Fullerene and Tungsten Oxide Nanostructures-based Electrocatalysts for All-Vanadium Redox Flow Batteries

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Fullerene and Tungsten Oxide Nanostructures-based Electrocatalysts for All-Vanadium Redox Flow Batteries

Farah Ahmed El Diwany

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science in Nanotechnology

School of Sciences and Engineering
The American University in Cairo
Fall 2020
Statement of Original Authorship

The work encompassed in this thesis has not been submitted before for fulfilling the requirements of any other degree or award at the American University in Cairo or any other research institution. I certify, at the best of my knowledge, that this thesis does not contain material written or published by other persons unless the work is referred to.

Signature: Farah Ahmed El Diwany

Date: January 7th, 2021
Keywords

Energy storage; vanadium redox flow battery (VRFB); G1 VRFBs; G3 VRFBs; mixed acids; positive-electrode; negative-electrode; carbon cloth; carbon felt; cyclic voltammetry; kinetics; reversibility; peak separation; electrochemical impedance spectroscopy; charge transfer resistance; overpotential; stability; thermal treatment; fullerene; hydrated tungsten oxide; reduced tungsten oxide; stoichiometric tungsten oxide; oxygen functional groups; conductivity; wettability; hydrogen evolution reaction; chlorine evolution; Nicholson’s method; heterogeneous-rate constant.
Abstract

The vanadium redox flow battery (VRFB) is one of the most promising long-term energy storage solutions mainly due to its long service life and the independence of its energy capacity on power rating and *vice versa*. However, its relatively high capital cost limits its widespread deployment. Economic analysis reveals that a high-power density VRFB with decreased cell stack size can dramatically reduce the cost. The energy efficiency of a VRFB primarily depends on the kinetics of vanadium redox reactions that take place in the stack. Therefore, studying the effect of surface chemistry of electrodes on the kinetics of each half-cell reaction is important. Accordingly, this thesis aims to enhance the kinetics of the redox reactions at the negative and positive electrodes. The thermal treatment of carbon cloth (CC) electrodes was studied and was found to improve the kinetics of both half-cell reactions. The incorporation of C\textsubscript{76} particles further enhanced the kinetics of the VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} redox reaction. A 99.5\% and 97\% decrease in the VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} electron transfer resistance was achieved, compared to thermally treated CC (TCC) and untreated CC (UCC). Less chlorine evolution and higher stability upon cycling were also achieved for C\textsubscript{76}, showing that treatment was not only unnecessary but also unsatisfactory in terms of cyclic stability.

\textbf{WO}_3.0.33\text{H}_2\text{O/W}_{32}\text{O}_{84} (hydrated tungsten oxide, HWO) was fabricated by a hydrothermal method and used primarily for the V\textsuperscript{2+}/V\textsuperscript{3+} redox reaction. It exhibited superior kinetics compared to TCC. In addition to inhibiting the parasitic hydrogen evolution reaction, HWO was found to enhance the stability of the negative electrode relative to TCC. As for the VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} reaction, a nanocomposite of HWO-50\% C\textsubscript{76} was found to not only decrease the charge transfer resistance and enhance the electrode stability, but also further inhibit chlorine evolution, relative to UCC, TCC and C\textsubscript{76}. This shows the great potential of HWO-50\% C\textsubscript{76} and HWO as electrocatalysts for VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} and V\textsuperscript{2+}/V\textsuperscript{3+} redox reactions, respectively, towards lower-cost VRFBs.
Acknowledgments

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List of Abbreviations

AC        Activated Carbon
ASA       Active Surface Area
BE        Binding energy
CB        Carbon Black
CC        Carbon Cloth
CF        Carbon Felt
CP        Carbon Paper
CNFs      Carbon Nanofibers
CNTs      Carbon Nanotubes
CS        Crystallite size
CV        Cyclic Voltammetry or Cyclic Voltammograms
DFT       Density Functional Theory
ECSA      Electrochemical Surface Area
EDX       Energy Dispersive X-ray Spectroscopy
EE        Energy Efficiency
EIS       Electrochemical Impedance Spectroscopy
ET        Electron Transfer
EU        Electrolyte Utilization
FESEM     Field Emission Scanning Electron Microscopy
FTIR      Fourier Transform Infrared Spectroscopy
G1        1st Generation
G2        2nd Generation
G3        3rd Generation
GF        Graphite Felt
GNP       Graphene Nanoplatelets
GO        Graphene Oxide
HER       Hydrogen Evolution Reaction
HT        Hydrothermal
<table>
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<tr>
<th>Abbreviation</th>
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<tr>
<td>HWO</td>
<td>WO$<em>3$.($\text{H}<em>2\text{O}$)$</em>{0.333}$/W$</em>{32}$O$_{84}$ (hydrated tungsten oxide)</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic Energy</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi-Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
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<tr>
<td>RFB</td>
<td>Redox Flow Battery</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
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<td>SCE</td>
<td>Saturated Calomel Electrode</td>
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<td>VRFB</td>
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<td>XRD</td>
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Chapter 1: Introduction

1.1 Energy Problem

The ever-growing population, intensive human activities, and the rapid industrial revolution have led to an increasingly high demand for electrical energy of more than $20 \times 10^3$ TWh per year worldwide, and this increases every year by more than 3%.\(^1\) Although fossil fuels have been used as an energy source for several decades, they have been associated with numerous environmental risks, not to mention their limited reservoirs are running out. The resulting increased greenhouse gas emissions have contributed to global warming (~1.5 °C increase in global mean land temperature), with more than 40% of global CO\(_2\) emissions produced only from fossil fuels.\(^2\) This has caused extreme weather conditions such as increased frequency and intensity of dust storms, heatwaves, droughts, and flooding, leading to desertification, land degradation, and food insecurity, which is affecting the whole human and ecosystem health.\(^3\) Approximately, 15-18 billion m\(^3\) of freshwater is contaminated by fossil fuel waste products every year, which threatens agriculture and the entire ecosystem, as well as contribute to communicable diseases.\(^4\) The high reliance on fossil fuels has also worsened ambient air pollution, which is considered as the fifth major risk factor, contributing to about 4.2 million worldwide deaths per year due to noncommunicable diseases.\(^5\) In fact, around 40,000 Egyptians annually die from pollution-related diseases, according to the World’s Health Organization (WHO).\(^6\) By 2030, it is estimated that about 1.1 million Egyptian may be at risk of Nile flooding annually, due to climate change, as reported by the WHO.\(^6\)
Chapter 1: Introduction

The Paris Agreement in 2015 has set the goal to minimize global emissions to limit the global temperature increase to 1.5 ºC.\textsuperscript{2} To achieve this, 45\% of the global anthropogenic CO\textsubscript{2} emissions needs to be reduced by 2030 compared to 2010 levels, according to the Intergovernmental Panel on Climate Change (IPCC).\textsuperscript{2} Therefore, the penetration of clean and renewable wind and solar energies is expected to significantly increase over the coming years (up to 37-75\% of the total electrical energy in 2050).\textsuperscript{1} However, they are unreliable as they only generate electricity when it is suitable weather or timing. Besides, the electrical grid becomes unstable when the power from renewable energy sources exceeds 20\% of the total generated power.\textsuperscript{1,7}

