC</td>
<td>1.24</td>
<td>114</td>
<td>75.0</td>
</tr>
</tbody>
</table>

In the case of both the GC-A and GC-H no significant changes in the Raman spectra were observed in Figure 3.2 (a) relative to GC-P, only a slight decrease in the I_D/I_G ratio for the GC-A was seen. This suggests that both the acid and heat treatment methods were not aggressive enough to induce any significant structural changes observable by Raman spectroscopy. However, the Raman spectra of the GC-R, GC-EC and GC-R+EC samples in Figure 3.2 (b), show significant changes after treatment. The most noticeable changes in the Raman spectra of the three samples is the peak broadening and the consequent
decrease in the $I_D/I_G$ intensity ratio (Table 3.2). In this case, the decrease in $I_D/I_G$ ratio corresponds to an increase in amorphisation and disorder in the GC surface. The peak broadening of the D-band further confirms the defect introduction for these three samples [103]. The D and G-bands also begin to overlap and the region around 1500 cm$^{-1}$ begins to increase in intensity as the two bands merge. Sadezky and co-workers have previously assigned signals in this region to the amorphous part of the carbon structure [104]. Thus, the changes observed for these three surfaces result from an increase in the amorphous part of the carbon structure and an increase in structural disorder.

3.4.2 Electrochemical characterisation

3.4.2.1 Voltammetric behaviour of modified GC surfaces in V(V) solution

The V(V) reduction reaction:

$$\text{VO}_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$$

was investigated at the modified GC electrode surfaces in this study. Peak separation ($\Delta E_p$/mV) between anodic and cathodic peak potentials was used as the activity descriptor in this study. The reversibility limits proposed by Nicholson were used as a guideline for assessing activity [82]. All GC electrodes showed peak separation values greater than the theoretical value of 59/n mV, which indicates non-Nernstian behaviour [27] (see Table 3.3). Figure 3.3 (a) shows the CVs obtained on the oxygen treated GC electrodes and Figure 3.3 (b) shows the CVs obtained for the GC-R and GC-R+EC surfaces.
3. Positive electrode – V(V)/(IV) redox couple

Figure 3.3 - Cyclic voltammograms measured at 50 mV s⁻¹ in 0.9 mol L⁻¹ V(V)/2 mol L⁻¹ H₂SO₄ for GC electrodes subject to (a) oxidative treatments and (b) mechanical and mixed treatments.

Table 3.3 - Activity (∆E_p / mV) measured at 50 mV s⁻¹.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Activity (∆E_p / mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-R+EC</td>
<td>165</td>
</tr>
<tr>
<td>GC-R</td>
<td>184</td>
</tr>
<tr>
<td>GC-EC</td>
<td>186</td>
</tr>
<tr>
<td>GC-A</td>
<td>501</td>
</tr>
<tr>
<td>GC-H</td>
<td>700</td>
</tr>
<tr>
<td>GC-P</td>
<td>710</td>
</tr>
</tbody>
</table>

The GC-P, GC-H and GC-A show peak separations ∆E_p >210 mV and fall into the irreversible region, showing poor activity towards V(V) reduction. The GC-EC, GC-R and GC-R+EC electrodes showed the greatest improvements in activity after treatment (∆E_p < 210 mV) falling into the ‘quasi-reversible’ region. These three electrodes will be considered for further discussion.
3. Positive electrode – V(V)/V(IV) redox couple

3.4.2.2 Surface area effect on activity (ΔEₚ)

It should be clarified at this point that the peak separation descriptor (ΔEₚ) used here, is a purely kinetic parameter related only to the intrinsic catalytic properties of the electrode surface under investigation. Increases in the geometric surface area of a given electrode with a given intrinsic activity, will only contribute to an increase in the peak current intensity measured in a CV. The peak separation itself will remain unchanged. This concept is confirmed in Figure 3.4 which shows the peak current and peak separation values (ΔEₚ) for an electrode (GC-EC) which has its full geometric area exposed to the electrolyte and a second CV where only half the geometric area is exposed to electrolyte during the CV measurement (see supplementary information section 3.6.2 for detailed discussion).

![Figure 3.4 - Cyclic voltammograms measured at 50 mV s⁻¹ in 0.9 mol L⁻¹ V(V) for GC-EC with half (0.098 cm²) and the full (0.196 cm²) geometric electrode surface area exposed to the electrolyte.](image)

3.4.2.3 Electrochemical impedance spectroscopy (EIS)

EIS was used to further investigate and validate the kinetic processes occurring at the electrode/electrolyte interface for the three GC electrodes showing the best activities, ΔEₚ < 210 mV. The EIS spectra in Figure 3.5 are made up of two distinct regions, a semicircle at high frequency whose radius depends on the charge transfer resistance (Rₜ) and a sloped line in the low frequency region associated with the Warburg impedance (W) corresponding to diffusion processes. The experimental data were fitted using the equivalent electrical circuit shown in Figure 3.5. The equivalent circuit consists of an
3. Positive electrode – V(V)/(IV) redox couple

solution/electrolyte resistance ($R_s$), a charge transfer resistance ($R_{ct}$), a Warburg impedance element ($W$), and a constant phase element (CPE) denoted by ‘Q’. A CPE was used to model the double layer capacitance ($C_{DL}$) and account for the non-ideal behaviour of the capacitive elements due to surface inhomogeneity’s including surface roughness and impurities [84,85]. Equation (3.2) gives the relationship between the CPE (Q) and the $C_{DL}$. Table 3.4 summarises the parameters determined from the model.

$$C_{DL} = Q \omega^{a-1}$$  \hspace{1cm} (3.2)

where: ‘a’ is a dimensionless parameter $0 < a < 1$ and $a=1$ corresponds to an ideal capacitor, ‘Q’ is a constant with units mF.s$^{(a-1)}$, ‘$\omega$’ is the frequency (s$^{-1}$) corresponding to the apex of the Nyquist diagram [85].

Figure 3.5 - Nyquist impedance plots for GC-P, GC-EC, GC-R and GCR+EC electrodes recorded at 10 mV overpotential. Experimental data are shown by markers and the model fit is shown by the solid lines.
Table 3.4 - Equivalent electrical circuit parameters obtained from fitting experimental EIS data measured at 10 mV overpotential in 0.9 mol L\(^{-1}\) V(V)/2 mol L\(^{-1}\) H\(_2\)SO\(_4\) to the model circuit in Figure 3.5.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(R_s/\Omega \text{ cm}^2)</th>
<th>(R_{ct}/\Omega \text{ cm}^2)</th>
<th>(W/\Omega \text{ s}^{-1/2})</th>
<th>(Q/mF \text{ s}^{(a)})</th>
<th>(a)</th>
<th>(\chi^2 10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-P</td>
<td>1.2</td>
<td>30.2</td>
<td>66.4</td>
<td>0.25</td>
<td>0.80</td>
<td>24.8</td>
</tr>
<tr>
<td>GC-EC</td>
<td>0.9</td>
<td>9.2</td>
<td>33.0</td>
<td>0.94</td>
<td>0.76</td>
<td>3.0</td>
</tr>
<tr>
<td>GC-R</td>
<td>1.0</td>
<td>8.7</td>
<td>46.6</td>
<td>0.57</td>
<td>0.90</td>
<td>3.0</td>
</tr>
<tr>
<td>GC-R+EC</td>
<td>0.9</td>
<td>5.4</td>
<td>21.5</td>
<td>3.10</td>
<td>0.69</td>
<td>13.5</td>
</tr>
</tbody>
</table>

\(\chi^2\) - fit accuracy

The \(R_{ct}\) of the GC electrodes in Table 3.4 decreases in the order pristine GC-P > GC-EC > GC-R > GC-R+EC indicating that the electron transfer rate has improved on these three modified GC electrodes. Moreover, this trend in the \(R_{ct}\) is in line with the \(\Delta E_p\) activity descriptor adopted in section 3.4.2.1 and validates the activity trends observed in terms of \(\Delta E_p\). Looking at the low frequency region of the impedance spectra in Figure 3.5, all GC electrodes show nearly ideal Warburg behavior with a phase angle close to 45°. High \(W\) values are characteristic of systems, which exhibit variations in ion diffusion path lengths, resulting in lower access of electrolyte ions to the active electrode surface [114]. The \(W\) values for the treated electrodes shown here decrease in the order GC-R > GC-EC > GC-R+EC. This behavior could be related to an increase in surface wettability when oxygen species are introduced onto the surface. As previously discussed, the GC-EC and GC-R+EC showed higher O/C ratios after treatment compared to the GC-R. The corresponding low \(W\) values for these two electrodes with high O/C ratios suggest that the surface oxygen groups lead to better electrolyte accessibility to the electrode surface. Furthermore, the GC-R electrode shows a higher \(W\) value compared to the GC-EC and GC-R+EC. However, the charge transfer resistance is similar on these three surfaces. This suggests that differences in O/C ratios only contribute to the wetting properties of the surface (reflected by the \(W\) element) and do not play a catalytic role in the charge transfer process itself, this is in agreement with suggestions by previous authors [78,79].

3.4.2.4 Influence of surface O/C ratio and carbon microstructure of GC on V(V) reduction activity

It has been proposed by several authors that oxygen functional groups play a key role in facilitating the electron transfer process for V(V) reduction at carbon electrode surfaces [52,54,58]. More recent studies have negated the catalytic role of oxygen groups towards V(V) reduction, and have suggested that other properties such as surface roughness and
3. Positive electrode – V(V)/(IV) redox couple

carbon microstructure play a role in improving electrode kinetics [53, 74, 107]. In order to gain further insight into the properties affecting activity from this study, activity trends with O/C ratio and carbon structure were investigated. Plots of activity versus O/C ratio and D-band peak width are shown in Figure 3.6.

Figure 3.6 - Activity ($\Delta E_p$ / mV) versus (a) surface oxygen to carbon ratio (O/C) and (b) peak width of the D-Band from the Raman spectra measured as the FWHM (cm$^{-1}$) (the dotted line serves as a guide for the eye only)

It is clear from Figure 3.6 (a) that there is no direct correlation between O/C ratio and activity. The GC-EC, GC-R and the GC-R+EC surfaces show similar activities; however, the O/C ratios differ significantly on these three surfaces. Furthermore, XPS did not reveal any convincing trends relating activity with a specific oxygen functional group. An increase in both the carbonyl and carboxyl groups was observed for all treated electrode except the GC-R. However, GC-A and GC-H showed a much poorer activity compared to GC-EC and GC-R+EC despite an increase in the relative amounts of these two functional groups. This finding is in line with several recent studies which have suggested that oxygen groups may not play a key role in improving electrode kinetics for V(V) reduction and that other factors such as surface roughness, wettability and carbon microstructure could be more important [53, 74, 107].

Figure 3.6 (b) shows the correlation between the activity and the D-band peak width (FWHM). The peak width of the D-band was chosen as the parameter indicating a
structural change, as it can be directly linked to the introduction of defects and disorder into the GC structure [102,110,112]. The D-band broadening itself appeared to be most prominent for the three most active surfaces in this study. Figure 3.6 (b) confirms that higher activities were seen for GC samples which showed significant peak broadening of the D-band after treatment. In all three cases, the peak broadening was accompanied by a reduction in the D-band peak intensity, and a consequent lowering of the \( I_D/I_G \) ratio. Thus a similar trend could be drawn for activity and \( I_D/I_G \), where low \( I_D/I_G \) ratios correspond to high activities. However, this interpretation is less intuitive and low \( I_D/I_G \) ratios could be misinterpreted as an increase in order or graphitisation, which is not the case for GC in this study. Carbon structure appears to be an important property playing a key role in improving the electrode kinetics of GC towards the V(V) reduction reaction. The rough GC surface exhibited Raman features similar to the GC-EC, and GC-R+EC with observable D-band peak broadening and a lowering of the \( I_D/I_G \) ratio, again interpreted as defect introduction. The O/C was slightly greater than that of the GC-P. Thus, the significant activity improvement observed for this surface, suggests that defect introduction alone can improve V(V) reduction activity, and oxygen functionalities may not play a catalytic role for this reaction. However, oxygen functionalities may play a role in improving the mass transport properties and wetting of the GC surface as was suggested by the impedance spectroscopy interpretation in section 3.4.2.3.

Finally further electrochemical oxidation of the rough GC surface (GC-R+EC), resulted in an increase in surface oxygen to carbon ratio and a further D-band broadening observed by Raman spectroscopy. It is interesting to note here that despite even further changes in structural disorder and an increased O/C ratio on the GC surface, the peak separation is not drastically improved, similar observations were made in a study by Cao et al. [107]. However, a lower Warburg impedance value indicates an improvement in mass transport (see Table 3.4.). This again suggests a mass transport improvement perhaps due to the increased surface O/C ratios. The results shown here suggest that there is a limit of surface roughness or structural disorder of GC beyond which the activity is not improved significantly.

3.5 Conclusions

In this study, the effect of oxygen functional groups and carbon microstructural changes on V(V) reduction activity were studied on a glassy carbon model electrode surface. No direct correlation between V(V) reduction activity and surface oxygen to carbon ratio or any specific oxygen functional group was found for this system. Significant structural changes were revealed by Raman spectroscopy for electrodes subjected to electrochemical...
oxidation, abrasive polishing and a combination of the two treatments. All of these surfaces showed improved activities and reduced charge transfer resistances towards V(V) reduction. The structural changes were interpreted as a disruption of the GC structure by introduction of defects, confirmed by D-band broadening and lowering of the $I_D/I_G$ ratio.

It appears that the heat and acid treatments were not aggressive enough to induce substantial structural changes observable by Raman spectroscopy. The activity improvement observed for the GC-R surface suggests that defect introduction and structural changes alone can improve V(V) reduction activity, and the oxygen functionalities are not crucial to improving the catalytic activity of GC. Additional electrochemical oxidation of the rough GC, did not result in substantial activity improvements, despite a further change in structure and increased O/C ratio. A possible explanation for this is that there is a limit of roughness or defect exposure and disorder, beyond which the activity ($\Delta E_p$) cannot be further improved. Findings from this study complement a recent study by Cao et al. where surface roughness and defects were thought to play a role in activity for V(V) reduction [107]. The combination of electrochemical characterisation and Raman peak width analysis in this study has revealed valuable activity trends, which have not been seen previously by the commonly applied $I_D/I_G$ analysis.
3. Positive electrode – V(V)/V(IV) redox couple

3.6 Supplementary material

3.6.1 XPS analysis

Figure 3.7 shows the deconvolution of the C1s peak measured by XPS for all samples in this study.

![XPS deconvolution of C1s peak for all GC samples in this study showing peak assignments of different oxygen functional group.]

**Figure 3.7** – XPS deconvolution of C1s peak for all GC samples in this study showing peak assignments of different oxygen functional group.