1.2 Energy Storage Systems

To satisfy the need for stable power, energy storage is required to not only store excess electricity at times when wind and solar energy sources are operating, but also avoid the instability of the grid as mentioned above. This will balance the supply and demand for energy, as well as match the power generation with load requirements. Energy storage also reduces costs for consumers and limits the need to upgrade electrical generating plants when in high demand.\textsuperscript{7} Conventional energy storage methods such as pumped hydro energy storage and compressed air energy storage have high construction costs, cannot quickly respond to power demands, and are only limited to suitable sites.\textsuperscript{8} Even though electric double layer supercapacitors have a higher power density, they suffer from very low energy density and cannot be used for long-term energy storage.\textsuperscript{8} Complications associated with regenerative fuel cells include energy storage via electrolysis and difficulty in storing inflammable hydrogen.\textsuperscript{8}
Batteries are a core technology to aid with the energy transition and are believed to be the best solution to achieve the Paris Agreement as shown in Figure 1.1 due to their substantial flexibility. That is, they could decarbonize transport, enable the shift from fossil fuels to renewable power generation and help to provide electricity to off-grid communities, especially that power and transport comprise ~40% of the global emissions. In fact, battery demand has been annually increasing by 30% for the past 10 years and is expected to keep growing at the same rate by 2030. However, cost-efficient and sustainable batteries are needed for broad customer acceptance. The lithium-ion battery technology is still the most mature energy storage system because of its high energy density. However, Li-ion batteries suffer from overcharging and aging, hence their limited life cycle, as well as present a fire risk.

In an alternative technology, redox flow batteries (RFBs) are thought to be an optimal solution for long-term energy storage (~30 years) when combined with renewable energy sources, especially that governments are stressing the need for integrating long life-cycle energy storage technologies into the so-called smart grids. The scalability (decoupling of energy storage and power density), site versatility, long-cycle life, and ease of operation of RFBs render them a suitable energy storage system. Among other batteries, RFBs have the lowest annualized cost, equal to $65/kWh, compared to $93-$140/kWh and $279-$420/kWh for Li-ion and lead-acid batteries, respectively, due to their longer cycle life.
1.3 Thesis Organization

The energy crisis and energy storage technologies were introduced in Chapter 1. Scientific background on RFBs, including their advantages, drawbacks and electrochemistry, in addition to the basic science of the electrochemical and physicochemical characterization techniques utilized throughout this thesis, will be discussed in Chapter 2. The recent literature on the kinetics of electrode material for vanadium redox flow batteries will be reviewed in Chapter 3. This chapter is divided into the treatment of commercial carbon-based electrodes, carbon nanostructures, and metal oxides with more focus on tungsten oxide. This is followed by the employed experimental procedures and the physicochemical and electrochemical characterization methods used in Chapter 4. The results and discussion will be presented in Chapter 5 in four main sections: the electrochemical performance of 1) treated carbon cloth on VO\(^{2+}/VO_2^+\), 2) C\(_{76}\) particles on VO\(^{2+}/VO_2^+\) (paper accepted for publication in Chem. Commun., 2020)\(^1\), 3) tungsten oxide nanostructures on VO\(^{2+}/VO_2^+\) and V\(^{2+}/V_3^+\), and 4) C\(_{76}\)/tungsten oxide nanocomposites on VO\(^{2+}/VO_2^+\) and V\(^{2+}/V_3^+\) redox reactions. Conclusion and future work will be presented in Chapter 6.
2.1 Advantages of RFBs

RFBs are large stationary electrochemical energy storage systems mainly used for long-term energy storage of renewable energy sources in decentralized and deregulated networks.\textsuperscript{7,8,10} Electricity coming from solar and wind sources is chemically stored in RFBs, then converted back to electricity upon demand by redox reactions between electroactive species dissolved in liquid electrolytes. They consist of two main parts: two tanks of electrolyte solutions where the energy is stored, and the cell stack where redox reactions take place to convert chemical into electrical energy. To be more specific, the catholyte (positive side) and the anolyte (negative side), containing different redox couples, are pumped from the external tanks into the cell stack upon operation, where they are separated by an ion exchange membrane to prevent mixing of the ions. Inside the cell, electrochemical reactions take place on the surface of electrodes. This design renders the RFB its most significant feature, which is the independence of power and energy densities. That is, while the size or the number of stacks govern the power rating, the energy capacity is defined by the amount of electrolyte stored in the tanks.

The operating voltage of the RFB system is determined by the difference in chemical potentials of both redox couples dissolved in the two half-cell electrolytes. So, just like any galvanic cell, the larger the difference between the positive and negative sides (determined by the selection of redox couple combinations), the higher the operating voltage. Whereas a plethora of redox couples could theoretically be used in RFBs, factors like chemical potential, electrochemical reversibility, solubility, toxicity, and cost limit their use for large-scale applications. Unlike conventional batteries (e.g., Li-ion batteries) where the electrodes are the active species, so they
get consumed during the electrochemical reaction, RFBs store energy by reversible redox processes taking place in solution. In fact, the electrodes only provide a surface area for the redox reaction to take place, hence their relatively long lifetime and low annualized cost. In addition, deep charging and discharging can take place without affecting the morphology of the electrode structure. Therefore, RFBs are suitable for frequency balancing, energy storage exceeding six hours, and fast response upon electrical demand by switching between charging and discharging within milliseconds.\(^\text{10}\)

### 2.2 Types of RFBs

There are three main different types of RFBs: hybrid, organic, and aqueous RFBs. Hybrid RFBs involve the deposition of solid species on the electrode during charging at one of the half cells. However, dendrites could form at high current densities which would lower the power and capacity. Also, power and energy densities are no longer decoupled, which is the main advantage of RFBs. An example is the Zn-Br RFB involving the deposition of Zn metal at the anode, but Br\(_2\) vapors are extremely toxic. Another type of hybrid RFBs is the presence of gaseous material (e.g., H\(_2\) or O\(_2\)) in one of the half-cell reactions. However, while the usage of H\(_2\) requires its storage and compression, O\(_2\) suffers from very slow kinetics. Even though organic RFBs are attractive as the cell voltage could increase beyond O\(_2\) and H\(_2\) evolution, organic electrolytes suffer from low conductivity, high toxicity, and high cost.

As for aqueous RFBs, they are comprised of two electrolyte tanks, in which the redox species are dissolved in aqueous solutions and the electrodes do not take part in the redox reaction, as described above. Many chemistries have been tried, such as the Mn\(^{2+}/\text{Mn}^{3+}\) catholyte in H\(_2\)SO\(_4\) combined with Ti\(^{3+}/\text{Ti}^{4+}\), Cr\(^{2+}/\text{Cr}^{3+}\), V\(^{2+}/\text{V}^{3+}\), Sn\(^{2+}/\text{Sn}^{4+}\), or Zn/Zn\(^{2+}\) anolytes,\(^\text{7,8,10}\) but their major problem is the instability of Mn\(^{3+}\) ions in solution. The Fe/Cr RFB was invented in the 1970s at
Chapter 2: Scientific Background

NASA, and was the first practical RFB. Its chemistry involves Fe\(^{2+}/\)Fe\(^{3+}\) and Cr\(^{2+}/\)Cr\(^{3+}\) redox couples dissolved in HCl in the positive and negative sides, respectively. However, it suffers from slow Cr kinetics. The most studied and advanced type is the all-vanadium RFB (VRFB), invented by Skyllas-Kazacos et al.\(^ {13}\) in 1986, is illustrated in Figure 2.1, and will be the subject of this thesis. Its advantage over all other RFBs is the reduced cross-contamination across the membrane as both sides contain the same metal species (vanadium), which decreases capacity fading/self-discharge hence prolongs the lifetime of the battery.

2.3 Electrochemistry of VRFBs

The chemistry of the VRFB is based on VO\(^{2+}/\)VO\(^{2+}\) (Equation 2.1) and V\(^{2+}/\)V\(^{3+}\) (Equation 2.2) ions dissolved in H\(_2\)SO\(_4\) electrolyte at the cathode and anode, respectively.

\[
\begin{align*}
\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- & \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O} & E^0 = +0.991 \ \text{V} \\
\text{V}^{3+} + \text{e}^- & \rightleftharpoons \text{V}^{2+} & E^0 = -0.255
\end{align*}
\]

(2.1) (2.2)

This gives an open-circuit voltage (OCV) of 
\[
E^0 = +0.991 - (-0.255) = 1.246 \ \text{V}.
\]

As illustrated in Figure 2.1 below, VO\(^{2+}\) is oxidized to VO\(^{2+}\) at the cathode, and V\(^{3+}\) is reduced to V\(^{2+}\) at the anode during charging (e.g., by electrical energy produced by solar or wind energy sources), while H\(^+\) ions move across an ion exchange membrane from the cathode to the anode to balance the charge transport. The reverse redox reactions take place upon discharging the battery when electricity is needed. As already mentioned, both vanadium redox reactions take place at the surface of inert electrodes (usually carbon-based electrodes).
Chapter 2: Scientific Background

The main factors controlling the performance of the VRFB system are: (1) thermodynamics, reflected $E^0$; (2) reversibility/electrode kinetics/electron transfer (ET) rate, embodied in $k^0$, the standard heterogeneous ET rate constant; and (3) mass transport (mainly diffusion) of vanadium ions to the electrode. The low energy density of VRFBs is governed by the limited solubility and stability of vanadium ions in $\text{H}_2\text{SO}_4$ in 1st Generation (G1) VRFBs. That is, $\text{VO}_2^+$ ions readily precipitate to form solid $\text{V}_2\text{O}_5$ at elevated temperatures ($>$40 ºC). Instead, an HCl/HBr electrolyte had been proposed for 2nd Generation (G2) VRFBs, but these suffered from Br2 vapor formation. Therefore, a 3rd Generation (G3) VRFB using mixed acids ($\text{H}_2\text{SO}_4$/HCl) was reported, demonstrating high solubility and stability over a wider temperature range by preventing deprotonation and hence the precipitation of $\text{V}_2\text{O}_5$. Another reason for the low energy density is the partial utilization of the active species in the electrolyte due to the electrochemical (2) and mass

**Figure 2.1:** Schematic diagram of the VRFB. Vanadium redox species are stored in external tanks and are pumped into the central cell stack to generate power by redox reactions.
transport (3) polarizations, especially at high current densities. As such, electrode kinetics have a massive impact on the energy density of the VRFB, as well as on the power ratings.

According to the Butler-Volmer (BV) (Equation 2.3), an overpotential (\(\eta\)) of a certain value must be applied to the electrode before any current, \(i\), could be obtained depending on the electrode kinetics. The higher activation energy barrier for ET between the vanadium ions and the electrode would require a higher overpotential. The BV equation also relates the current flowing at the electrode with the standard heterogeneous ET rate constant, \(k^0\), and the transfer coefficient, \(\alpha\), which is a measure of the reaction mechanism.

\[
i = A F k^0 \{ [R] \exp \left( \frac{(1-\alpha)F \eta}{RT} \right) - [O] \exp \left( \frac{-\alpha F \eta}{RT} \right) \} \tag{2.3}
\]

An electrochemically reversible reaction requires a small \(\eta\) as it has a large \(k^0\), and vice versa for an irreversible reaction. An intermediate case is the quasi-reversible reactions, which is the case for \(\text{VO}^{2+}/\text{VO}_2^+\) and \(\text{V}^{2+}/\text{V}^{3+}\) redox reactions in the VRFB system. The \(\eta\) also changes the \(E^0 (=1.245 \text{ V})\) giving an output voltage of \(V_{\text{out}} = E^0 - \eta\), and an input voltage of \(V_{\text{in}} = E^0 + \eta\).\textsuperscript{15,16}

However, even though VRFBs have lower annualized cost than other batteries, their extensive commercialization is still impeded by their relatively high system capital cost ($399/kWh), primarily due to the cell stack.\textsuperscript{11} Therefore, improving the cell stack performance by improving electrodes’ efficiency can reduce the size of the stack and, consequently, the cost. In particular, the energy stored and power delivered, in the VRFB, are proportional to \(V_{\text{out}}\). Therefore, fast ET at the electrode’s surface is needed, which depends on the structure of the electrode. It is for that reason that this thesis is focused on the electrode material and kinetics to improve the overall battery performance. To study the kinetics of the materials, certain electrochemical techniques were used as will be discussed in the next section.
2.4 Electrochemical Characterization

The electrocatalytic activity of the electrode materials was investigated by two methods: cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Both techniques were conducted in a three-electrode setup (shown in Figure 4.1), consisting of the working, counter, and reference electrodes placed in the electrolyte of interest. The working electrode is the material under study where the redox reaction takes place, and the current flows between itself and the counter electrode. The working electrode potential is measured against the reference electrode.

In CV, the potential of the electrode is swept from a potential where no reaction takes place to a potential where the reaction is diffusion-controlled, and then back to the starting potential (Figure 2.2a). The potential is swept at a constant rate, called the scan rate, \( \nu \), and the current is measured with respect to the potential. The cyclic voltammogram (CV) produced consists of two main regions: (1) the ET kinetics region when the current increases exponentially according to the BV model (Equation 2.3), and (2) the mass transport (mainly diffusion) controlled region when the current reaches a maximum. The difference in potentials, \( \Delta E_p \), at oxidation and reduction peak currents, as shown in Figure 2.2a, is indicative of the kinetics of the reaction.\(^{17}\) A larger \( \Delta E_p \) means that a larger \( \eta \) was required for the reaction to take place, indicating slower ET. A reversible reaction has a \( \Delta E_p = 59 \text{ mV/n} \), where \( n \) is the number of electrons involved in the redox reaction.\(^{18}\) Another property that reflects the reversibility of the reaction is the peak current ratio, \( I_{pc}/I_{pa} \), between the cathodic and anodic currents, which approaches one as the reaction becomes more reversible. If \( \Delta E_p \) changes with \( \nu \) then the reaction is quasi-reversible or irreversible.
Figure 2.2: (a) CVs of three main electrochemical systems. $\Delta E_p$ is larger for more irreversible redox reactions. Taken from ref. 17 (b) Nyquist plot with the equivalent circuit displayed for a typical VRFB system.