3.6.2 Capacitance measurements

CV measurements in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) were carried out to investigate changes in the capacitance signals of the electrode surfaces after each treatment method. The capacitance is related to the total electrode surface area in contact with the electrolyte, it does not necessarily represent the electrochemically active surface area for the given reaction. The CVs in Figure 3.8 and the corresponding capacitance values in Table 3.5 show the relationship between capacitance as measured in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) and the corresponding cathodic peak current intensity from the CV measured in 0.9 mol L\(^{-1}\) V(V)/2 mol L\(^{-1}\) H\(_2\)SO\(_4\).
3. Positive electrode – V(V)/(IV) redox couple

**Figure 3.8** - Cyclic voltammograms for all treated and untreated GC electrodes measured at 50 mV s\(^{-1}\) in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\).

**Table 3.5** - Capacitance (C) measured in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) and peak current of sample i (\(i_i\)) measured in 0.9 mol L\(^{-1}\) V(V)/2 mol L\(^{-1}\) H\(_2\)SO\(_4\).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Capacitance of sample i</th>
<th>Cathodic peak current of sample i, (i_i)</th>
<th>Roughness factor (RF)</th>
<th>Normalised peak current</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-P</td>
<td>38 (\mu)F cm(^{-2}) \text{geometric}</td>
<td>3.1 mA</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>GC-H</td>
<td>255 (\mu)F cm(^{-2}) \text{geometric}</td>
<td>3.4 mA</td>
<td>6.7</td>
<td>1.08</td>
</tr>
<tr>
<td>GC-R</td>
<td>1229 (\mu)F cm(^{-2}) \text{geometric}</td>
<td>8.5 mA</td>
<td>32.5</td>
<td>2.71</td>
</tr>
<tr>
<td>GC-A</td>
<td>1403 (\mu)F cm(^{-2}) \text{geometric}</td>
<td>6.2 mA</td>
<td>37.1</td>
<td>1.99</td>
</tr>
<tr>
<td>GC-EC</td>
<td>5623 (\mu)F cm(^{-2}) \text{geometric}</td>
<td>12.4 mA</td>
<td>149</td>
<td>3.97</td>
</tr>
<tr>
<td>GC-R+EC</td>
<td>6243 (\mu)F cm(^{-2}) \text{geometric}</td>
<td>11.8 mA</td>
<td>165</td>
<td>3.77</td>
</tr>
</tbody>
</table>

Comparing the RF values and the normalised peak currents, it is clear that the cathodic peak current in this case does not scale with the capacitance. The peak separation (\(\Delta E_p\)) values however, have changed relative to the pristine GC for all the treated samples. This is an indication that the treatment methods do not simply induce a roughening effect that increases the geometric surface area of the glassy carbon, while maintaining the same intrinsic catalytic properties of the pristine glassy carbon. Rather, the surface properties of the GC samples have changed after each treatment, resulting in different surfaces with different intrinsic catalytic properties compared to the pristine GC (GC-P). Increases in
geometric surface area were shown to only affect the peak current density and not the peak separation (see section 3.4.2.2). Thus, improvements in activity ($\Delta E_p$) should be correctly assigned to catalytic surface properties of the electrode itself and not simply to an increased geometric surface area effect.
Chapter 4. Negative electrode – V(II)/V(III) redox couple

This chapter covers a detailed study of the kinetics of the V(II) oxidation reaction on model carbon electrode surfaces. Insights into activity and stability are gained in sections 4.1 and 4.2 respectively. Section 4.1 investigates the influence of surface oxygen groups on the V(II) oxidation activity. Section 4.2 presents a detailed study on the stability of oxidised edge and basal plane pyrolytic graphite electrodes in the potential range of the V(II)/V(III) reaction. Correlations between carbon material properties and electrode activity and stability are discussed.

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4. Negative electrode – V(II)/V(III) redox couple

4.1 Electrode activity for V(II) oxidation

4.1.1 Abstract

The role of surface oxygen groups on the kinetics of the V(II) oxidation reaction was studied on modified glassy carbon (GC) electrodes by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The reaction was found to be sensitive to the presence of oxygen groups on the electrode surface. Higher O/C ratios determined by x-ray photoelectron spectroscopy (XPS) corresponded to higher activities and lower charge transfer resistances measured in a 1 mol L\(^{-1}\) V(II) electrolyte. The stability of an oxidised GC surface was also investigated in a 1 mol L\(^{-1}\) V(II) electrolyte by potential holding and cycling experiments. It was found that after holding and cycling to successively more negative potentials up to -0.8 V/RHE, the electrode surface lost its initial activity.

4.1.2 Introduction

The surface chemistry and structure of the carbon electrodes used in the all-vanadium redox flow cell have been found to play a key role in improving the kinetics of both the V(II) oxidation and V(V) reduction reactions [52,58,74,107]. Significant efforts have been made to understand and optimise the surface properties of the carbon electrodes and identify the limiting half-cell reaction in this system [48,115]. A common approach to improving electrode performance has been the introduction of functional groups, particularly oxygen-containing groups onto the electrode surface. The observed improvements in electrode performance have been attributed to a wetting or surface area effect and/or a catalytic effect of these surface groups [52,60,78]. However, the exact role of surface oxygenated groups on the kinetics of both reactions is unclear and the limiting half-cell reaction is still a topic of debate. Contrary to reports that V(V) reduction has the slower reaction kinetics of the two redox reactions, recent studies have shown that the V(II) oxidation limits the overall cell performance [53,60,61,66,78,108,115–118]. It has also been suggested that surface oxides could play a catalytic role in improving the kinetics of this reaction [53,60,61,116]. Early studies by McDermott et al. showed that V(II) oxidation follows an inner-sphere reaction mechanism involving bridging of hydrated V(II) ions with the surface oxide groups [71]. While the catalytic role of surface oxides for V(II) oxidation in the all-vanadium system has been suggested by several authors, discrepancies still remain in the literature regarding this point. It is the purpose of this study to gain further insight into the influence of surface oxygen groups on the kinetics of the V(II) oxidation reaction. Glassy carbon electrodes treated by oxidative and surface roughening methods were used to study V(II) oxidation reaction kinetics by Cyclic
Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). Trends of activity vs. oxygen content determined by x-ray photo electron spectroscopy (XPS) were investigated. Finally, the stability of surface oxygen groups in the potential range of V(II/III) oxidation/reduction was studied.

4.1.3 Experimental

4.1.3.1 Electrolyte preparation
A 1 mol L\(^{-1}\) V(II) electrolyte solution was prepared by electrolysis of 1 mol L\(^{-1}\) V(IV) solution (\(\text{VOSO}_4 \cdot n\text{H}_2\text{O}\), Alfa Aesar 99.9%, dissolved in 2 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\), Sigma Aldrich 99.999%) using a commercial redox flow cell system (Scribner\(^{®}\)) and carbon paper electrodes (SGL39AA). The concentration of V(II) was confirmed by UV-visible spectroscopy (Metrohm\(^{®}\)) to be 1 mol L\(^{-1}\).

4.1.3.2 Electrode materials and treatment methods
Glassy carbon (GC) disk electrodes were supplied by Hochtemperaturwerkstoffe GmbH (Sigradur\(^{®}\) G, 5 mm OD x 4 mm thickness, mirror polished). The GC electrodes were treated oxidatively, by acid and electrochemical treatments and non-oxidatively by abrasive polishing on sandpaper (3M\(^{TM}\) Grit size-600). A mixed treatment involving abrasive polishing followed by electrochemical oxidation was also carried out (see reference [48] for detailed experimental conditions). Five GC electrode surfaces were investigated in this study using the same nomenclature as in our previous study on V(V) reduction [48]: pristine (GC-P), acid treated (GC-A), electrochemically treated (GC-EC), rough (GC-R) and mixed treatment (GC-R+EC).

4.1.3.3 Surface characterisation
X-ray photoelectron spectroscopy (XPS) was used to determine the oxygen content (O/C ratio) of the treated GC electrodes. A VG ESCALAB 220iXL spectrometer (Thermo Fischer Scientific) equipped with an Al K\(\alpha\) monochromatic source and a magnetic lens system was used. High resolution spectra of the C1s and O1s peaks were used to determine the surface oxygen to carbon ratio (O/C ratio) for all electrode samples. All curves were fitted according to a Gaussian-Lorentzian function. Background subtraction has been performed according to the Shirley method, and the atomic sensitivity factors (ASF) of Scofield were applied to estimate the atomic composition.

4.1.3.4 Electrochemical characterisation
Electrochemical measurements were carried out using a standard three-electrode setup with a platinum-mesh counter electrode and a Hg/Hg\(\text{SO}_4\) reference electrode (Gamry
4. Negative electrode – V(II)/V(III) redox couple

Instruments Inc.® at room temperature. Cyclic voltammograms (CVs) were recorded at 50 mV/s in an argon purged 1 mol L⁻¹ V(II) electrolyte and reported against the reversible hydrogen electrode (RHE). All CVs were corrected during data analysis for ohmic resistance. Electrochemical Impedance Spectroscopy (EIS) measurements were carried out at ~10 mV overpotential for V(II) oxidation with a voltage amplitude of 10 mV in the frequency range: 1 MHz - 50 mHz. The experimental data was fitted to the equivalent electrical circuit by a randomize-simplex procedure using Z Fit EC Lab® software. In order to assess the stability of an oxidised GC electrode in the potential range of the V(II)/V(II) redox couple, potential holding and cycling experiments were carried out in 1 mol L⁻¹ V(II) electrolyte. For potential holding measurements, the electrode was held at OCV for 10 seconds before recording the initial CV, then three negative potentials were applied successively to the electrode: -0.6, -0.7, -0.8 V/RHE for 10 seconds each. A CV was recorded after each potential holding step. Cycling experiments were carried out in two potential ranges: potential range 1 (∆E₁), from -0.6 to 0.2 V/RHE and potential range 2 (∆E₂), from -0.8 to 0.2 V/RHE. 150 cycles were recorded for each potential range. The surface oxygen content (O/C) was determined by XPS after the final potential holding step of -0.8 V/RHE and after cycling in ∆E₂.

4.1.4 Results and Discussion

4.1.4.1 Effect of electrode treatment on V(II) oxidation reaction kinetics

The V(II) oxidation reaction:

\[ \text{V}^{2+} \rightleftharpoons \text{V}^{3+} + e^- \]  

was studied at the modified GC electrodes to investigate the influence of surface oxygen groups on electrode activity. The peak potential separation (∆Eₚ) measured by CV and the charge transfer resistance (Rₜ) measured by EIS were determined to give an indication of electrode activity [27]. Figure 4.1 shows the CVs and Nyquist impedance plots of the pristine and modified GC electrodes measured in V(II) solution. The activity data is summarised in Table 4.1.
Figure 4.1 - Cyclic voltammograms measured at 50 mV s⁻¹ in 1 mol L⁻¹ V(II)/2 mol L⁻¹ H₂SO₄ for GC electrodes subject to (a) oxidative treatments and (b) abrasive polishing and mixed treatment (c) Nyquist impedance plots for all GC electrodes, markers show experimental data, solid lines show the fitted data using the equivalent electrical circuit diagram shown in the inset (d) activity (ΔEₚ) versus O/C ratio determined by XPS for all GC electrodes.
4. Negative electrode – V(II)/V(III) redox couple

**Table 4.1 - Summary of CV, XPS and EIS data**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>O/C ratio</th>
<th>Activity</th>
<th>$\Delta E_p$ /mV</th>
<th>$R_o$ /Ω cm$^2$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-R+EC</td>
<td>0.30</td>
<td>140</td>
<td>0.6</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>GC-EC</td>
<td>0.19</td>
<td>200</td>
<td>0.9</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>GC-A</td>
<td>0.23</td>
<td>240</td>
<td>1.7</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>GC-R</td>
<td>0.14</td>
<td>310</td>
<td>3.7</td>
<td>9.8E-3</td>
<td></td>
</tr>
<tr>
<td>GC-P</td>
<td>0.12</td>
<td>630</td>
<td>28</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

where: $R_o$ – charge transfer resistance, $\chi^2$ - fit accuracy

The GC-EC, GC-A and GC-R+EC electrodes showed the best activity towards V(II) oxidation. These surfaces showed the smallest $\Delta E_p$ values in Figure 4.1 (a) and 4.1 (b) and analysis of the impedance data in Figure 4.1 (c) revealed a decrease in the charge transfer resistance. This indicates an enhancement of the reaction kinetics of V(II) oxidation at these three surfaces. XPS analysis confirmed an increase in the oxygen content (O/C ratio) after treatment for these three surfaces (see Table 4.1). It is notable that the roughened GC electrode with a low O/C ratio, showed a poor activity towards V(II) oxidation. The small improvement in peak separation for GC-R compared to GC-P could be attributed to either a kinetic and/or a diffusional effect [119]. After electrochemical oxidation of the GC-R and a consequent increase in O/C ratio, a substantial improvement in activity was observed at the GC-R+EC surface. The effect of defect exposure by roughening the GC surface did not have the same positive effect on activity as was seen for the V(V) reduction reaction in our previous study [48]. Only after the introduction of surface oxygen groups was a notable activity improvement observed. A plot of oxygen content (O/C ratio) versus peak separation ($\Delta E_p$) in Figure 4.1 (d) indicates that the V(II) oxidation reaction is sensitive to the amount of oxygen present on the surface. Higher O/C ratios correspond to better activity and low $R_o$. The observations made here are in line with several earlier and more recent studies involving V(II) oxidation at oxidised carbon surfaces [53,60,71,120]. It was suggested previously that V(II) oxidation follows an inner-sphere reaction mechanism involving surface oxygen groups [120]. Thus, unlike V(V) reduction, V(II) oxidation appears to be sensitive to the presence of surface oxygen groups on the carbon electrode.
4. Negative electrode – V(II)/V(III) redox couple

4.1.4.2 Stability of surface oxygen groups

The V(II)/V(III) redox couple occurs at a standard redox potential of -0.26 V/SHE. This is well below 0V/SHE where it is common for an oxidised surface to undergo reduction processes [120]. It was seen in section 4.1.4.1 that the V(II) oxidation reaction is sensitive to the surface oxygen content. Thus the question of stability of an oxidised carbon surface in this potential range becomes crucial if oxidised electrodes are to be used in an applied system. The stability of an electrochemically oxidised glassy carbon surface was studied by potential holding and cycling experiments and the effect on peak separation ($\Delta E_p$) was studied (Figure 4.2).

![Cyclic voltammograms](image)

**Figure 4.2** - Cyclic voltammograms measured at 50 mV s$^{-1}$ in 1 mol L$^{-1}$ V(II)/2 mol L$^{-1}$ H$_2$SO$_4$ for a GC-EC electrode (a) subject to potential holding steps at OCV, -0.6, -0.7 and -0.8 V/RHE for 10 seconds per step and (b) 150 cycles in two different potential ranges $\Delta E_1$ and $\Delta E_2$, CVs show the 1$^{st}$ and 150$^{th}$ cycle.