EIS uses a purely electronic model to represent an electrochemical system, in which a redox reaction at the electrode’s interface is analogous to an electric circuit with resistors and capacitors. This gives accurate kinetic and mass transport information as, unlike the CV, EIS can separate both contributions. A sinusoidal potential with a small amplitude (max. 10 mV) of fixed frequency is applied to the working electrode around a time-independent DC potential, and the current response is measured. This is done for a wide range of frequencies (0.001 Hz – $10^5$ Hz) to compute the impedance at each frequency. The data produced is usually presented using the so-called Nyquist plot (Figure 2.2b), in which the imaginary part of the impedance is plotted against the real part of the impedance. An equivalent circuit is then needed to analyze the system and obtain the required parameters. For VRFBs, a complete Randles cell is used, where $R_\Omega$ is the ohmic resistance, $R_{CT}$ is the charge transfer resistance, $C$ is the capacitance and $W$ is the Warburg slope related to the diffusion of the ions. A smaller semi-circle means a smaller $R_{CT}$ value, hence fast ET, and a higher $W$ slope means faster diffusion of ions.$^{19}$
2.5 Physicochemical Characterization

Field emission scanning electron microscopy (FE-SEM) was employed for the examination of the microstructure surface morphology. Electrons are generated by a field emission source, accelerated in a field gradient under ultra-high vacuum, and focused by electromagnetic lenses and apertures onto the sample surface. The incident electron beam then interacts with the sample by elastic and inelastic scattering, producing different signals with different energies emitted from varying depths. In one of the inelastic processes, loosely bound electrons emitted from regions close to the surface (~50 nm deep) are called the secondary electrons. These electrons are then detected by a detector and amplified to be used in imaging and analyzing the sample. Another form of signal is the emission of characteristic X-rays which are specific to each element present in the sample. Energy-dispersive X-ray spectroscopy (EDX) detects these X-rays to provide a surface elemental mapping of the samples.

Transmission electron microscopy (TEM) was used to provide atomic resolution lattice images, as well as reveal the crystal structure. TEM also consists of a field emission gun, electromagnetic lenses, apertures, and a data recording system. However, as the TEM name implies, electrons are transmitted through the sample (<100 nm thick) so the detector, unlike in SEM, is placed below the specimen stage. Electrons passing through the sample with unchanged trajectory make up the transmitted electrons, which are used to reveal the microstructure of the sample through bright-field imaging. Other interactions occur between the sample and the incident beam of electrons, such as elastic Bragg diffraction. These diffracted electrons, in addition to the transmitted electrons, are used to obtain high-resolution imaging of the lattice planes. In a polycrystalline material, randomly oriented crystallites diffract the incident electrons to produce a
ring pattern, in which the d-spacings (d) and Miller planes (hkl) could be obtained, hence the crystal structure.

Powder X-ray diffraction was conducted to study the phase and crystal structure of the samples. X-rays generated by a cathode ray tube are filtered to produce monochromatic radiation with a wavelength, $\lambda = 1.54$ nm. When the incident X-ray beam hits the sample at an angle $\theta$ with the planes, coherent waves are scattered by the periodic lattice, leading to constructive interference between the diffracted rays satisfying Bragg's Law ($2dsin\theta = \lambda$). These diffracted X-rays are detected and a diffraction pattern is then produced. Because each crystalline material has unique d-spacings, information about the crystal structure can be obtained. Due to the random orientation of the grains in a powdered sample with respect to the incident beam, all possible diffractions (d-spacings) of the lattice could be detected by scanning over a wide range of $2\theta$ angles. Results from XRD were compared with those from TEM analysis.

X-ray photoelectron spectroscopy (XPS) was utilized to identify the surface carbon functional groups and the oxidation state of metal oxide. Under ultra-high vacuum, a monoenergetic X-ray beam with energy, $E_{\text{photon}}$, hits the sample, resulting in the ejection of core-level electrons from the sample based on the photoelectric effect. Photoelectrons are detected and their respective kinetic energies (KE) are measured. Using KE of the ejected photoelectrons, the binding energy (BE) of core electrons can be calculated (also using the spectrometer work function, $\phi$) by $\text{BE} = E_{\text{photon}} - \text{KE} - \phi$. The chemical shift in BE values gives information about the environment around each atom in the sample. Hence, oxidation states and surface functional groups could be determined.

Fourier transform infrared spectroscopy (FT-IR) was used to determine the functional groups on the surface of the samples to be compared with the XPS results. FTIR involves the
bombardment of the sample of interest with an IR beam. The sample absorbs specific IR frequencies of energy based on the covalent bonds available. That is, energy is absorbed only when it is equal to the natural frequency of the vibration of the bond, in which the vibrations are usually stretching and bending. The frequency absorbed is characteristic of the molecular bond in the sample. The transmitted beam then reaches an underneath detector forming an interferogram (raw data in the time domain), which is converted to the IR absorption spectrum (data in the frequency domain) by FT.

Raman spectroscopy was used to study the defects and conductivity present in carbon materials. An ultraviolet/visible light laser is used as an energy source of a specific frequency. The sample under study absorbs the radiation and re-emits it by scattering to be detected. The frequency of the re-emitted beam is shifted up or down relative to the incident monochromatic radiation, which is called the Raman effect. That is, the incident radiation excites and polarizes the molecule, so it starts to vibrate with a characteristic frequency then emits the radiation. The emitted radiation could have a frequency equal to (Rayleigh scattering), lower than (Stokes) or higher than (Anti-Stokes) that of the incident radiation. This shift is in the IR range, hence provides information about the vibrational transitions in a molecule.
Chapter 3: Electrode Advancements in VRFBs

The first study on different electrode materials than graphite for VRFB systems was investigated by Rychcik and Skyllas-Kazacos in 1987. This study showed that the graphite electrodes corrode under the oxidizing environment of the VO$_2^+/VO_2^{2+}$ reaction, causing the formation of carbon suspension in the positive electrolyte. This finding shifted the research attention to the replacement of graphite electrodes with metal electrodes, even though they are more expensive. Fortunately, subsequent studies showed that, by controlling the cut-off voltage during the charging process, it is possible to prevent the disintegration of carbon-based electrodes and achieve long-term stability. In 2015, the focus then shifted back to the modification of carbon-based electrodes with different functional groups and electrocatalysts aiming to improve their reversibility toward vanadium redox reactions, to reduce the cost of the VRFB system, which is the goal for market penetration. Modifications with transition metals (e.g., Pt$^{4+}$, Pd$^{2+}$, Ir$^{3+}$, and In$^{3+}$) have been used due to their good catalytic activity related to their partially filled d orbital. However, many of these are noble and rare-earth metals, so they are not practical for large-scale VRFBs due to their high cost, in addition to their promotion of parasitic reactions, especially hydrogen evolution reaction (HER). Other metal catalysts have been used by dissolving their ions in the vanadium electrolyte solution. This would, however, result in the accumulation of deposited metal during charge/discharge cycles. Also, a portion of the charge would be directed to depositing the metal layer rather than charging the vanadium ions. This would defeat the purpose of using VRFB systems in the first place. As a result, massive attention has been given to modifying carbon-based electrodes.

Graphitized carbon-based electrodes are widely used in VRFB systems to provide a low cost, electrically conductive, high surface area, porous structure for a sufficient flow of electrolyte.
These are usually graphite felt (GF), carbon felt (CF) or carbon cloth (CC) electrodes, all of which consist of interlaced fibers with diameters in the micrometer range (~10 µm), with high chemical robustness and stability in a wide potential range in acidic media. However, the poor reversibility (slow kinetics) of both vanadium half electrochemical reactions at these carbon electrodes limits their implementation as high-performance VRFB electrodes. These slow kinetics require a large overpotential, \( \eta \), due to the large activation energy needed for electron transfer (ET). As discussed in Section 2.3, this leads to a low output voltage \( (V_{out} = E^0 - \eta) \) and a high input voltage \( (V_{in} = E^0 + \eta) \), and hence low capacity and energy efficiency.\(^{15}\) Along with the sluggish kinetics of the graphitized carbon electrodes, their unsatisfactory mass transport (i.e., diffusion of vanadium ions to and from the electrode) reduces the power density of the VRFB.\(^{31}\) This is due to their intrinsic hydrophobicity that hinders the surface area accessibility (i.e., no close contact between the vanadium electrolyte and electrode), prohibiting the tunneling of electrons to/from the electrode’s surface from/to the active species in solution. Because both vanadium redox reactions occur through an inner layer mechanism, the lack of oxygen functional groups on the surface of carbon-based materials also inhibits the kinetics.\(^{16,32}\)

Therefore, suitable surface modifications should be carried out on the pristine carbon electrodes to increase their wettability, as well as introduce surface functionalities as catalytically active sites for the redox reactions.\(^{15,16,28-31}\) Increasing the surface defects, conductivity, and surface area should also be targeted. These strategies would evidently overcome the activation polarization towards the vanadium redox reactions taking place within the VRFB architecture. Consequently, this would allow for improved power density, electrolyte utilization (EU), and energy efficiency (EE), especially at high current densities, where polarization losses are more pronounced. Ultimately, reduced capital cost and broader VRFB market commercialization will
be achieved. This is why the research has focused on the surface chemistry of the electrodes by employing different treatment methods, and developing carbon and metal oxides electrocatalysts, which will be discussed in the following sections.

3.1 Treatment of Commercial Carbon Electrodes

One way to alter the surface chemistry of commercial carbon electrodes is via treatment methods, such as thermal and chemical treatment. B. Sun and M. Skyllas-Kazacos thermally treated GF at 400 °C in air and found that it exhibited a lower activation potential than untreated GF towards the VO$_2^+/VO^{2+}$ reaction. This was ascribed to the increased surface concentration of oxygen functional groups, C=O and C-OH, which act as active sites towards vanadium ions. They also hypothesized a mechanism for the catalysis of VO$_2^+/VO^{2+}$ in the charging process, as shown in Figure 3.1a. The first step involves the transport of VO$_{2}^{+}$ ions from the bulk electrolyte to the surface of the electrode, mainly by diffusion. Adsorption of positively charged VO$_{2}^{+}$ ions on highly electronegative oxygen atoms takes place by an ion-exchange reaction with hydrogen ions of the phenolic functional groups on the carbon surface; thus, bonding onto the electrode surface, forming a (-C-O-V-) bond. The second step is electron transfer from VO$_{2}^{+}$ to the electrode surface though the (-C-O-V-) bond. The transfer of one of the oxygen atoms on the C-O functional group to the VO$_{2}^{+}$ takes place, forming VO$_{2}^{+}$ at the surface. VO$_{2}^{+}$ could also be formed by the transfer of oxygen from H$_2$O molecules in solution. The third and final step includes the exchange of VO$_{2}^{+}$ at the surface with H$^+$ from the electrolyte and diffuses back into the bulk solution.

As for the discharge process, the reverse reactions would take place, with the difference that VO$_{2}^{+}$ is bulkier causing steric hindrance, and hence its slower kinetics. The same mechanism was also proposed for the negative reaction (Figure 3.1b) by W. Li et al., but without the oxygen transfer. However, a charge imbalance could be noticed in step 2 (should be V$_2^{2+}$ instead of V$^{3+}$).
Interestingly, the kinetics of the $V^{2+}/V^{3+}$ redox reaction was found to be more dependent on abundant oxygen functional groups. These findings suggested that both half-reactions occur via an inner-sphere species, such as the (-O') bond. It is worth mentioning that the same mechanism in Figure 3.1 occurs if COOH, C=O, or N functional groups were available, as positive vanadium ions adsorb onto the surface of the electrode via an electronegative species and electron transfer takes place though (-C-O-V-) or (-C-N-V-) bonds. The kinetics of both half-reactions were also found to be improved at higher surface-defect concentration. Even though the literature still lacks an in-depth understanding of this, it could be that defects more readily form oxygen functional groups when the electrode is placed in solution, acting as functionalized active sites for vanadium redox reactions.

![Electrochemical Reaction Mechanism](image)

**Figure 3.1:** Schematic illustration of the electrochemical reaction mechanism proposed by Sun and Skyllas-Kazacos for the (a) positive and (b) negative reactions. Adapted from ref. 16 and 33.

Since the first paper by Skyllas-Kazacos, thermal treatment has been widely adopted to activate carbon-based electrodes. However, the properties that contribute to enhancement were not well understood. Therefore, K. V. Greco *et al.* studied the effect of temperature on the performance of carbon paper (CP) electrodes towards both half-cell reactions. They found that a balance
Chapter 3: Electrode Advancements in VRFBs

between electrochemical surface area (ECSA), wettability, oxygen content, defects, and mechanical stability was needed to achieve the highest kinetics. Treatment at 450 ºC showed the best kinetics, hence energy efficiency (EE), despite not exhibiting the highest ECSA or oxygen content. In another study, T. Liu et al. thermally treated CP in the presence of CO₂ to create pores and introduce oxygen functional groups. They achieved peak separation ($\Delta E_p$) values of 246 mV and 224 mV, instead of 590 mV and 607 mV for pristine CP, for the negative ($V^{+3}/V^{2+}$) and positive ($VO_2+/VO^{2+}$) half-reactions, respectively. Likewise, S. Abbas et al. created nanopores onto the surface of CP electrodes using cobalt acetate tetrahydrate as an etching agent, along with thermal oxidation. $\Delta E_p$ was reduced from 369 mV for pristine CP to 142 mV, leading to an enhanced electrolyte utilization (EU) for the $VO_2+/VO^{2+}$ half-reaction, attributed to the functional groups, defected nanopores, and wettability. To enhance the number of active sites, S. C. Kim et al. incorporated O and N functional groups to GF by urea thermolysis and obtained a lower activation potential for the $VO_2+/VO^{2+}$ reaction with a $\Delta E_p$ of 210 mV instead of 420 mV for pristine GF. This was caused by the synergistic effect between oxidation and N doping, which created a negatively charged surface to attract vanadium ions.