The CVs in Figure 4.2 (a) show that after the first potential holding step at -0.6V/RHE, the peak separation has increased, indicating a loss in activity at the GC-EC surface. After progressive potentiostatic steps at -0.7 V/RHE and finally -0.8V/RHE, the peak separation grows larger and the surface loses its initial activity. This is in line with recent findings by Bourke et al. and Miller et al. [60,61]. Similarly, after cycling the GC-EC electrode in two different potential ranges, the electrode surface loses its initial activity. A larger peak separation is observed after 150 cycles in $\Delta E_2$ than $\Delta E_1$. Both these experiments highlight the detrimental effects of progressively more negative potentials on electrode activity. The O/C ratio decreased from 0.19 to 0.14 after potential holding at -0.8V/RHE and to 0.17 after cycling in $\Delta E_2$. The decrease in O/C ratio in both cases does
4. Negative electrode – V(II)/V(III) redox couple

not correspond directly with the decrease in activity. This is an indication that other surface phenomena such as passivation may also contribute to the loss in activity, as has been suggested previously [121]. Furthermore the type of carbon may also play a role in the observed stability of an oxidised carbon electrode. The same experiments carried out on an oxidised edge plane pyrolytic graphite electrode revealed more stable behaviour than the EC-GC under the same stability test conditions. Further studies on the stability of oxidised carbon surfaces is needed to better understand the nature of the potential degradation observed here. Nonetheless it is evident that the negative potential limit has a detrimental effect on the stability of an oxidised carbon surface. This finding is particularly relevant for applied systems in which the electrode at the V(II) side is exposed to negative potentials for extended periods of time during charging.

4.1.5 Conclusions

In this study, we have explicitly shown that improvements in the V(II) oxidation reaction kinetics observed by EIS and CV correspond to an increase in the total surface oxygen content (O/C). Furthermore, the stability of surface oxygen groups in the potential range of V(II) oxidation appears to be a critical issue. An oxidised GC surface loses its initial activity after a series of potentiostatic steps and cycling measurements. The negative potential limit seems to have a detrimental effect on the stability of an oxidised carbon surface and further investigations into the mechanisms behind this effect are required. Oxygen treatment may not be the most effective long-term solution to improving V(II) oxidation kinetics at the negative electrode in an applied system. The stability could be a decisive issue for long-term operation and alternative, stable surface treatments and materials should be explored. Nonetheless, there is still much to be learned regarding the mechanism of V(II) oxidation and the catalytic role of surface oxygen groups. Further understanding of the reaction mechanism will help in optimising and developing a more suitable and stable negative electrode material for this reaction.
4.2 Electrode stability

4.2.1 Abstract
The V(II)/V(III) reaction occurring at the negative electrode in the all vanadium redox flow battery has been identified as performance limiting in the system. Given the complexity of the commercial carbon electrodes typically used for this application, a model electrode approach is adopted in this work to study electrode activity and stability. This was done using edge and basal plane pyrolytic graphite electrodes modified by electrochemical oxidation. Differential electrochemical mass spectrometry was used for the first time in this work to investigate the parasitic hydrogen evolution reaction on the oxidized carbon surfaces. The Basal plane surface showed a higher faradaic efficiency for V(III) reduction compared to the edge plane surface. The oxidized surfaces were subject to extended cycling, after which the basal electrode showed a dramatic loss in activity compared to the edge surface which was relatively stable. This activity loss was related to the poor mechanical stability of the basal plane surface. The electrodes were analysed before and after cycling by different techniques including: X-ray photoelectron spectroscopy, Raman spectroscopy and scanning electron microscopy. The influence of the type of carbon and its related properties on electrode activity and stability are discussed.

4.2.2 Introduction
All-vanadium redox flow batteries (VRBs) have gained significant attention as load levelling devices for large scale energy storage applications [22,25]. The performance limiting reaction in this system has been established in recent literature to be the V(II)/V(III) redox reaction occurring at the negative electrode in the VRB [62,108,115,116,122,123]. The surface chemistry and carbon structure are key properties affecting the reaction kinetics of the V(II)/V(III) redox reaction [60,72,108]. Research efforts have been focused on understanding and improving the kinetics of this reaction by modifying the carbon surface by different treatment methods [47,48,78,116,124,125]. Typically, surface oxygen-containing groups are introduced onto the carbon surface and are thought to play a catalytic role by facilitating the electron transfer for the V(II)/V(III) redox reaction [53,60,61,116,124,125]. Despite these improvements observed upon oxidation, long-term cycling experiments have revealed significant losses in electrode performance over time. These losses have been reported to originate mainly from the negative electrode [59,62,115]. Several explanations regarding the cause for negative electrode degradation have been proposed in the literature. These include: exposure to highly reducing negative potentials, the parasitic hydrogen evolution reaction (HER) as
well as losses in surface area related to peeling of the surface of the carbon fibers [44,59–61,122,126,127]. Miller et al. suggested that the range of potentials experienced by the negative electrode correspond to a region where reducing potentials play a role in electrode deactivation resulting in slower kinetics for the V(II)/V(III) couple [60,61]. On the other hand, several authors have reported the detrimental effects of hydrogen evolution on negative electrode performance [44,86,122]. The standard potential of the negative electrode in the VRB system occurs below the standard potential for hydrogen evolution; therefore the lower potential thermodynamically allows simultaneous hydrogen evolution and V(III) reduction [86].

\[
2H^+ + 2e^- \rightleftharpoons H_2 \quad E^0 = 0 \text{ V vs. SHE} \tag{4.2}
\]

\[
V^{3+} + e^- \rightleftharpoons V^{2+} \quad E^0 = -0.26 \text{ V vs. SHE} \tag{4.3}
\]

In the presence of V(III) ions the onset potential of the HER has been reported to shift to more negative potentials, indicating that the HER and V(III) reduction compete strongly with each other [108]. This means in some cases that a fraction of the measured current goes towards the HER, resulting in performance losses in the form of capacity decay and electrolyte imbalance at the negative side of the VRB [123,128]. Furthermore, hydrogen gas formation can present mass transport issues as well as blockage and even removal of active sites on the carbon electrode surface. In a recent in situ study by Wei et al., hydrogen gas evolution was visible during operation of a transparent VRB cell. The hydrogen bubble formation visibly blocked active electrode area, resulting in reduced electrode performance [86]. In another study, a loss in electrode activity corresponding to a loss in surface oxygen-containing groups was observed after hydrogen evolution had occurred on the graphite electrode surface [126]. Rudolph et al. also claimed that the loss in surface oxygen-containing groups after extended operation contributed to increased cell polarisation at the negative electrode [121,129]. The mechanism of oxygen removal has been suggested to occur by breaking of carbon-oxygen bonds and the recombination with adsorbed hydrogen atoms to form water [86]. Pezeshki et al. rule out the loss of surface oxides as a reason for decreased electrode performance [123], while other authors suggest a loss in active surface area by peeling of carbon fibres could contribute to losses in performance [59]. There are conflicting reports in the literature regarding the mechanisms of carbon electrode degradation. Most of these stability studies are carried out on commercial carbon materials such as carbon felt or carbon paper electrodes, which makes it difficult to decouple all the contributing effects on such complex 3D electrode systems. There is a need to simplify the electrode system, in order to gain a better
understanding of the influence of different material properties on carbon electrode degradation, which was the purpose of this study.

In this work, a well-defined model electrode system based on edge and basal plane pyrolytic graphite electrodes was used. The quantitative influence of the HER on the V(II)/V(III) reaction was studied on the oxidised edge and basal surfaces by differential electrochemical mass spectrometry (DEMS). In this way, the average faradaic efficiency for V(III) reduction over one complete potential sweep was determined on the two oxidised surfaces. The stability of the oxidised surfaces was studied by cyclic voltammetry in a fixed potential window. Post mortem analysis of cycled electrodes was carried out by scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Correlations between electrode activity, stability and carbon material properties are discussed.

4.2.3 Experimental Section

4.2.3.1 Electrolyte preparation

A 1.6 mol L\(^{-1}\) V(II) electrolyte was prepared by electrolysis of commercially available 1.6 mol L\(^{-1}\) vanadium electrolyte solution supplied by OXKEM® (50:50, V(III): V(IV) in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\)) using a commercial Scribner® redox flow cell test system with carbon felt electrodes (SGL SIGRACELL GFD4.6 EA) and a Nafton® 117 membrane. The solution was considered fully charged (100% state of charge, SoC) at a current density of 2 mA cm\(^{-2}\).

4.2.3.2 Electrode materials and oxidation treatment

Edge and basal plane pyrolytic graphite disk electrodes supplied by Pine Research® (5.0 mm OD including 1 mm epoxy shroud) were used in this study. All electrodes were compatible with the standard E4 series Pine Research® RDE tips. Electrochemical (EC) oxidation was carried out in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution (Alf Aesar® 99.9 %) by potential holding at 2.2 V/RHE for 5 min followed by a second potential holding step at 0.1 V/RHE for 30 s [49]. The electrode surfaces are referred to in the text by shorthand sample names according to the respective states of the electrode surface. The following samples names are used throughout the text: Pristine-Edge and Pristine-Basal refer to the pristine as-received electrode surfaces, EC-Edge and EC-Basal refer to the electrochemically oxidised surfaces and EC-Edge \(\text{cycled}\) and EC-Basal \(\text{cycled}\) refer to the electrochemically oxidised surfaces after 150 cycles in 1.6 mol L\(^{-1}\) V(II) electrolyte.
4. Negative electrode – V(II)/V(III) redox couple

4.2.3.3 Scanning electron microscopy (SEM)
SEM images of pristine, EC oxidised and cycled edge and basal plane electrodes were taken using a FESEM Ultra 55 microscope (Carl Zeiss) with an acceleration voltage of 2 keV.

4.2.3.4 X-ray photoelectron spectroscopy (XPS)
X-ray photoelectron spectroscopy (XPS) was used to determine the oxygen content of the pristine, EC oxidised and cycled electrode surfaces. A VG ESCALAB 220iXL spectrometer (Thermo Fischer Scientific) equipped with an Al Kα monochromatic source and a magnetic lens system was used. High resolution spectra of the C1s and O1s peaks were used to determine the surface oxygen to carbon ratio (O/C ratio) for all electrode samples. All curves were fitted according to a Gaussian Lorentzian function. Background subtraction has been performed according to the Shirley method, and the atomic sensitivity factors (ASF) of Scofield were applied to estimate the atomic composition. Deconvolution of the C1s core level spectra was carried out fitting the following peaks: 284.1 eV, 284.9 eV, 285.96 eV, 288.2 eV, 290.4 eV and 291.61 eV which arise from C-C, C-H, C-OR (including C-OH and O-C-O), C=O, COOH and shakeup satellite contributions respectively [43,100].

4.2.3.5 Raman spectroscopy
A Raman microscope (Labram HR800 Horiba-Jobin Yvon, Japan) with a He-Ne laser (632.8 nm) and a 50x lens (ULWDM Plan 50, NA¼0.55, Olympus, Japan) was used to investigate the near-to-surface region of the edge and basal electrodes in this study. The measurements were performed with a grating of 600 line/mm and a laser power of 20 mW. First order Raman spectra were recorded in the range 1000 - 2000 cm⁻¹ for the pristine, EC oxidised and cycled edge and basal plane electrode surfaces.

4.2.3.6 Electrochemical characterisation
Electrochemical measurements were carried out at room temperature using a standard three-electrode setup with a platinum-mesh counter electrode and a Hg/HgSO₄ (+0.658 V/SHE) reference electrode (C3 Prozess - und Analysentechnik GmbH). Cyclic voltammograms (CVs) were recorded at a scan rate of 50 mV s⁻¹ in an argon purged 1.6 mol L⁻¹ V(II) solution using a Biologic VSP-300 potentiostat. All CVs were corrected during data analysis for ohmic resistance and all potentials are reported versus the reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy (EIS) measurements were carried out at ~10 mV overpotential for V(II) oxidation with a voltage amplitude of 10 mV in the frequency range of 1 MHz to 50 mHz. The
experimental data was fitted to the equivalent electrical circuit by a randomize-simplex procedure using Z Fit EC Lab® software.

The influence of 150 ‘charge/discharge’ cycles on the reaction reversibility of the oxidised carbon electrode surfaces was studied in a fixed potential window (0 to -0.8 V). The lower potential limit was fixed relatively low at -0.8 V to see the influence, if any, of the HER and negative potentials on the reactivity of the two oxidised surfaces after cycling. An initial CV was recorded for each freshly oxidised surface at 50 mV s\(^{-1}\) in 1.6 mol L\(^{-1}\) V(II) before each cycling measurement. After 150 cycles at 50 mV s\(^{-1}\) in 1.6 mol L\(^{-1}\) V(II), the electrolyte was replaced with a fresh solution of 1.6 mol L\(^{-1}\) V(II) and a final CV was recorded.

4.2.3.7 **Differential electrochemical mass spectrometry (DEMS)**

The DEMS cell setup used in this work has been described elsewhere.[31] The setup is similar to the cell design used by Ashton [130]. In this work, gold mesh counter electrodes and a Hg/Hg\(_2\)SO\(_4\) reference electrode (C3 Prozess - und Analysentechnik GmbH) were used. Measurements were carried out with an electrolyte flow rate of 100 μl min\(^{-1}\) at room temperature. The vacuum system incorporates a commercial Pfeiffer Vacuum QMA 422 quadrupole mass analyser with a 90° off-axis secondary electron multiplier (SEM) and cross-beam electron impact ion source (CB-IS). The quadrupole mass analyser (QMS) was calibrated for detection of H\(_2\) (m/z=2). An electron energy of 70 eV was used for ionization with an emission current of 1 mA, a focus plate of 14.0 V, extraction 250 V and resolution 50. H\(^+\) ions were detected by SEM with a detector voltage of 1030 V. With these settings, a data point was recorded every 200 ms.

Electrochemical measurements in the DEMS setup were carried out using a VSP-300 Biologic potentiostat. CVs were measured for the freshly oxidised edge and basal surfaces in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) and in 1.6 mol L\(^{-1}\) V(III). The potential was swept from 0 to -0.8 V and back, at a scan rate of 50 mV s\(^{-1}\), recording a total of 5 cycles for each measurement. The measurements in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) were used to calculate the calibration factor (\(\alpha\)), relating the mass ion charge (QQMS) to the faradaic charge (QF). The average faradaic efficiencies for V(III) reduction over one complete potential sweep were calculated from the measurements in 1.6 mol L\(^{-1}\) V(III) electrolyte (see supplementary material section 4.3.2 for a detailed calculations).
4. Negative electrode – V(II)/V(III) redox couple

4.2.4 Results and Discussion

4.2.4.1 Electrode surface characterisation

SEM images of the pristine, EC oxidised and cycled edge and basal plane surfaces are shown in Figure 4.3 (a – f). The Pristine-Edge electrode in Figure 4.3 (a) shows a relatively homogenous surface, characterised by very small and randomly distributed shallow pits in the surface structure. The Pristine-Basal surface in Figure 4.3 (b) is made up of what appear to be a number of basal oriented graphite platelets. Figure 4.3 (c) and Figure 4.3 (d) illustrate the effects of EC oxidation on both edge and basal surfaces. For the case of the EC-Edge, the surface appears relatively rough with large cracks of ~3 µm in size visible on the surface, Figure 4.3 (c). The EC-Basal surface has a very different morphology after EC oxidation, Figure 4.3 (d). Delamination of the basal surface occurs, resulting in a number of loose graphite-like platelets of a few tens of micrometres in size. EC oxidation is known to result in an expansion and exfoliation of the graphite structure [131]. Furthermore, this process of surface exfoliation by oxidation leads to an apparent increase in surface area visible by SEM. This can be confirmed by capacitive charge measurements in 2 mol L⁻¹ H₂SO₄ (see supplementary material Figure 4.9). After extended cycling, the surface of the EC-Edge electrode appears rougher. The cycled EC-Basal electrode displays a much smoother surface, still made up of layers of large graphite flakes.
Figure 4.3 - SEM images of (a) Pristine-Edge (b) Pristine-Basal (c) EC-Edge, (d) EC-Basal, (e) EC-Edge cycled (f) EC-Basal cycled.
The O/C ratios and corresponding fractions of different oxygen functional groups for the pristine, EC oxidised and cycled surfaces are summarised in Figure 4.4 (a – d).