Sun and Skyllas-Kazacos also treated GF electrodes using boiled concentrated H$_2$SO$_4$ to introduce C=O and C-O functional groups. EE values increased and were similar to those obtained by thermal treatment. K. Zhang et al. treated carbon felt (CF) with H$_2$SO$_4$ and ozone gas and correlated the increase in oxygen functional groups (C=O and C-OH) and defects, as well as wettability, with the enhancement in electroactivity towards the $V^{3+}/V^{2+}$ redox reaction. Whereas no redox peaks were observed for pristine CF, a $\Delta E_p$ of 149 mV was obtained for the treated CF, leading to a higher EE and stability at high current densities. Density functional theory (DFT) calculations showed that the incorporation of surface oxygen functionalities shifts the adsorption
energy of vanadium ions to more negative values, thereby facilitating the interactions between carbon and $V^{2+}/V^{3+}$ and enhancing the charge transfer. In another study, A. Hassan and T. Tzedakis used boiled $K_2Cr_2O_7$ in concentrated $H_2SO_4$ to introduce oxygen functional groups. The $\Delta E_p$ of $VO_2^+/VO^{2+}$ decreased from 990 mV to 610 mV, owing to the increased electrode roughness, oxygen functionalities, number of adsorption sites and hydrophilicity. It should be noted that the small number of adsorption sites and oxygen functionalities on the untreated GF could be the result of its high hydrophobicity; hence, preventing the electrolyte penetration through the fibers.

X. L. Zhou et al. used KOH to activate carbon cloth (CC) electrodes, for both half-cell reactions, by creating nanopores to increase the hydraulic permeability of the electrode and enhance ion transport. The enhanced surface area and oxygen functional groups improved the EE and EU at high current densities. They also compared CC to CP and found that activated CC exhibited a higher charge-discharge depth by $\sim 26.7\%$, indicating better transport properties attributed to the lower ion transport resistance.

Apart from thermal oxidation, X. Wu et al. investigated the effect of microwave treatment on GF. They found an enhancement in the charge transfer of the positive reaction, as a result of the O-H groups, as well as the increased surface roughness. A. B. Shah et al. incorporated N and S functional groups into the GF structure via hydrothermal treatment using ammonium persulfate and found that the impact on the cathodic peak ($VO_2^+$ to $VO^{2+}$) was higher than that on the anodic peak. This was indicative of either slower kinetics in the reverse direction, or a different reaction mechanism, as mentioned in Sun and Skyllas-Kazacos’s study. They attributed the improved kinetics to the increased oxygen (from sulfate groups) and nitrogen content. But it is worth mentioning that the crystallinity of GF was also improved upon the treatment, which could have contributed to the enhancement.
3.2 Carbon Nanostructures

Apart from the treatment methods mentioned above, various carbon morphologies have been synthesized and used as electrocatalysts to enhance the kinetics of both half-reactions in VRFBs (Tables 3.1 and 3.2). Carbon nanostructures are highly conductive, stable in acidic media, and provide active sites (though functionalization and defects) for vanadium electrochemical reactions, enabling them to be suitable active materials for VRFBs.

3.2.1 Graphene-based Structures

Graphene has been extensively used as electrode material due to its high surface area, good conductivity, and ease of functionalization. P. Han et al. examined graphene oxide (GO) nanoplatelets for \( \text{VO}_2^+/\text{VO}^{2+} \) and \( \text{V}^{3+}/\text{V}^{2+} \) redox reactions,\(^{47}\) and found that the \( \text{V}^{3+}/\text{V}^{2+} \) reversibility more strongly depended on the abundant oxygen functional groups, in line with W. Li’s study\(^ {33}\). Despite the positive correlation between the amount of oxygen functional groups and the enhanced electroactivity (i.e., lower \( \Delta E_p \)), GO with a lower O/C ratio showed less polarization at high scan rates, owing to their higher electrical conductivity. The same group later incorporated multiwalled carbon nanotubes (MWCNTs) into the GO structure to increase the electrical conductivity of the GO and hence decrease the charge transfer resistance (\( R_{\text{CT}} \)).\(^ {48}\) The \( \Delta E_p \) was found to decrease from 220 mV for GO to 150 mV for the composite electrode for \( \text{VO}_2^+/\text{VO}^{2+} \). In another study, J. Jin et al. used N-doped graphene as a positive electrode and achieved excellent reversibility with a \( \Delta E_p \) value of 100 mV, compared to 120 mV for graphene.\(^ {35}\) This enhancement was specifically attributed to the more quaternary nitrogen active sites towards the \( \text{VO}_2^+/\text{VO}^{2+} \) couple, rather than the increase in the total nitrogen content, even though it could oddly be noticed that all graphene electrodes with different nitrogen ratios displayed the same \( \Delta E_p \). Parasitic oxygen evolution reaction was also observed for all N-doped graphene electrodes, however, it was not
discussed by the authors. Z. Gonzalez et al. also found that GO decreased the $\Delta E_p$ from 636 mV for CF to 241 mV for $\text{VO}_2^+/\text{VO}^{2+}$, attributed to the oxygen functional groups.\textsuperscript{49} Likewise, they previously prepared graphene sheets perpendicular to Au substrate as an electrode material for the positive reaction and achieved good kinetics ($\Delta E_p = 190$ mV), due to the exposed edge planes and oxygen functional groups.\textsuperscript{50} In another study, M. Etesami et al. claimed that P-doped GO enhanced the electroactivity towards both half-cell reactions due to the increased negative charge density on the surface, relative to plain GO.\textsuperscript{51} However, the enhancement was very minor and a $\Delta E_p$ value of 350 mV was observed for the positive redox reaction, which is considered to be relatively high.

More recently, D. Opar and coworkers fabricated a 3D mesoporous graphene structure to enhance the electroactivity of the positive and negative electrodes, achieving $\Delta E_p$ values of 355 mV (583 mV for CF) and 274 mV (469 mV for CF), respectively.\textsuperscript{52} Even though graphene exhibited less oxygen functional groups than CF, it showed higher activity due to the higher conductivity and structural defects. They have also incorporated nitrogen into the same structure in a subsequent study and achieved a higher energy efficiency (EE) at the same high current density, owing to the introduction of structural defect sites as well.\textsuperscript{53} Besides, $\Delta E_p$ values were slightly reduced; that is, 323 mV was attained for the positive electrode, and 235 mV for the negative side. It was also concluded that the electrocatalytic activity is not only dependent on nitrogen content but the balance between active sites, conductivity, and active surface area (ASA). This is opposing the findings of Jin et al.’s study,\textsuperscript{35} as in D. Opar et al.’s study the number of quaternary nitrogen sites was not directly correlated with the activity. In another study, M. Jing et al. synthesized a free-standing oxygen-functionalized 3D reduced GO porous electrode with a high ASA.\textsuperscript{54} Compared to CF, superior reversibility for both half-reactions was observed for the
modified electrodes with $\Delta E_p$ values of 99 mV for $\text{VO}_2^+/\text{VO}_2^{2+}$ (481 mV for CF) and 92 mV for $\text{V}^{3+}/\text{V}^{2+}$.