After EC oxidation the O/C ratio increased for both edge and basal electrodes from ~0.16 and ~0.12 respectively, to approximately 0.3 in both cases (Figure 4.4 (a) and Figure 4.4 (b)). A loss in total oxygen is seen for both the edge and basal surfaces after 150 cycles in 1.6 mol L$^{-1}$ V(II). The O/C ratio decreased from 0.3 to 0.23 for the EC-Edge surface. A more dramatic decrease was observed for the oxidised basal surface after cycling from 0.3 to 0.14, almost back to the original O/C ratio of the Pristine-Basal surface (Table 4.2). Figure 4.4 (c) and Figure 4.4 (d) illustrate the distribution of the different oxygen functional groups on the respective surfaces. Electrochemical oxidation resulted in an increase in the fraction of C=O groups on the edge plane surface and a reduction in the fractions of C-OH and COOH groups. After extended cycling, the

Figure 4.4 - O/C ratios and distribution of different oxygen functional groups for (a), (c) Edge electrode surfaces (b), (d) Basal electrode surfaces.
fraction of C=O decreased on the edge plane surface. A small increase in the C=O fraction after oxidation was observed on the basal plane surface, while the COOH fraction remained almost constant. After cycling the composition of oxygen groups for the basal plane surface was similar to the pristine basal electrode. In general, the EC-Edge surface displayed a greater fraction of C=O groups compared to the EC-Basal surface.

Raman spectroscopy was used to track changes in the carbon microstructure after EC oxidation and after extended cycling. The first order Raman spectra below exhibit two characteristic peaks, the D-band at 1360 cm⁻¹ and G-band at ~1580-1600 cm⁻¹. The D-band is typically associated with the ‘disorder’ and defects in the carbon structure, while the G-band is related to the graphitic or ‘ordered’ domains in the carbon structure [102,103].

![Raman Spectra of Edge and Basal Electrodes](image)

**Figure 4.5** - Raman spectra of all (a) edge PG and (b) basal PG electrodes in this study.

In Figure 4.5 (a), the surface of the Pristine-Edge electrode is characterised by two sharp D and G band peaks with a I_D/I_G ratio of 1.04. The narrow G-band is an indication of a graphitic-type material, the defects or edge sites present in the structure of the edge oriented graphite give rise to the significant D-band peak. The small peak at 1620 cm⁻¹, referred to as the D2-band is typically observed as a shoulder of the G-band peak and also accounts for structural disorder [104]. After EC oxidation of the edge surface, a significant increase in the D-band intensity and a notable broadening and merging of the D and G-band peaks was observed. The I_D/I_G ratio increased from 1.04 to 1.27 for the oxidised surface. The higher I_D/I_G ratio and peak broadening are related to the
introduction of lattice defects and disorder into the carbon structure as the surface is disrupted by EC oxidation [69,112]. After cycling in V(II) electrolyte, the $I_D/I_G$ ratio increased slightly to 1.46 indicating further defect/disorder introduction. In contrast to the edge surface, the Raman spectra of the Pristine-Basil electrode was characterised by a much sharper and more intense G-band peak, resulting in a lower $I_D/I_G$ ratio of 0.36. The Pristine-Basil electrode represents a more ordered carbon material with fewer defects present in the pristine structure. After EC oxidation, the intensity of the G-band decreased dramatically and significant D and G band peak broadening was observed. The resulting $I_D/I_G$ ratio of 1.37 was much higher than for the pristine surface (0.36). This again indicated disorder and defect introduction. After extended cycling in V(II) the $I_D/I_G$ ratio was relatively unchanged for the basal electrode. EC oxidation of both edge and basal electrodes resulted in defect and disorder introduction into the carbon structure in line with previous studies [69,132].

Table 4.2 - Summary of O/C ratios and $I_D/I_G$ ratios determined by XPS and Raman spectroscopy respectively for pristine, EC oxidised and cycled edge and basal electrode surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Edge</th>
<th></th>
<th>Basal</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O/C ratio</td>
<td>$I_D/I_G$</td>
<td>O/C ratio</td>
<td>$I_D/I_G$</td>
</tr>
<tr>
<td>Pristine</td>
<td>0.16</td>
<td>1.01</td>
<td>0.12</td>
<td>0.36</td>
</tr>
<tr>
<td>EC</td>
<td>0.30</td>
<td>1.27</td>
<td>0.32</td>
<td>1.47</td>
</tr>
<tr>
<td>cycled</td>
<td>0.23</td>
<td>1.46</td>
<td>0.14</td>
<td>0.37</td>
</tr>
</tbody>
</table>

4.2.4.2 Activity of electrochemically oxidised edge and basal plane electrodes for V(II)/V(III) reaction

Figure 4.6 (a-d) illustrates the cyclic voltammograms measured in 1.6 mol L$^{-1}$ V(II) solution and the Nyquist impedance plots for both pristine and EC oxidised edge and basal plane electrode surfaces.
4. Negative electrode – V(II)/V(III) redox couple

Figure 4.6 - CVs measured in 1.6 mol L\(^{-1}\) V(II) at 50 mV s\(^{-1}\) for pristine and EC oxidised (a) edge and (b) basal plane electrode surfaces and Nyquist impedance plots for (c) pristine and (d) EC oxidized edge and basal plane electrodes, markers in Nyquist plots represent experimental data and solid lines represent the model fitted data using the equivalent electrical circuit diagram seen in the insets.

In the case of both pristine electrodes, the CVs show very large peak separations \(\Delta E_p > 500\) mV. The \(\Delta E_p\) gives an indication of the electrochemical reversibility of a redox system at a given surface. A large peak separation indicates an irreversible redox reaction with slow reaction kinetics and poor electrode activity [82]. After EC oxidation, the \(\Delta E_p\) decreased significantly for both electrodes, indicating a large improvement in electrochemical reversibility. The oxidised electrodes are more active for the V(II)/V(III) redox reaction compared to the pristine surfaces. The peak currents of the oxidised surfaces however were not the same. The EC-Basal electrode showed higher peak currents compared to the EC-Edge electrode in Figure 4.6, this could be related to the different surface areas of the two oxidised electrodes. Measurements in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) were carried out to determine the capacitive charge of the oxidised electrodes and give an indication of the actual surface area. These measurements revealed the EC-basal surface had approximately double the capacitive charge of the EC-Edge electrode (see supporting
information Figure 4.9 and Figure 4.10). Electrochemical impedance spectroscopy was in line with these observations. The charge transfer resistances ($R_{ct}$) were determined from the Nyquist impedance plots in Figure 4.6 (c) and 4.6 (d). The respective $\Delta E_p$ and $R_{ct}$ values are summarised in Table 4.3.

**Table 4.3** - Peak separation ($\Delta E_p$) measured at 50 mV s$^{-1}$ in 1.6 mol L$^{-1}$ V(II) and charge transfer resistance ($R_{ct}$) for pristine and EC oxidised edge and basal electrodes normalised to geometric surface area (cm$^2$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_p$/mV ± 6 mV</th>
<th>$R_{ct}$/Ω cm$^2$</th>
<th>$\chi^2$ 10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine-Basal</td>
<td>500 &lt;</td>
<td>254</td>
<td>0.046</td>
</tr>
<tr>
<td>Pristine-Edge</td>
<td>500 &lt;</td>
<td>123</td>
<td>2.34 x 10$^{-3}$</td>
</tr>
<tr>
<td>EC-Basal</td>
<td>132</td>
<td>1.75</td>
<td>0.2 x 10$^{-3}$</td>
</tr>
<tr>
<td>EC-Edge</td>
<td>117</td>
<td>0.47</td>
<td>0.5 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

Large semi-circular features are seen in the Nyquist plots for the pristine surfaces in Figure 4.6 (c) and are an indication of a high charge transfer resistance and slow kinetics (Table 4.3). The absence of the diffusion element is a further indication of the extremely slow reaction kinetics as the system does not reach any diffusion limitation during the measurement and is entirely limited by the charge transfer process of the V(II)/V(III) reaction. A comparison of the two pristine surfaces reveals that the $R_{ct}$ is lower on the Pristine-Edge surface (123 Ω cm$^2$) compared to the Pristine-Basal surface (254 Ω cm$^2$). This is in line with a previous study by Pour et al. where an edge oriented carbon provided faster kinetics for the V(II)/V(III) reaction compared to the basal oriented carbon [72]. After EC oxidation, the charge transfer ($R_{ct}$) resistance decreased by several orders of magnitude for both surfaces. The basal surface showed a decrease in $R_{ct}$ from 254 Ω cm$^2$ on the pristine to 1.75 Ω cm$^2$ on the oxidised surface. The $R_{ct}$ of the Pristine-Edge surface decreased form 123 Ω cm$^2$ to 0.47 Ω cm$^2$ after EC oxidation. The $R_{ct}$ values are in line with the dramatic decrease in $\Delta E_p$ observed in the CVs in Figure 4.6 (a) and 4.6 (b). This improvement in reaction kinetics is in agreement with our previous work on glassy carbon and carbon paper and felt electrodes [62,125] and has typically been attributed to the introduction of surface oxygen functional groups [53,60,61].
4. Negative electrode – V(II)/V(III) redox couple

4.2.4.3 Influence of parasitic hydrogen evolution reaction on V(III) reduction

The average faradaic efficiencies (FE) for the V(III) reduction were determined using DEMS over one complete potential sweep between 0 to 0.8 V for the oxidised edge and basal plane surfaces. Figure 4.7 illustrates the FE efficiencies of the two oxidised surfaces. Detailed information regarding the methodology for faradic efficiency estimation is given in the supplementary material section 4.3.2.

![Figure 4.7 - Average FE for V(III) reduction on EC-Edge and EC-Basal electrodes. FE expressed as % determined according to equation (4.10) in supplementary material section 4.3.](image)

The EC-Edge surface was found to be more active for the HER in both 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) and in 1.6 mol L\(^{-1}\) V(III) compared to the EC-Basal surface. The average faradaic efficiency for V(III) reduction was calculated to be 80 % for the EC-Edge surface and 92 % for the EC-Basal surface. It was also observed that more hydrogen was detected on both surfaces when the measurements were carried out in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) compared to the case when V(III) ions were present. This observation is in line with Langner et al. who also reported a change in hydrogen evolution rates in the presence of V(III) ions [108].

4.2.4.4 Extended cycling of oxidised electrodes in 1.6 mol L\(^{-1}\) V(II)

The stability of the oxidised edge and basal electrode surfaces was studied in 1.6 mol L\(^{-1}\) V(II) by extended cycling in a fixed potential window (0 to -0.8 V). In our previous work, it was shown that an oxidised glassy carbon surface was unstable upon cycling in the potential range of the V(II)/V(III) couple. Losses in electrode activity were related to a loss in surface oxygen groups after cycling [125]. However, the study was not exhaustive to all possible activity loss mechanisms. In this work, a more detailed investigation into
the cycling stability of two oxidised model carbon electrode surfaces was carried out. Figure 4.8 shows the initial and final CVs recorded in 1.6 mol L\(^{-1}\) V(II) after 150 cycles, Table 4.4 summarises the ∆E\(_p\) values.

![Initial and final CVs after 150 cycles between 0 and -0.8 V, measured at 50 mV s\(^{-1}\) in 1.6 mol L\(^{-1}\) V(II) for (a) EC-Edge and (b) EC-Basal electrodes](image)

**Table 4.4 - ∆E\(_p\) before and after 150 cycles in 1.6 mol L\(^{-1}\) V(II).**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cycle 1 ∆E(_p) / mV</th>
<th>cycle 150 ∆E(_p) / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC-Basal</td>
<td>190</td>
<td>&gt;300</td>
</tr>
<tr>
<td>EC-Edge</td>
<td>183</td>
<td>225</td>
</tr>
</tbody>
</table>

After 150 cycles between 0 and -0.8 V, the peak separation (ΔE\(_p\)) of the EC-Edge surface increased from 183 mV to 225 mV, indicating a loss in electrode activity. A much greater increase in ΔE\(_p\) (from 190 mV to > 300 mV) was observed for the EC-Basal surface after cycling. The peak current was also seen to decrease significantly after cycling for the EC-Basal surface. This could be related to a loss in active surface area. CVs measured in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) showed a dramatic decrease in capacitive charge before and after cycling for the EC-Basal surface (see Figure 4.11). Thus a significant loss in reaction reversibility and electrode activity was observed for the EC-Basal electrode compared to the EC-Edge electrode after the same number of cycles. The loss in activity was gradual in both cases and it was noted that the same cycling protocol carried out between 0 to -0.6 V did not result in such a dramatic loss in electrode activity for either the EC-Basal or the EC-Edge surface (see Figure 4.12). This observation suggests that cycling to more negative potentials detrimentally affects the electrode activity. Finally, it was also noted that rejuvenation of the electrode activity by re-oxidation after cycling could only be carried out once in the case of the EC-Basal surface, subsequent oxidations resulted in further
surface delamination and the electrode was completely destroyed. It was possible however to regain the initial activity of the edge electrode for a number of re-oxidations.

### 4.2.4.5 Influence of different carbon properties on V(II)/V(III) reaction reversibility and electrode degradation

In this work the initial activity and faradaic efficiency of freshly oxidised edge and basal plane electrodes was determined. The cycling stability of the two surfaces was also studied using cycling voltammetry. The surfaces were analysed before and after cycling by SEM, XPS and Raman spectroscopy. Electrochemical oxidation of both edge and basal electrodes resulted in significantly improved reversibility’s towards the V(II)/V(III) redox reaction. The two surfaces displayed similar ΔE_p values after oxidation. These improvements were attributed to the introduction of oxygen functional groups onto the carbon surface [53,60,61,116,124,125]. Furthermore, these findings fit with the suggestion of a transition from an outer to an inner sphere reaction mechanism for the V(II)/V(III) reaction involving catalytic oxygen groups. This idea was proposed in early studies by Chen and McCreery et al. and confirmed in a more recent study by Jiang et al. [65,133]. While it is clear that the oxygen groups contribute to improving the reaction kinetics, the changes in surface structure observed by Raman spectroscopy after oxidation are also important. The Raman spectra of both the oxidised edge and basal surfaces were characterised by high ID/IG ratios of 1.27 and 1.47 respectively, as well as significantly broad D and G-band peaks after oxidation. These features are synonymous with defect and disorder introduction into the carbon structures after EC oxidation. It has also been suggested that edge and defect sites are active for the V(II)/V(III) redox reaction [72,108,134]. SEM images revealed very important differences between the appearance of the two oxidised surfaces. Significant delamination of the EC-Basal surface occurred after oxidation, and the surface was made up of a number of loosely held graphite-like flakes. The EC-Edge surface appeared more robust in comparison. Using DEMS it was shown that the EC-Edge electrode was more active for the HER compared to the EC-Basal electrode in both 2 mol L⁻¹ H₂SO₄ and 1.6 mol L⁻¹ V(III). The presence of edge sites has been suggested to strongly decrease the overpotential for the HER compared to basal planes [135]. The higher activity for the HER translates to a lower FE for V(III) reduction for the EC-Edge electrode. In a real system this would have a detrimental effect on capacity and overall performance [123,128]. Furthermore hydrogen evolution has been suggested to negatively influence electrode stability [86].
4. Negative electrode – V(II)/V(III) redox couple

EC-Edge surface was found to be more stable than the EC-Basal electrode after a number of cycles in 1.6 mol L⁻¹ V(II). In both cases XPS analysis showed a loss in surface oxygen content (O/C ratio) after cycling. The oxygen content of the EC-Edge surface decreased by ~ 20% after cycling, while a more severe loss in oxygen was observed for the EC-basal surface of ~ 50% after cycling. The loss in oxygen groups, thought to be active sites for V(II)/V(III) reaction, could be one possible reason for the observed loss in electrode activity. Exposure to such negative electrode potentials is known to have a reducing effect on the electrode surface and could contribute to the loss in oxygen groups seen for both surfaces [60,61]. For the EC-basal electrode however, the dramatic loss in surface oxygen of ~50% may not be related solely to the effects of reducing potentials. After cycling the EC-Basal electrode, the loosely held surface layers of the EC-Basal electrode became detached and could be seen in the electrolyte after the measurement. SEM images after cycling also indicate that these loose flakes are no longer present and the surface appears smoother. This could explain the dramatic decrease in surface oxygen content seen by XPS. The removal of the oxidised surface layers could lead to exposure of non-oxidised layers below, which would result in the much lower O/C ratio, similar to that of the pristine surface. The cycled basal surface had an O/C ratio and surface distribution of oxygen groups similar to that of the pristine basal surface. Furthermore, the surface area of the electrode would likely become smaller after losing these surface flakes. This could explain the decrease in peak current intensity in Figure 4.8 (b) and the reduced capacitive charge measured in 2 mol L⁻¹ H₂SO₄ after cycling (see Figure 4.11). The EC-Edge surface was more stable in comparison, showing a much less drastic loss in activity in terms of ΔEp. The loss in oxygen seen for this surface after cycling could be related to the reducing effects of negative electrode potentials [60,61]. Furthermore, since this surface showed a higher activity for HER, it is also possible that the mechanical stability of the surface was affected by bubble formation, resulting in a similar but not as drastic, flaking of the surface as was seen for the basal electrode. However, in this case the mechanical stability was not as critical as for the basal surface.

This work demonstrates that two different types of carbon electrodes oxidised by the same method, produce two surfaces with similar initial activities but very different structural and surface properties and importantly different FE for V(III) reduction. The cycling stabilities of the oxidised surfaces also differed significantly. The poor mechanical stability of the oxidised basal surface appears to be the main issue responsible for the drastic activity loss observed here. However, as mentioned previously other factors such as exposure to excessively negative potentials could also have a negative influence on
electrode activity. Furthermore, the negative effects of hydrogen evolution on activity as suggested by previous authors, should also be considered [44,86]. These findings are important and can be extended to more complex in situ studies on carbon felt and carbon paper electrodes. In our previous work in a full cell system, two different types of carbon materials both treated by the same thermal oxidation method showed vastly different stabilities upon extended cycling [62]. It was suggested that the different material properties could be responsible. The issue of carbon electrode degradation is complex and the mechanism of degradation of one carbon material does not necessarily apply globally to all carbon materials used as negative electrode in the VRB. The structural, morphological and surface chemical properties as well as the HER activity are all key factors to be considered.

4.2.5 Conclusions

In this work the activity and faradaic efficiency of oxidised edge and basal model carbon electrodes was investigated for the V(II)/V(III) reaction. Oxygen functional groups were found to play a catalytic role for this reaction improving reaction kinetics independent of the initial type of carbon used. DEMS was used for the first time in this work to determine the FE for V(III) reduction at the oxidised carbon electrodes. The EC-Edge surface showed a higher activity for the HER and subsequently a lower FE for V(III) reduction compared to the EC-Basal surface. Extended cycling to -0.8 V resulted in a loss in activity for both oxidised surfaces. The activity loss was more dramatic for the EC-Basal electrode and was related to the poor mechanical stability of this surface. The importance of the type of carbon and its related properties on (i) the HER activity and faradaic efficiency for V(III) reduction and (ii) the stability of the electrode surface upon cycling, are brought to light in this work. In this work we determined the influence of the HER on FE, however further work could be carried out to assess the influence of the HER on electrode stability; this is a possible avenue of future research following this study. Nonetheless, it is clear from this work that oxidised carbon electrodes with low HER activities and good mechanical stabilities should be considered when designing stable, high performance negative carbon electrodes for the VRB system.

4.3 Supplementary material

4.3.1 Capacitive charge measurements in 2 mol L^{-1} H_{2}SO_{4}

The capacitive charge of both pristine and EC oxidised electrodes was measured in 2 mol L^{-1} H_{2}SO_{4} at 50 mV s^{-1} between 0 and 1.0 V/RHE. The capacitive charge was calculated
4. Negative electrode – V(II)/V(III) redox couple

as the integrated area between 0.2 to 0.8 V/RHE, the values reported in coulombs (C) are summarised in Table 4.5.

Figure 4.9 - CVs measured in 2 mol L⁻¹ H₂SO₄ at 50 mV s⁻¹ for (a) pristine edge and basal electrodes and (b) EC oxidised edge and basal electrodes.

Table 4.5 - Capacitive charge values for pristine and EC oxidised electrodes.

<table>
<thead>
<tr>
<th></th>
<th>Edge</th>
<th>Basal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>9.76 x 10⁻⁶</td>
<td>5.36 x 10⁻⁶</td>
</tr>
<tr>
<td>EC oxidised</td>
<td>4.8 x 10⁻³</td>
<td>1.2 x 10⁻²</td>
</tr>
</tbody>
</table>

The current normalised by capacitive charge for both EC oxidised electrodes is shown in Figure 4.10.
Figure 4.10 - CVs of oxidised edge and basal electrodes normalised by capacitive charge from Table 4.5.

The CVs measured in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) before and after cycling the EC-Basal surface are shown in Figure 4.11.

Figure 4.11 - CVs measured in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) at 50 mV s\(^{-1}\) for EC-Basal and EC-Basal cycled.

CVs showing cycling between 0 to -0.6 V/RHE is shown in Figure 4.12 below.
4. Negative electrode – V(II)/V(III) redox couple

**Figure 4.12** - CVs showing 150 cycles between 0 and -0.6 V, measured at 50 mV s$^{-1}$ in 1.6 mol L$^{-1}$ V(II) for (a) EC-Edge and (b) EC-Basal electrodes.

The hydrogen evolution current measured in 2 mol L$^{-1}$ H$_2$SO$_4$ for both oxidised edge and basal surfaces normalised by the geometric surface area is shown in Figure 4.13.

**Figure 4.13** - Hydrogen evolution currents measured in 2 mol L$^{-1}$ H$_2$SO$_4$ at 50 mV s$^{-1}$ on oxidised edge and basal surfaces, current normalised to geometric surface area.

4.3.2 **DEMS data analysis**

4.3.2.1 **Sample calculations**

This is an example calculation using the EC-Edge data obtained by DEMS measurements to determine the calibration factor ($\alpha$) and the average faradaic efficiency (FE) for V(III)
reduction over a complete potential cycle. The same analysis was carried out for the data on the EC-Basal electrode.

4.3.2.2 Calculation of calibration factor
The measurements carried out in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) were used to calculate the calibration factor (\(\alpha\)). Figure 4.14 shows the current (A) versus time (s) plots for measurements in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) recorded by (a) the QMS (m/z=2) and (b) the corresponding electrochemical current measured by the Biologic potentiostat for the EC-Edge surface.

![Figure 4.14](image)

**Figure 4.14** - (a) QMS signal for m/z=2 (b) electrochemical signal in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) for one cycle (0 to -0.8 V/RHE) measured at 50 mV s\(^{-1}\) on the EC-Edge electrode sample. Shaded regions indicate integrated areas used for charge determination (\(Q = A \cdot s = C\)).

The shaded regions represent the integrated areas used to determine the charge (C) for one cycle. The background capacitive current in the electrochemical signal in Figure 4.10 (b) was subtracted and only the charge associated with the faradaic processes was considered. The calibration factor (\(\alpha\)) was calculated according to equation (4.4)

\[
\alpha = \frac{Q_{\text{HER}}}{Q_{\text{QMS}}^\text{m/z=2}} \quad (A \cdot s)
\]
4. Negative electrode – V(II)/V(III) redox couple

where:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{m/z=2}^{QMS}$</td>
<td>(C)</td>
<td>Ion charge from the QMS signal recorded for m/z=2</td>
</tr>
<tr>
<td>$Q_{HER}^{F}$</td>
<td>(C)</td>
<td>Faradaic charge for the hydrogen evolution reaction (HER)</td>
</tr>
</tbody>
</table>

Using the integrated charge values obtained from Figure 4.10, the calibration factor for the EC-Edge electrode was calculated as follows (all calculated data is summarised in Table 4.6).

$$\alpha = \frac{0.022 \ C}{2.3 \times 10^{-9} \ C} = 9.56 \times 10^6$$  \hspace{1cm} (4.5)

### 4.3.3 S3.1.1 Calculation of average faradaic efficiency (FE)

Figure 4.15 shows the results for measurements carried out in 1.6 mol L$^{-1}$ V(III) showing current (A) versus time (s) plots for the data recorded by (a) the QMS (m/z=2) and (b) the corresponding electrochemical current measured by the Biologic potentiostat for the EC-Edge surface.
In this case, the measured electrochemical current/charge is made up of a combination of the V(III) reduction current/charge and the HER current/charge, equation (4.6).

\[ Q_{Total}^F = Q_{V(III)/V(II)}^F + Q_{HER}^F \]  
(4.6)

Since the faradaic contribution of the HER \( Q_{HER}^F \) is unknown, the calibration factor (\( \alpha \)) determined previously for the EC-Edge electrode is needed to convert the charge determined by the QMS \( Q_{m/z=2}^{QMS} \) into a corresponding faradaic charge \( Q_{HER}^F \), equation (4.7).

\[ Q_{HER}^F = \alpha \cdot Q_{m/z=2}^{QMS} \]  
(4.7)

Substitution of equation (4.7) into equation (4.6) allows determination of the faradaic charge associated with V(III) reduction \( Q_{V(III)/V(II)}^F \) by equations (4.8) and (4.9).

\[ Q_{Total}^F = Q_{V(III)/V(II)}^F + \alpha \cdot Q_{m/z=2}^{QMS} \]  
(4.8)

\[ Q_{V(III)/V(II)}^F = Q_{Total}^F - \alpha \cdot Q_{m/z=2}^{QMS} \]  
(4.9)
Finally, the faradaic efficiency (FE) for V(III) reduction can be calculated according to equation (4.10)

\[
FE \left( V(III)/V(II) \right) = \frac{Q_{V(III)/V(II)}^{F}}{Q_{Total}^{F}}
\]  

where:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{m/z=2}^{QMS} )</td>
<td>C</td>
<td>Ion charge from the QMS signal recorded for m/z=2</td>
</tr>
<tr>
<td>( Q_{HER}^{F} )</td>
<td>C</td>
<td>Faradaic charge for the hydrogen evolution reaction (HER)</td>
</tr>
<tr>
<td>( Q_{Total}^{F} )</td>
<td>C</td>
<td>Total faradaic charge</td>
</tr>
<tr>
<td>( Q_{V(III)/V(II)}^{F} )</td>
<td>C</td>
<td>Faradaic charge for reduction of V(III) to V(II)</td>
</tr>
<tr>
<td>( \alpha )</td>
<td></td>
<td>Calibration factor</td>
</tr>
</tbody>
</table>

Using the charge values determined from the integration of the current versus time plots in Figure 4.15, and the data in Table 4.6, the value for the average faradaic efficiency for V(III) reduction over one potential sweep at the EC-Edge surface was calculated as follows:

\[
Q_{V(III)/V(II)}^{F} = Q_{Total}^{F} - \alpha \cdot Q_{m/z=2}^{QMS}
\]  

\[
= 0.0264 \ C - (9.56 \times 10^{6}) \cdot (5.73 \times 10^{-10}) = 0.021 \ C
\]

\[
FE \left( V(III)/V(II) \right) = \frac{Q_{V(III)/V(II)}^{F}}{Q_{Total}^{F}} = \frac{0.021 \ A.s}{0.0264 \ A.s} = 80 \%
\]  

Tables 4.6 and 4.7 summarise the measured and calculated data used to determine the average faradaic efficiencies for both the EC-Edge and EC-Basal electrodes over one complete potential sweep.

**Table 4.6 - Summary of DEMS data for the EC-Edge electrode**

<table>
<thead>
<tr>
<th>2 mol L(^{-1}) H(_2)SO(_4)</th>
<th>1.6 mol L(^{-1}) V(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{m/z=2}^{QMS} )</td>
<td>( Q_{m/z=2}^{QMS} )</td>
</tr>
</tbody>
</table>
4. Negative electrode – V(II)/V(III) redox couple

<table>
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<tr>
<th></th>
<th>(C)</th>
<th>(C)</th>
<th>(C)</th>
<th>(C)</th>
<th>(C)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3 x 10^{-9}</td>
<td>0.022</td>
<td>9.56 x 10^{6}</td>
<td>5.73 x 10^{10}</td>
<td>0.0264</td>
<td>0.0054</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Faradaic efficiency for V(III) reduction = 80 %

**Table 4.7 - Summary of DEMS data for the EC-Basal electrode**

<table>
<thead>
<tr>
<th></th>
<th>(C)</th>
<th>(C)</th>
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<th>(C)</th>
<th>(C)</th>
<th>(C)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mol L^{-1} H_{2}SO_{4}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q_{\text{m/z=2}}^{\text{QMS}} )</td>
<td>8.9 x 10^{10}</td>
<td>0.0093</td>
<td>( Q_{\text{HER}}^{\text{HER}} )</td>
<td>7.14 x 10^{6}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q_{\text{HER}}^{\text{HER}} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( x^* )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6 mol L^{-1} V(III)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q_{\text{m/z=2}}^{\text{QMS}} )</td>
<td>3 x 10^{10}</td>
<td>0.041</td>
<td>( Q_{\text{Total}}^{\text{Total}} )</td>
<td>0.0021</td>
<td></td>
<td></td>
<td>0.038</td>
</tr>
<tr>
<td>( Q_{\text{HER}}^{\text{HER}} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q_{\text{V(II)/V(II)}}^{\text{V(II)/V(II)}} )</td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Faradaic efficiency for V(III) reduction = 92 %

4.3.4 **QMS signals measured in 2 mol L^{-1} H_{2}SO_{4} and 1.6 mol L^{-1} V(III)**

Figure 4.16 summarises the QMS signals recorded for m/z=2 during one full cycle (0 to -0.8 V/RHE) measured in 2 mol L^{-1} H_{2}SO_{4} and 1.6 mol L^{-1} V(III) electrolytes for the EC-Edge and EC-Basal electrodes.
4. Negative electrode – V(II)/V(III) redox couple

**Figure 4.16** - QMS signal recorded for EC-Edge and EC-Basal surfaces for one cycle measured in (a), (b) 2 mol L⁻¹ H₂SO₄ and (c), (d) 1.6 mol L⁻¹ V(III) electrolyte.