### 3.2.2. Carbon Nanofibers and Nanotubes

Another carbon morphology that has been widely investigated is the carbon nanofibers (CNFs) due to their high ASA. S. Liu et al. were the first to fabricate CNFs on GF electrodes by chemical vapor deposition for the $\text{VO}_2^+/\text{VO}_2^{2+}$ reaction and reported a decrease in the overpotential, as evinced by the reduced $\Delta E_p$ from 414 mV for GF to 194 mV. They attributed this kinetics enhancement to the presence of C=C functional groups exposed on the surface of CNFs, and proposed a mechanism as shown in Figure 3.2. That is, during charging, the two C atoms in the C=C bond could combine with $\text{VO}_2^+$ and -OH from H$_2$O, respectively. $\text{V}^{4+}$ could then substitute the H atom to form a bond with O, releasing H$^+$, followed by the detachment of $\text{VO}_2^+$ from CNFs. G. Wei et al. synthesized CNFs via electrospinning and found a decrease in $\Delta E_p$ relative to CF (174 mV for $\text{VO}_2^+/\text{VO}_2^{2+}$ and 168 mV for $\text{V}^{3+}/\text{V}^{2+}$), as a result of the improved conductivity rather than oxygen functional groups. However, parasitic reactions such as oxygen and hydrogen evolution were observed. C. Xu et al. prepared an ultrathin free-standing electrospun CNFs electrode to enhance the activity towards vanadium ions. However, severe mass polarization was observed due to the small pores, leading to a low electrolyte utilization (EU) and EE at low current densities. Therefore, in a more recent study, they fabricated CNFs that have larger pores, by blend-electrospinning, and compared their activity against conventional CNFs. The concentration polarization was enhanced as revealed by the full-cell measurements as expected. However, the kinetics of both half-reactions were found to be more sluggish (especially for $\text{V}^{3+}/\text{V}^{2+}$, $\Delta E_p = 648$ mV compared to 116 mV), owing to the decreased number of functional groups. To balance between electroactivity and mass transfer, L. Zeng et al. prepared different diameter-sized
electrospun CNFs with oxygen and nitrogen functional groups. Even though CNFs with the largest diameter suffered from the highest resistance and lowest ASA, they achieved the highest EU and EE at high current densities, owing to the improved mass transfer. In another study, D. Cheng et al. decorated CNFs with Ir metal to enhance their electrocatalytic activity towards the positive reaction. A $\Delta E_p$ of 170 mV was achieved compared to 220 mV for pure CNFs, owing to the oxygen active sites and the catalytic activity of Ir towards $\text{VO}_2^+/\text{VO}^{2+}$, leading to a 12% increase in EE. To make use of the good conductivity of the carbon nanotubes (CNTs) and the active sites (edge planes) of the CNFs, M. Park et al. prepared a CNFs/CNTs composite and tested their effect on enhancing the CF activity. The decreased $\Delta E_p$ from 375 mV (CF) to 136 mV for the positive redox reaction was attributed to the increased amount of oxygen functional groups, in addition to the already-mentioned advantages. The negative reaction also exhibited defined peaks, compared to pristine CF, owing to the suppressed HER, but the $\Delta E_p$ was still considered large (615 mV).

**Figure 3.2:** Schematic illustration of the $\text{VO}_2^+/\text{VO}^{2+}$ electrochemical reaction mechanism proposed by S. Liu et al. Adapted from ref. 55.

As for CNTs, A. Sodiq et al. reported excellent electrode kinetics of N-CNTs towards the $\text{V}^{3+}/\text{V}^{2+}$ and $\text{VO}_2^+/\text{VO}^{2+}$ electrochemical reactions, with $\Delta E_p$ values of 80 mV (190 mV for CNTs) and 100 mV (210 mV for CNTs), respectively. High stability of the anode, mostly affected by pyridinic-N and oxygen functional groups, was achieved during cycling. The higher efficiency of the N-doped electrode was attributed to the nitrogen active sites, as well as the higher
graphitization degree leading to less corrosion at high potentials. In another study, they used black pearl carbon to catalyze both redox reactions. An enhanced $\Delta E_p$ of 150 mV was obtained for $V^{3+}/V^{2+}$, compared to 280 mV and 170 mV for MWCNTs and GNPs, respectively. Similarly, good reversibility was attained for $VO_2^+/VO^{2+}$, with a $\Delta E_p$ of 120 mV (250 mV for MWCNTs and 210 mV for GNPs). However, it was found that black pearl could not be used as a cathode material due to its corrosion at high potentials. The $\Delta E_p$ values for MWCNTs were supported by a previous study by G. Wei et al., who attributed the enhanced activity to the presence of carboxylic groups on the surface of the CNTs. However, looking closely at the XPS analysis revealed very small percentages of oxygen, so maybe the improved conductivity of the electrode was the main reason for the enhancement.

### 3.2.3. Other Synthesized Carbon Structures

In addition to the widely used graphene, CNFs, and CNTs structures discussed above, other carbon morphologies were also investigated. S. Jeong et al. used a high surface area, oxygen-functionalized carbon foam to promote both redox reactions. They have also incorporated Pt particles within the structure, which very slightly enhanced the reversibility of the positive electrode ($\Delta E_p$ from 286 mV to 281 mV) but promoted HER on the negative side. Y. Gao et al. incorporated O, N, and P-doped carbon sheets onto CF to enhance the reversibility of both reactions, from 564 mV to 355 for $VO_2^+/VO^{2+}$, and from no redox peaks to 340 mV for $V^{3+}/V^{2+}$. This was attributed to the boosted wettability and active sites, leading to a high EE and good stability at a high current density.
3.2.4. Naturally-derived Carbon

Apart from the synthetic carbon structures already reviewed, naturally-derived ones have recently been of great interest. Y. Lv et al. synthesized a nano-porous biomass structure using Scaphium Scaphigerum as a carbon source. The resulting highly graphitized, large surface area carbon structure was found to improve the kinetics of the negative electrode, compared to pristine GF. Using kiwifruit as a natural carbon source, the same group produced nitrogen-doped, highly graphitized porous carbon structure for both electrochemical reactions. The $\Delta E_p$ achieved by the ferric ammonium citrate, thermally activated electrode was 140 mV for $V^{3+}/V^{2+}$ and 180 mV for $VO_2^+/VO^{2+}$, compared to no redox peaks for the as-prepared electrode. This resulted in higher stability and EE, compared to the pristine GF cell. In another study, C. Wan et al. compared activated carbon (AC) derived from chitin to that derived from pine wood for both half-reactions. Chitin-derived AC exhibited the highest kinetics as a negative electrode ($\Delta E_p = 242$ mV vs. 526 mV for wood-derived), as well as a positive electrode ($\Delta E_p = 147$ mV vs. 198 mV for wood-derived). This was due to the higher ECSA and nitrogen doping, and hence more active sites for vanadium redox reactions. This ultimately resulted in a ~30% increase in maximum power density, compared to heat-treated CF.