Figure 4.16 shows that the m/z=2 signal recorded in 2 mol L⁻¹ H₂SO₄ is much larger than in 1.6 mol L⁻¹ V(III) for both the oxidised edge and basal surfaces. The background current measured in 2 mol L⁻¹ H₂SO₄ is therefore not a true representation of the actual HER current contribution measured in the V(III) electrolyte. A comparison of the edge and basal surfaces reveals that more H₂ is evolved on the EC-edge compared to the EC-basal surface in H₂SO₄. In the V(III) electrolyte, the EC-edge surface still evolves more hydrogen than the EC-basal surface. Only a very small amount of H₂ was detected on the oxidised basal surface in V(III).
Chapter 5. Full-cell VRB studies

In this chapter, a full-cell study was carried out to investigate the performance of commercially relevant carbon electrode materials used in VRBs. The effect of thermal treatment on four commercial materials was studied, the two best performing materials were considered for further investigation. By use of a reference electrode in the system, the contribution of the two half-cell reactions to the overall performance was determined. The stability of the two electrode materials namely carbon felt and carbon papers, was evaluated and compared. Relevant material properties were identified and their influence on the observed stability is discussed in detail in this chapter.

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5. Full-cell VRB studies

5.1 Abstract
This work focuses on the performance and stability of selected commercial carbon electrode materials before and after heat treatment in an operating all-vanadium redox flow battery (VRB). Heat treatment results in improved cell performance for all tested materials, with SGL® 39 AA carbon papers and SIGRACELL® GFD4.6 EA carbon felt showing the best performance. Further investigation of these two materials by in situ reference electrode measurements reveal improvements after heat treatment originate mainly from the negative electrode or V(II)/V(III) side of the cell. Upon extended cycling, carbon felt is found to be stable. Carbon papers however, show significant performance losses originating from the negative electrode side. The potential limit during charging and the exposure to very negative potentials appears to be a critical issue at the negative electrode in the VRB. Analysis of both materials after cycling by scanning electron microscopy, Raman spectroscopy and x-ray photoelectron spectroscopy reveal significant differences in their surface chemistry, structure and morphology. These differences give valuable insights into the behaviour and degradation of different carbon materials used in VRBs.

5.2 Introduction
Redox flow batteries (RFBs) are a promising technology for efficient energy storage and grid stabilisation [6,136]. The all-vanadium redox flow battery (VRB), which uses vanadium ions in different oxidation states at the positive and negative electrodes, is the most advanced RFB to date [137]. The electrodes are a crucial component of the VRB, as they provide the surface on which the respective electrochemical reactions occur. Thus, catalytic activity, wettability and mass transport properties of the electrodes strongly affect VRB performance. Ideal electrodes for the VRB should provide both: long term durability and stable catalytic activity. Various materials have been considered as electrodes for the use in VRBs including non-carbon based dimensionally stable anode electrodes and carbon based electrodes such as carbon felt, carbon paper, carbon nanotubes, carbon nanofibres or graphene oxides [22]. To enhance electrochemical activity and wettability of carbon based materials in VRBs, different surface modification methods have been used. Carbon electrodes have been coated with metals such as iridium [138], doped with nitrogen [139] or decorated with nanomaterials such as graphene-nanowalls [140] or graphite carbon nanotubes [141]. Recently, Zhou et al. reported activation of carbon papers and carbon cloth by heat treatment and subsequent etching with KOH [142,143]. The performance of carbon materials have also been shown to be
improved by means of thermal [78,116,144], chemical [47,145], electrochemical [45], plasma [146] or a combination of corona discharge and hydrogen peroxide treatment [51].

Most of these surface treatment approaches introduce functional groups, commonly oxygen onto the carbon electrode surface. This leads to increased wettability and redox activity, which is generally attributed to the increased concentration of surface-active oxygen functional groups [116]. Among the various surface modifications, heat treatment is still regarded as the most common and facile approach to incorporate oxygen groups onto the surface of carbon materials [22]. In an effort to better understand the role of oxygen functional groups on electrode performance, Fink et al. studied pristine and heat-treated Rayon (a regenerated cellulose fibre) based GFA carbon felt and a polyacrylonitrile (PAN) based GFD carbon felt. According to this study, the normalized rate constant for the V(II)/V(III) redox reaction increased with increasing number of oxygen functional groups, the rate constant for the V(IV)/V(V) redox reaction decreased for both types of carbon felt electrodes [53]. Miller et al. demonstrated that the introduction of oxygen containing functionalities enhances the kinetics of V(II)/V(III) and inhibits the kinetics of V(IV)/V(V) [61]. Similar observations were made in a study by our group, where oxygen groups alone were not found to play a crucial role in the activity of glassy carbon electrodes for vanadium (V) reduction. However, surface modification leading to increased roughness and number of defects appeared to play a positive role for this reaction [48]. Many recent studies focusing on both vanadium redox reactions involved in the VRB have shown that the overpotential associated with the negative half-cell dominates the voltage losses of the VRB and limits performance [59,108,115,147].

Many efforts have been successfully undertaken to improve the electrochemical activity of various carbon materials, which result in better VRB performance. However, despite these improvements, some of the modified carbon materials are not suitable for use in the VRB because of their poor operational lifespan. The use of heat treated carbon materials such as Rayon based carbon felt GFA6 or PAN based carbon papers SGL 10 AA resulted in an initial performance increase in the VRB. However, the cycling stability of both modified carbon electrodes was found to be very poor, with electrodes losing their initial activity after a number of charge/discharge cycles [59,123].

In this study, the performance of a set of commercial carbon materials before and after heat treatment is investigated in a commercial VRB test system. The two best performing materials were selected and studied in more detail. Reference electrode measurements were used to decouple the positive and negative reaction contributions to the overall
performance. Cycling stability of the two selected materials was investigated over an extended period. The materials were characterized by x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and scanning electron microscopy (SEM) before and after cycling. Valuable insights into the limiting reaction of this system and the differing stabilities of two carbon based materials are discussed.

5.3 Experimental

5.3.1 Electrode materials and preparation
Four commercial PAN based carbon materials were used in this work: SGL 39 AA carbon papers (thickness: ~280 µm), SGL 10 AA carbon papers (thickness: ~360 µm), Toray carbon papers TGP-H-120 (thickness: ~370 µm) and SGL SIGRACELL® GFD4.6 EA carbon felt electrodes (thickness: ~4300 µm). The heat treatment (HT) was carried out according to the procedure described in the literature [78]. The carbon electrodes were placed in a tube furnace at 400°C under a steady flow of synthetic air (30 mL min⁻¹) for 30 hours. HT has been used to denote heat treated materials throughout the text.

5.3.1 Cell architecture and electrolyte preparation
A commercial redox flow test system (Model 857, Scribner®) with an active area of 25 cm², serpentine flow fields and a Nafion® 117 membrane was used. Nafion® 117 was pretreated at 80°C in 32 % nitric acid for 1 h, followed by rinsing and boiling for 1 h in water. A 1 mol L⁻¹ vanadium solution was prepared by dissolving VOSO₄·nH₂O (Alfa Aesar, 99.9 % purity, where n was determined to be 3 by thermogravimetric analysis) in 2 mol L⁻¹ H₂SO₄. The solutions were charged following a typical protocol and considered fully charged (100% state of charge, SoC) at a current density of 2 mA cm⁻² [148]. Three layers of SGL 10 AA carbon papers was identified previously as the optimum number for best performance in a VRB and this number was used here [144]. To maintain the same thickness of layered carbon papers in the cell, three Toray TGP-H-120 and four SGL 39 AA papers was used on either side of the cell. One piece of carbon felt (GFD6.4 EA) was used on either side of the cell.

5.3.2 Polarisation curves and reference electrode measurements
Discharge polarisation curves were recorded galvanostatically with freshly charged electrolytes (100% SoC) at an electrolyte flow rate of 30 mL min⁻¹. A single-pass method was used to measure polarisation curves, whereby no recirculation of the electrolyte into the storage tanks occurred and the discharged electrolyte was collected externally. This ensured a 100% SoC electrolyte entered the cell throughout the experiment. Data points were measured at current densities of 0, 20, 40, 60, 100, 140, 180, 220, 260 mA cm⁻².
5. Full-cell VRB studies

holding for 20 seconds at each point. The current limit of this system was 280 mA cm\(^{-2}\). A Hg/Hg\(_2\)SO\(_4\) reference electrode (C3 Prozess - und Analysentechnik GmbH) was connected to the cell in an ‘edge-type’ configuration in which an extension of the Nafion\(^{®}\)117 membrane was placed in contact with the reference electrode used in the cell [88–90]. The junction region was kept hydrated with a 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution.

### 5.3.3 Charge/discharge cycling

Charge/discharge cycling was carried out at 30°C, with a flow rate of 30 mL min\(^{-1}\) at current density of 40 mA cm\(^{-2}\) using 70 mL of 1 mol L\(^{-1}\) vanadium electrolyte at each side of the cell (poor performance of pristine carbon felt required a reduced current density of 20 mA cm\(^{-2}\)). The upper and lower cell voltage cut-off limits were set to 1.7 V and 0.8 V respectively. Coulombic efficiency (CEff), voltage efficiency (VEff) and energy efficiency (EEff) were calculated from the 2\(^{\text{nd}}\) cycle following a procedure in the literature [91].

Extended cycling stability of selected heat treated materials (HT-SGL 39 AA and HT-GFD6.4 EA) was carried out with 100 mL of 1 mol L\(^{-1}\) vanadium electrolyte at each side of the cell, 35 charge/discharge cycles at 100 mA cm\(^{-2}\) and an additional 38 cycles at 120 mA cm\(^{-2}\) were measured under the same conditions described previously.

### 5.3.4 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used determine the total oxygen content (O/C ratio) and identify the different oxygen groups on the surface of the carbon materials. Samples of pristine and freshly heat treated GFD4.6 EA and SGL 39 AA were analysed as well as HT-GFD4.6 EA and HT-SGL 39 AA after extended cycling. As a comparison for the cycled materials, HT-GFD4.6 EA and HT-SGL 39 AA electrodes were each soaked in 2 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution for a week (duration of a typical cycling experiment) to evaluate the influence of sulfuric acid alone on the oxygen content of the electrodes. Electrodes were rinsed thoroughly using deionised water and dried before being analysed by XPS. A VG ESCALAB 220iXL spectrometer (Thermo Fischer Scientific) equipped with an Al K\(\alpha\) monochromatic source and a magnetic lens system was used. High resolution spectra of the C1s and O1s peaks were used to determine the surface oxygen to carbon ratio (O/C ratio) for all electrode samples. All curves were fitted according to a Gaussian-Lorentzian function. Background subtraction was performed according to the Shirley method, and the atomic sensitivity factors (ASF) of Scofield were applied to estimate the atomic composition. Deconvolution of the C1s core level spectra was carried out fitting the following peaks: 284.1 eV, 284.9 eV, 285.96 eV, 288.2 eV, 290.4
eV and 291.61 eV (±0.8eV) arising from C-C, C-H, C-OR (including C-OH and O-C-O), C=O, COOH and shakeup satellite contributions, respectively [43,100].

5.3.5 **Raman Spectroscopy**

A Raman microscope (Labram HR800 Horiba-Jobin Yvon, Japan) with a He-Ne laser (632.8 nm) and a 50x objective (ULWDMS Plan 50, NA = 0.55, Olympus, Japan) was used to investigate the near-to-surface region of both untreated and heat treated SGL 39 AA carbon papers and GFD4.6 EA carbon felt electrodes and HT-SGL 39 AA and HT-GFD4.6 EA electrodes after cycling. The measurements were performed with a grating of 600 line mm⁻¹ and a laser power of 20 mW. First order Raman spectra were recorded in the range 1000 to 2000 cm⁻¹.

5.3.6 **Scanning Electron Microscopy (SEM)**

The surface morphology of carbon materials was analyzed by scanning electron microscopy (SEM). SEM images were taken using a FESEM Ultra 55 from Carl Zeiss with an acceleration voltage of 2 keV.

5.4 **Result and Discussion**

5.4.1 **Performance of carbon materials before/after heat treatment**

The performance of four pristine, commercially available carbon electrode materials was studied in an operating VRB cell. The effect of heat treatment on these materials was investigated. Carbon felt electrodes (GFD4.6 EA) that are widely used in VRBs were compared to various carbon papers including SGL 10 AA, SGL 39 AA and Toray TGP-H-120. Figure 5.1 shows the polarisation curves measured for the untreated and heat treated materials and the key performance indicators for these materials are summarised in Table 5.1.
5. Full-cell VRB studies

Figure 5.1 - Discharge polarisation curves measured in an operating VRB (SoC: 100 %) with (a) untreated and (b) heat treated commercial carbon electrode materials.

Among the untreated materials, the SGL 39 AA carbon papers showed the best performance (Figure 5.1 (a)). After heat treatment, all electrode materials showed an improvement in overall cell performance. The HT-GFD4.6 EA carbon felt and HT-SGL 39 AA carbon papers showed the best performance of all heat treated materials tested in this study (Figure 5.1 (b)).
5. Full-cell VRB studies

Table 5.1 - Key performance indicators for untreated and heat treated carbon materials. Coulombic efficiency (CEff), voltage efficiency (VEff), energy efficiency (EEff) and discharge capacity (Qdis) determined from the 2nd cycle at 40 mA cm\(^{-2}\) (20 mA cm\(^{-2}\) in case of untreated carbon felt*). Discharge capacity (Qdis) calculated as Q\(_{\text{dis,measured}}\)/Q\(_{\text{dis,theroretical}}\) expressed in %. Flow rate: 30 mL min\(^{-1}\), upper and lower cutoff voltages of 1.7 V and 0.8 V respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CEff</th>
<th>VEff</th>
<th>EEff</th>
<th>Qdis</th>
<th>CEff</th>
<th>VEff</th>
<th>EEff</th>
<th>Qdis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toray TGP-H-120</td>
<td>42</td>
<td>59</td>
<td>25</td>
<td>13</td>
<td>89</td>
<td>68</td>
<td>61</td>
<td>56</td>
</tr>
<tr>
<td>SIGRACET® SGL 39 AA</td>
<td>91</td>
<td>75</td>
<td>68</td>
<td>59</td>
<td>91</td>
<td>87</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>SIGRACET® SGL 10 AA</td>
<td>87</td>
<td>73</td>
<td>64</td>
<td>53</td>
<td>92</td>
<td>79</td>
<td>73</td>
<td>71</td>
</tr>
<tr>
<td>SIGRACELL® GFD4.6EA</td>
<td>88*</td>
<td>54*</td>
<td>48*</td>
<td>34*</td>
<td>92</td>
<td>88</td>
<td>81</td>
<td>88</td>
</tr>
</tbody>
</table>

Untreated SGL 39 AA showed the highest energy efficiency (68%) and discharge capacity (59%) for the pristine materials. Carbon felt showed the worst performance, even at a reduced current density (20 mA cm\(^{-2}\)) a very low energy efficiency (48%) and discharge capacity (34%) was observed. After heat treatment the HT-SGL 39 AA carbon papers and HT-GFD4.6 EA carbon felt showed the highest energy efficiencies of 79% and 81% respectively of all the heat treated materials (see supplementary material Figure 5.7 for further details related to cycling history with various untreated and heat treated carbon electrode materials from this work). These materials were selected for further investigation and will be the focus of the remainder of this work.
5.4.2 Polarisations curves with reference electrode

A reference electrode included in the operating system allowed the decoupling of the contributions of the positive and negative electrode reactions to the overall performance. Figure 5.2 (a) and (b) show the polarisation curves for both carbon paper and carbon felt before and after heat treatment and illustrate the overpotential contributions from both the positive and negative electrode reactions.

![Figure 5.2](image)

**Figure 5.2** - Discharge polarisation curves (SoC: 100 %) for untreated and heat treated (a) SGL 39 AA carbon papers and (b) GFD4.6 EA carbon felt showing contributions from the positive and negative reactions to the overall full-cell voltage. The observed improvements after heat treatment originate from the negative electrode side for both materials. The V(II)/V(III) redox reaction appears to benefit significantly after heat treatment of the electrode materials. This observation is in line with several previous studies [59,61,75,108,115]. The positive half-cell does not show any significant changes in overpotential before and after heat treatment of the electrode materials.

5.4.3 Cycling stability

Cycling stability of HT-GFD6.4 EA carbon felt and HT-SGL 39 AA carbon papers was investigated under VRB operating conditions. At the high current densities (100 and 120 mA cm⁻²), HT-GFD6.4 EA carbon felt showed superior cycling performance, including higher VE and charge/discharge capacity. However, both systems experienced slight VE decreases and significant capacity fading during the cycling experiments, this effect was more pronounced for HT-SGL 39 AA carbon papers, Figure 5.3 (a). In general, capacity fading and decrease in VE during cycling experiments can be explained by two reasons: (1) as a result of high vanadium cross-over through the Nafion® 117 membrane and/or (2) as a result of electrode degradation under VRB operating conditions.
conditions. To separate the effect of electrolyte cross-over and possible electrode degradation, the vanadium electrolyte was replaced after cycling with a fresh electrolyte and the cell was charged and discharged again. If capacity / VE decline was solely a consequence of electrolyte imbalance caused by cross-over through the membrane, replacement of the imbalanced electrolyte should allow the restoration of the original cycling performance observed before the cycling experiments. If however electrolyte imbalance was accompanied by electrode degradation, it would not be possible to restore the original cycling performance by replacing the electrolyte with a fresh one.

In the case of HT-GFD6.4 EA carbon felt, the use of fresh electrolyte allowed the full recovery of the original cycling performance (Figure 5.3 (d)). Only a very small decrease in discharge capacity (2%) and VE (2%) was observed. In this case the losses observed during cycling were associated only with electrolyte imbalance and not with carbon felt degradation. In contrast to this, the original cell performance could not be restored for HT-SGL 39 AA carbon papers upon replacement of the electrolyte (Figure 5.3 (e)). Discharge capacity decreased by 22% and VE by 4%. This is an indication that the performance decline is not only associated with electrolyte imbalance but also with electrode degradation. Polarisation curves measured after extended cycling support these observations. The HT-GFD6.4 EA carbon felt showed almost no change in overall performance before and after cycling (Figure 5.3 (f)). However, a significant performance loss was observed for HT-SGL 39 AA carbon papers after cycling (Figure 5.3 (e)). The performance loss originated mainly from the negative electrode side.
5. Full-cell VRB studies

Although both carbon materials were activated using the same heat treatment method, HT-GFD4.6 EA carbon felt showed superior cycling stability compared to HT-SGL 39 AA carbon papers under VRB operating conditions. Other studies in the literature have reported poor stability of heat treated SGL 10AA carbon papers and GFA6 carbon.
5. Full-cell VRB studies

[59,123]. Following these observations, the surface properties of the stable and unstable electrode materials before and after extended cycling experiments were investigated by XPS, Raman spectroscopy and SEM.

5.4.4 **Electrode characterisation before and after cycling**

5.4.4.1 *Investigations of surface oxygen functionalities by XPS*

XPS was used to investigate changes in surface oxygen content on the carbon materials before/after heat treatment and after extended cycling and soaking experiments. Figure 5.4 shows the changes in total oxygen content (O/C) and the distribution of different oxygen groups on the carbon materials under investigation.

![Figure 5.4](image)

**Figure 5.4** - XPS analysis of pristine, heat treated, acid soaked and cycled electrodes showing O/C ratios for (a) SGL 39 AA carbon papers (CP) and (b) GFD4.6 EA carbon felt (CF) and comparison of different oxygen functional groups for (c) SGL 39 AA carbon papers and (d) GFD4.6 EA carbon felt.

After heat treatment, the oxygen content (O/C ratio) increased slightly for HT-SGL 39 AA carbon papers from 0.02 to 0.03 (Figure 5.4 (a)). A slight decrease in O/C ratio was observed from 0.075 to 0.05 for HT-GFD4.6 EA carbon felt (Figure 5.4 (b)). This decrease was also observed by Zhong et al. and explained by the removal of volatile C-O
contaminants during heat treatment [75]. The different behaviour upon heat treatment is an indication that the two materials interact differently with oxygen, this could be related to the different structures of the two pristine materials. The O/C ratio after acid soaking increased significantly for both materials, in line with findings by previous authors [123]. After long term cycling the oxygen content of both cycled materials were compared to the acid-soaked samples as a baseline. A decrease in O/C ratio of approximately 33% was observed for both carbon materials from the negative half-cell. The O/C ratio for HT-GFD4.6 EA carbon felt from the positive half-cell showed a slight decrease in O/C ratio compared to the acid soaked samples. However, HT-SGL 39 AA carbon papers showed an increase in the O/C ratio after cycling at the positive half-cell.

In both cases the negative electrode showed lower oxygen content after cycling compared to the positive side. It is known that highly oxidising potentials experienced by the positive electrodes are well in the limit of known electrochemical oxidation of carbon [149]. Additionally the vanadium ions themselves have also been suggested to induce changes in the oxygen content of carbon electrodes [123]. The type of oxygen groups is shown in Figure 5.4 (c) and (d). C-OR, C=O and COOH groups were present on the surface of heat treated and acid soaked carbon paper and carbon felt with C-OR groups being the most abundant. After long term cycling experiments, C-OR groups were still the dominant groups on the surface of both materials.

The surface of pristine carbon papers showed a large amount of higher oxide groups (such as C=O and COOH) compared to carbon felt. After thermal treatment, the amount of higher oxide groups decreased for carbon papers and increased for carbon felt. Interestingly, in the case of both carbon electrodes, the most oxygen functionalities were introduced onto the surface not as a consequence of thermal treatment but after soaking in 2 mol L⁻¹ H₂SO₄ (see Figure 5.4 (a) and 4 (b)). In this case, the bonding nature of the groups introduced was not the same for the two materials. For carbon papers, the amount of higher oxides was reduced after soaking in acid, with C=O/C-OH ratio decreasing from 0.38 to 0.28 and COOH/C-OH ratio from 0.28 to 0.20. For carbon felt, a reduction in the concentration of the higher oxide groups (C=O and COOH) was also observed, but was more pronounced in this case. The C=O/C-OH ratio changed from 0.46 to 0.23 and the COOH/C-OH ratio decreased even more from 0.23 to 0.08. It appears that the presence of COOH groups relative to C-OH groups is much less favoured on the surface of carbon felt than on the surface of carbon papers in 2 mol L⁻¹ H₂SO₄ (see supplementary material, Table 5.3).
5. Full-cell VRB studies

After extended cycling experiments, COOH groups disappear completely from the surface of carbon felt on both the positive and negative electrodes. The C=O/C-OH ratio increases from 0.23 to 0.50 and 0.45 for the negative and positive sides respectively. In contrast to this, the amount of COOH and C=O groups relative to COH groups remains very similar after cycling for carbon papers.

Changes in the amount of oxygen functionalities on the surface of carbon materials and in their bonding nature may occur for a number of different reasons. We have shown here the effect of 2 mol L$^{-1}$ sulphuric acid on the amount of surface oxygen functionalities and their bonding nature for two different carbon materials. Vanadium ions have also been shown to influence the amount of oxygen containing functional groups on the surface of carbon electrodes. For instance V(II) and V(III) ions have been reported to reduce the oxygen content on the carbon surface, while V(V) ions have been shown increase the oxygen content [123]. Thus, the very similar decrease (around 33%) in oxygen content observed at the negative electrode for both materials after cycling could be related to the presence of V(II) and V(III) ions. Changes in O/C ratio on the surface of electrodes from the positive half-cell (decrease for GFD4.6 EA carbon felt and increase for SGL 39AA carbon papers) this may be caused by interactions of both carbon electrodes with V(V) ions. Moreover, exposure to highly positive potentials as well as very negative potentials during cycling can also influence the oxygen content of the surface.

5.4.4.2 Investigation of carbon materials by Raman spectroscopy and SEM

The extent of graphitisation and amount of defects present in the carbon materials was investigated by Raman spectroscopy. The peaks at $\sim$1350 (D), 1590 (G) and 1620 cm$^{-1}$ (D2) in the Raman spectrum of carbon can be assigned to the disordered graphitic lattice (edges), the ideal graphitic lattice and disordered graphitic lattice (surface layer) respectively [104,108]. The Raman spectra of the carbon papers and carbon felt after heat treatment and extended cycling experiments are shown in Figure 5.5.
5. Full-cell VRB studies

Heat treatment of carbon papers resulted in an increase in the $I_D/I_G$ ratio from 0.48 to 0.72, indicating an increase in the defects at the surface of the carbon fibres. XPS revealed the introduction of oxygen functionalities onto the surface of the carbon fibres, which is in line with the increase in defect density observed by Raman spectroscopy [150]. In contrast to this, heat treatment of carbon felt resulted in a decrease in the $I_D/I_G$ ratio from 1.97 to 1.34. This decrease in the $I_D/I_G$ ratio indicates an increase in the size of graphitic domains in the material after heat treatment [92]. XPS in this case showed a decrease in surface oxygen functionalities after heat treatment, which is in line with the increased degree of graphitisation observed by Raman spectroscopy. The effect of extended cycling on both the positive and negative electrodes was examined. It appears that both positive and negative electrodes undergo similar structural changes after cycling. In the case of the HT-SGL 39 AA carbon papers, a further increase in the $I_D/I_G$ ratio is observed for both heat treated electrodes after cycling. Again, this can be interpreted as a further increase in disorder and defects (edge sites) at the surface of this material in line with the increase in oxygen functionalities observed by XPS. The HT-GFD4.6 EA carbon felt however sees a further decrease in the $I_D/I_G$ ratio after cycling. The appearance of the peak at 1620 cm$^{-1}$

Figure 5.5 - Raman spectra showing SGL 39 AA carbon papers and GFD4.6 EA carbon felt before/after heat treatment and after cycling the heat treated electrodes at the positive and negative side of the VRB.
5. Full-cell VRB studies

is notable and is attributed to defects in the graphite lattice at the surface layer and could be linked to the increased oxygen observed after cycling.

Furthermore, the surface morphology was examined by SEM, see Figure 5.6. Based on the SEM results, the pristine carbon felt and carbon papers differ in the surface appearance of the fibres. The carbon felt has an uneven surface morphology with sharp edge-structures and apparent grooves in the fibres. Carbon papers exhibit a smoother fibre surface with small flakes scattered on the surface. Heat treatment did not cause any visible changes in the morphology of the fibres for both carbon materials. However, after long term cycling HT-GFD4.6 EA carbon felt appears to have a rougher surface morphology compared to the pristine material.

![SEM images showing morphological changes of SGL 39 AA carbon papers and GFD4.6 EA carbon felt before/after heat treatment and after cycling the heat treated electrodes at the positive and negative side of the VRB.](image)

**Figure 5.6** - SEM images showing morphological changes of SGL 39 AA carbon papers and GFD4.6 EA carbon felt before/after heat treatment and after cycling the heat treated electrodes at the positive and negative side of the VRB.

5.4.4.3 *Comparison and overview of different carbon materials*

In order to investigate the influence, if any, of the starting precursor used to synthesise the carbon materials and their performance, the results from this work on two heat treated PAN based carbon materials (HT-SGL 39 AA and HT-GFD4.6 EA) were
compared with a heat treated Rayon based carbon felt (GFA6) used in a previous study by Derr. et al. [59] Table 5.2 summarises the key findings.

**Table 5.2 - Comparison of surface and electrochemical properties of selected heat treated PAN based carbon materials from this study (HT-SGL 39 AA and HT-GFD6.4 EA) and Rayon based carbon felt (GFA6) from a previous study [59].**

<table>
<thead>
<tr>
<th></th>
<th>PAN based carbon papers</th>
<th>PAN based carbon felt</th>
<th>RAYON based carbon felt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SGL 39 AA</td>
<td>GFD4.6 EA</td>
<td>GFA6†</td>
</tr>
<tr>
<td>cycling stability</td>
<td>unstable</td>
<td>stable</td>
<td>unstable</td>
</tr>
<tr>
<td>in potential window</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8-1.7 V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>period of time between</td>
<td>long</td>
<td>short</td>
<td>long</td>
</tr>
<tr>
<td>1.6-1.7 V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oxygen groups present</td>
<td>C-OR*; C=O; COOR</td>
<td>C-OR*; C=O</td>
<td>C-OR*, COOR</td>
</tr>
<tr>
<td>on stressed electrodes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after cycling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>I_D/I_G ratio of</strong></td>
<td>0.48</td>
<td>1.97</td>
<td>-</td>
</tr>
<tr>
<td><strong>pristine materials</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

†reference [59] *major functional groups detected on the carbon surface

No correlation between the precursor materials used to synthesise the carbon electrodes and their operational lifespan can be seen. A notable difference between the three carbon materials shown in Table 5.2 is their residence times at cell voltages between 1.6 – 1.7 V during charging. HT-SGL 39 AA carbon papers and Rayon based carbon felt (GFA6) from Derr et al. were exposed to cell voltages above 1.6 V for a significantly longer period of time during charging compared to the stable HT-GFD4.6EA carbon felt from this study. It follows that the polarisation at either or both positive and negative electrodes is greater for these materials, resulting in the higher cell voltages observed during charging. During charging at a fixed current density, the negative half-cell potential is seen to become more negative with time (see supplementary material Figure 5.8). Since the degradation of the carbon papers is observed mainly at the negative electrode side, it can be deduced that more negative potentials at the negative electrode have a detrimental effect on electrode stability. This was confirmed by measurements in which the cut-off cell voltage during charging was reduced from 1.7 V to 1.6 V. In this case, less performance losses were observed at the negative electrode for HT-SGL 39 AA carbon papers after extended cycling measurements (see supplementary material, Figure 5.9).
Thus it appears that the electrode degradation is strongly related to the potential at the negative electrode, particularly during the charging stage.

It has been shown previously that the range of negative potentials experienced by the negative electrode in the VRB fall into a region in which the electrode can be deactivated by reduction [59]. Oxygen surface groups have been shown to have a positive influence on V(II)/V(III) redox reaction kinetics. However, the stability of oxidised carbon surfaces has also been found to be affected by very negative electrode potentials [60,61,125]. In this study, XPS analysis revealed that after cycling, the oxygen content at the negative electrode decreased for both carbon materials relative to the acid soaked samples. This decrease in oxygen content could result from exposure to very negative electrode potentials and ultimately contribute to the loss in activity observed at the negative electrode. However, this observation alone does not fully explain the loss in activity observed for the carbon papers and not for carbon felt. Previous studies have suggested that activity losses at the negative electrode could be due to a combination of factors including hydrogen evolution, passivation effects and losses in surface active groups such as oxygen [44,60,121,125]. The two materials in this study differ significantly in their structures, observed by Raman spectroscopy and surface morphology seen by SEM. The structural properties and morphology of the carbon materials could also play a key role in the different stabilities of the carbon materials studied here. It appears that stability and degradation of carbon materials in VRBs is a complex issue. It is likely that a combination of different effects is responsible, including material properties and surface chemistry as is seen in this work. However, other issues such as hydrogen evolution and mass transport also need to be considered in order to gain a full overview of factors contributing to electrode stability and degradation in VRBs.

5.5 Conclusions

A preliminary investigation into performance and electrode stability of selected commercial materials under VRB operating conditions was carried out in this study. Heat treatment was found to be beneficial for cell performance with all materials, HT-SGL 39 AA carbon papers and HT-GFD4.6 EA carbon felt showed the best overall performance. Reference electrode measurements with these two materials revealed that most of the improvements after heat treatment came from the negative electrode or the V(II)/V(III) side. Upon extended cycling, HT-GFD4.6 EA carbon felt was found to be stable and no significant performance losses could be observed. HT-SGL 39 AA carbon papers however showed significant losses in performance which originated primarily from the negative electrode. The degradation of carbon papers at the negative electrode appears to
be related to the negative electrode potential itself. Interestingly, even if the cut off voltage limits are the same during the charging process (1.7 V/RHE), unstable carbon papers experience more negative potentials than stable carbon felt over the same charging period.

XPS revealed very similar losses in oxygen at the negative electrode after cycling for both, stable and unstable, carbon electrodes. Losses in surface oxygen could contribute to the losses in activity observed for HT-SGL 39 AA carbon papers, however it does not appear to be the only factor responsible. Raman spectroscopy and SEM revealed significant structural and morphological differences between the two materials with different stability. The formation of different oxygen functional groups upon thermal treatment and acid soaking appears to be influenced by the carbon materials itself and can result in their different cycling stabilities. The combination of XPS complemented by Raman spectroscopy shown here provides valuable insights into the correlation between structure, surface oxygen functionalities and cycling stability of different carbon electrode materials. These insights will help in the understanding and optimisation of a more stable negative electrode material for the VRB system. Further investigations into other possible contributing effects such as mass transport and material structural properties including porosity and morphology are ongoing in our group.

5.6 Supplementary material

Figure 5.7 shows the charge/discharge curves for four commercial carbon electrode materials used in this work (a) before and (b) after thermal treatment.

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**Figure 5.7** - Charge/discharge curves for various carbon electrodes before/after thermal treatment. Carried out at a current density of 40 mA cm\(^{-2}\) (20 mA cm\(^{-2}\) for untreated carbon felt). 70 mL of 1 mol L\(^{-1}\) vanadium electrolyte on each side, flow rate: 30 mL min\(^{-1}\), voltage cut-off 0.8 V to 1.7 V.
5. Full-cell VRB studies

Table 5.3 below gives a comparison of the ratios of different oxygen functional groups present on the surface of the pristine and heat treated SGL 39 AA carbon papers and GFD4.6 EA carbon felt.

Table 5.3 - Comparison of different oxygen functional groups on the surface of SGL 39 AA carbon papers and GFD4.6 EA carbon felt.

<table>
<thead>
<tr>
<th>SGL 39AA</th>
<th>pristine</th>
<th>thermally treated</th>
<th>acid soaked</th>
<th>after cycling (-) side</th>
<th>after cycling (+) side</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O/COH</td>
<td>0.45</td>
<td>0.38</td>
<td>0.28</td>
<td>0.31</td>
<td>0.27</td>
</tr>
<tr>
<td>COOH/COH</td>
<td>0.42</td>
<td>0.28</td>
<td>0.20</td>
<td>0.22</td>
<td>0.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GFD4.6 EA</th>
<th>pristine</th>
<th>thermally treated</th>
<th>acid soaked</th>
<th>after cycling (-) side</th>
<th>after cycling (+) side</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O/COH</td>
<td>0.32</td>
<td>0.46</td>
<td>0.23</td>
<td>0.50</td>
<td>0.45</td>
</tr>
<tr>
<td>COOH/COH</td>
<td>0.15</td>
<td>0.23</td>
<td>0.08</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 5.8 shows the effect of charging and discharging on the positive and negative half-cell potentials over time. During charging the negative half-cell potential becomes progressively more negative with time and the positive half-cell potential becomes more positive with time. During discharge the opposite process occurs.

![Graph showing charge and discharge curves](image)

Figure 5.8 – (a) Charge and (b) discharge curves measured for thermally treated SIGRACELL® GFD4.6 EA carbon felt at a current density of 40 mA cm⁻². Insight into contributions of the positive and negative electrode reactions to the overall performance determined with reference electrode for both charging and discharging processes.
Figure 5.9 shows a comparison of performance of heat treated carbon papers before and after 73 cycles in two different potential windows. Figure 5.9 (a) shows the initial and final performance after 73 cycles between 0.8 V and 1.7 V. Figure 5.9 (b) shows the initial and final performance after 73 cycles between 0.8 V and 1.6 V. It is apparent that after 73 cycles between 0.8 and 1.6 V the losses in overall performance are reduced, Figure 5.9 (b). Furthermore, the losses originating from the negative electrode are reduced compared to the case when the cycling was carried out between 0.8 V to 1.7 V, Figure 5.9 (a).

**Figure 5.9** - Polarisation curves measured for heat treated SGL 39 AA carbon papers before and after 73 cycles (with freshly prepared electrolyte) between (a) 0.8 V and 1.7 V and (b) 0.8 V and 1.6 V, showing overpotential contributions from positive and negative electrode reactions.
Chapter 6. Summary, conclusions and outlook
6. Conclusions and outlook

6.1 Summary and conclusions

The work presented here has addressed the reaction kinetics of the two redox reactions in the all-vanadium redox flow cell on (i) a fundamental level on model surfaces and (ii) an application level in a full-cell system on commercially relevant carbon electrodes. The ultimate goal was to understand and identify properties affecting electrode activity and stability in order to improve power density.

The influence of surface modification of glassy carbon electrodes on the kinetics of the V(V) reduction reaction and the V(II) oxidation reaction was studied. The role of oxygen functional groups and carbon microstructure on electrode activity was investigated. For the V(V) reduction reaction, no direct correlation between activity and surface oxygen content or any particular oxygen group was observed. However, surfaces which were subject to structural changes upon treatment, showed improved activities and reduced charge transfer resistances for V(V) reduction. The structural changes constituted a disruption of the glassy carbon surface by introduction of disorder and defects. Raman spectroscopy was used to determine for the first time a correlation between V(V) reduction activity and disorder/defects expressed by the FWHM of the D-band in this study. This was a valuable finding and showed that defect introduction alone could improve V(V) reduction activity and oxygen functionalities may not play a crucial catalytic role for this reaction.

A similar study conducted for the V(II) oxidation reaction revealed quite different results. The catalytic effects of surface oxygen on V(II) oxidation kinetics has been suggested by many authors, however this work provided a quantitative proof by XPS of the dependence of V(II) oxidation activity on the total oxygen content. The stability of an oxidised carbon surface in the potential range of the V(II)/V(III) reaction was seen however to be an issue. The negative potential limit was identified as a crucial parameter affecting stability of an oxidised carbon electrode surface. Further stability studies were carried out on oxidised edge and basal plane pyrolytic graphite electrodes. These studies revealed deeper insights into possible reasons for losses in electrode activity over time. XPS revealed that both edge and basal plane surfaces lose oxygen after 150 cycles in the potential range 0 to -0.8 V/RHE. The oxygen loss was more extreme for the basal plane surface which also showed a dramatic loss in activity after cycling. The edge plane surface was much more stable in comparison. The degradation mechanisms were thought to be a function of the type of carbon. The basal plane surface suffered from mechanical stability issues involving delamination of the surface, which was thought to be responsible for the dramatic activity loss. Furthermore the parasitic hydrogen evolution reaction was
investigated for the first time using an in-house DEMS setup developed by our group. The DEMS analysis revealed the oxidised edge plane surface had a higher activity for the HER compared to the basal surface. The faradaic efficiency for V(III) reduction on the edge plane surface was consequently lower than that of the basal plane carbon.

Full-cell studies investigated the performance and stability of commercial electrode materials before after thermal treatment. By the inclusion of a reference electrode in the system, the V(II) oxidation reaction was identified as the performance limiting reaction during discharge. This was a significant finding at the time, as it was not well-established in the literature which reaction was limiting the overall performance. Extended cycling measurements revealed that carbon felt electrodes were stable and carbon paper electrodes were unstable after 73 cycles between 0.8 and 1.7 V/RHE. The main losses in performance originated from the negative electrode or V(II) side on the thermally treated carbon papers. Furthermore, lowering the upper cut-off potential limit during extended cycling from 1.7 V to 1.6 V, resulted in better stability of the negative electrode in the carbon paper system. This was an indication that the negative potential limit during cycling had a significant effect on electrode stability. It was suggested that carbon properties such as oxygen content, microstructure and morphology all play a role in the observed stability of these two different materials.

This PhD work has allowed valuable correlations to be made between model carbon electrodes and commercial carbon electrodes used in the VRB system. This has in turn provided significant insights and understanding into possible factors affecting carbon electrode activity and stability. The main conclusions of this work are summarised here:

- A correlation between activity for V(V) reduction and the disorder and defects in the carbon structure was established for the first time on model glassy carbon electrodes. Oxygen was not seen to play a crucial catalytic role for this reaction.
- Full-cell studies were in agreement with model V(V) reduction studies. No significant improvement in performance was seen at the positive electrode after introduction of oxygen onto carbon paper and carbon felt electrodes by thermal treatment.
- Quantitative analysis by XPS revealed for the first time a trend between V(II) oxidation activity and total surface oxygen content on modified glassy carbon electrodes.
- The performance limiting reaction in the full system was identified as the V(II) oxidation reaction occurring at the negative electrode during discharge.
6. Conclusions and outlook

- Losses in performance of thermally treated carbon papers after extended cycling in the full system originated mainly from the negative electrode and were influenced by the negative potential limit.

- A quantitative measure of hydrogen evolution and FE for V(III) reduction on model carbon surfaces was determined for the first time using an in-house DEMS setup.

- The EC-Edge surface showed a lower FE for V(III) reduction compared to the EC-Basal surface, indicating that the EC-Basal surface is more active for V(III) reduction.

- The EC-Basal surface did not maintain its initial activity after extended cycling and this was attributed to the poor mechanical stability of the basal surface itself.

- The type of carbon and its associated structural and chemical surface properties have a significant influence on the resulting electrochemical activity and stability of the electrodes used in the VRB system.

6.2 Outlook

Through the present research an idea of the properties influencing activity and stability have been established and could be used to design optimised electrodes for the VRB application. However there are several gaps in understanding that require further research. The model electrode systems provide a well-defined simplification of the real commercial carbon electrodes used. However, some aspects of the porous commercial electrodes are not accounted for in the model systems. An understanding of the macroscopic properties of commercial electrode materials (e.g. porosity, wettability) on performance is required. The diffusion limitations within a porous carbon fibre-based electrode should also be investigated.

The influence of the HER on electrode activity and system performance over time in the full-cell could also be investigated. DEMS is a valuable tool which should be exploited in this context, as it allows in-situ investigations of the electrochemical processes occurring at the electrode surfaces in the system. A similar study to the one carried out in this work, investigating the faradaic efficiencies for V(III) reduction could be conducted on different commercially relevant carbon materials. It would be possible to identify carbon materials with low HER activity, which is desirable for this application. Knowledge of the materials properties of carbons with low HER activity could be used in the design of stable negative electrodes.
Finally, from a kinetic perspective it would be valuable to combine further model electrode research with theoretical studies to try and identify an active site or active sites for both redox reactions. This would add great value in tailoring the design of the positive and negative electrodes to optimise activity for the respective redox reactions.
Bibliography


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Bibliography


[142] X.L. Zhou, T.S. Zhao, Y.K. Zeng, L. An, L. Wei, A highly permeable and enhanced surface area carbon-cloth electrode for vanadium redox flow batteries, J.


## List of symbols, abbreviations and constants

### Symbols

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<tr>
<td>I</td>
<td>Current</td>
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<tr>
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<td>Cell voltage</td>
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<tr>
<td>e⁻</td>
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</tr>
<tr>
<td>n</td>
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<td>negative (i = -) electrode or full cell (i = cell)</td>
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<td>$ΔE_p$</td>
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List of symbols, abbreviations and constants

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<td>Potential of anodic peak current</td>
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<td>$E_{p,c}$</td>
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<td>$\lambda_{scattered}$</td>
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### List of symbols, abbreviations and constants

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<td>m</td>
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<tr>
<td>α</td>
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### Abbreviations

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<th>Abbreviation</th>
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<td>RFB</td>
<td>Redox flow battery</td>
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<tr>
<td>VRB</td>
<td>Vanadium redox flow battery</td>
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<tr>
<td>EES</td>
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<td>CAES</td>
<td>Compressed air energy storage</td>
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<td>Pumped hydroelectric storage</td>
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<tr>
<td>PSI</td>
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<td>SHE</td>
<td>Standard hydrogen electrode</td>
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<td>Reference electrode</td>
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<td>Working electrode</td>
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### List of symbols, abbreviations and constants

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<td>Hydrogen evolution reaction</td>
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<td>Quadrupole mass spectrometer</td>
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### Constants

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Publication list

Peer reviewed publications


Annual reports PSI, Electrochemistry Laboratory (LEC)


Conference talks


Conference and summer school posters