M. Park et al. synthesized carbon black (CB) particles derived from corn protein, with oxygen and nitrogen active sites, as well as high conductivity. Results showed a $\Delta E_p$ of 146 mV for the positive electrode (353 mV for CF) and 500 mV for the negative electrode (no redox peaks for CF), indicating fast ET; hence, high EE and stability. Using the same protein, Md. A. Aziz et al. synthesized electrospun N-nanorods and obtained a $\Delta E_p$ of 280 mV, in comparison with a value of 390 mV for GC. They concluded that a balance between nitrogen content, oxygen content, and electrical conductivity was needed to achieve the lowest $R_{CT}$. In another study, R. Wang and
Y. Li fabricated a self-standing cocoon-derived carbon electrode to promote the kinetics of both half redox reactions via a cost-effective method. The abundant nitrogen and oxygen active sites allowed for fast electrolyte diffusion, thereby enhancing the EE and stability of the VRFB. While the $\Delta E_p$ of the positive electrode was 166 mV, compared to 329 mV for CP, a value of 470 mV was obtained for the negative side with no cathodic peaks for CP.

Interestingly, M. Jiao et al. designed a wood-based electrode that naturally has 3D hierarchical channels with pores for fast electrolyte transport. $\Delta E_p$ values of 540 mV and 350 mV were obtained for the VO$_2^+/VO^{2+}$ and V$^{3+}$/V$^{2+}$ reactions, respectively. Even though these results showed sluggish kinetics relative to the other studies, the presence of holes in the structure showed enhanced mass transfer, compared to the same structure without holes, leading to a 4.5 X improvement in discharge capacity. In another paper, M. Mahajan et al. used sal wood to prepare oxygen functionalized-AC electrodes with a high surface area. A decrease in $R_{CT}$ values was achieved for both redox reactions. However, the qualitative CV results were not satisfactory, and the EE was only improved by 1%.

Table 3.1: Summary of $\Delta E_p$ and $I_{pc}/I_{pa}$ values of different carbon structures mentioned above for V$^{3+}$/V$^{2+}$.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Electrolyte</th>
<th>$v$ (mV s$^{-1}$)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$I_{pc}/I_{pa}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO nanoplatelets-GC</td>
<td>2 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>10</td>
<td>330</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td>Mesoporous graphene-CF</td>
<td>0.05 M V$^{3.5+}$/1 M H$_2$SO$_4$</td>
<td>5</td>
<td>274</td>
<td>0.44</td>
<td>52</td>
</tr>
<tr>
<td>N-mesoporous graphene-CF</td>
<td>0.05 M V$^{3.5+}$/1 M H$_2$SO$_4$</td>
<td>5</td>
<td>235</td>
<td>0.53</td>
<td>53</td>
</tr>
<tr>
<td>CNFs-CF</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>5</td>
<td>168</td>
<td>-</td>
<td>56</td>
</tr>
<tr>
<td>CNFs-CNTs-CF</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>5</td>
<td>615</td>
<td>0.45</td>
<td>60</td>
</tr>
<tr>
<td>MWCNTs-CF</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>2</td>
<td>272</td>
<td>0.45</td>
<td>34</td>
</tr>
<tr>
<td>N-CNTs-CP</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>10</td>
<td>80</td>
<td>0.86</td>
<td>61</td>
</tr>
<tr>
<td>Black pearl carbon-GC</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>10</td>
<td>150</td>
<td>0.46</td>
<td>62</td>
</tr>
<tr>
<td>Carbon sheets-CF</td>
<td>0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>10</td>
<td>340</td>
<td>-</td>
<td>64</td>
</tr>
<tr>
<td>N-doped biomass GC</td>
<td>1.6 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>20</td>
<td>140</td>
<td>0.67</td>
<td>66</td>
</tr>
<tr>
<td>Chitin-derived AC</td>
<td>1 M V$^{2+}$/2 M H$_2$SO$_4$</td>
<td>50</td>
<td>242</td>
<td>-</td>
<td>67</td>
</tr>
<tr>
<td>Corn protein CB-CF</td>
<td>0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>5</td>
<td>500</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>Cocoon-derived carbon</td>
<td>1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>5</td>
<td>470</td>
<td>0.76</td>
<td>70</td>
</tr>
<tr>
<td>Wood-based carbon</td>
<td>0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>20</td>
<td>350</td>
<td>-</td>
<td>71</td>
</tr>
</tbody>
</table>
Table 3.2: Summary of $\Delta E_p$ and $I_{pc}/I_{pa}$ values of different carbon structures mentioned above for VO$_{2}^+/VO_2^+$.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Electrolyte</th>
<th>v (mV s$^{-1}$)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$I_{pc}/I_{pa}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO nanoplatelets-GC</td>
<td>2 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>10</td>
<td>230</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td>GO-CNTs</td>
<td>2 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>5</td>
<td>220</td>
<td>-</td>
<td>48</td>
</tr>
<tr>
<td>Graphene-GF</td>
<td>0.05 M V$^{4+}$/1 M H$_2$SO$_4$</td>
<td>5</td>
<td>241</td>
<td>0.9</td>
<td>49</td>
</tr>
<tr>
<td>N-graphene-GC</td>
<td>1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>50</td>
<td>100</td>
<td>0.72</td>
<td>35</td>
</tr>
<tr>
<td>Mesoporous graphene-CF</td>
<td>0.05 M V$^{3.5+}$/1 M H$_2$SO$_4$</td>
<td>5</td>
<td>355</td>
<td>0.89</td>
<td>52</td>
</tr>
<tr>
<td>N-mesoporous graphene-CF</td>
<td>0.05 M V$^{3.5+}$/1 M H$_2$SO$_4$</td>
<td>5</td>
<td>323</td>
<td>0.86</td>
<td>53</td>
</tr>
<tr>
<td>Carbon nanowalls</td>
<td>0.5 M V$^{4+}$/1 M H$_2$SO$_4$</td>
<td>5</td>
<td>190</td>
<td>0.83</td>
<td>50</td>
</tr>
<tr>
<td>CNFs-CF</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>5</td>
<td>174</td>
<td>-</td>
<td>56</td>
</tr>
<tr>
<td>Ir-CNFs-GC</td>
<td>1.6 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>20</td>
<td>170</td>
<td>0.64</td>
<td>59</td>
</tr>
<tr>
<td>CNFs-CNTs-CF</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>5</td>
<td>136</td>
<td>0.84</td>
<td>60</td>
</tr>
<tr>
<td>MWCNTs-CF</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>2</td>
<td>252</td>
<td>0.85</td>
<td>34</td>
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<tr>
<td>N-CNTs-CP</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>10</td>
<td>100</td>
<td>-</td>
<td>61</td>
</tr>
<tr>
<td>Black pearl carbon-GC</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>10</td>
<td>120</td>
<td>0.92</td>
<td>62</td>
</tr>
<tr>
<td>Carbon foam-GC</td>
<td>1 M V$^{4+}$/1 M H$_2$SO$_4$</td>
<td>100</td>
<td>286</td>
<td>0.85</td>
<td>63</td>
</tr>
<tr>
<td>Carbon sheets-CF</td>
<td>0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>10</td>
<td>355</td>
<td>0.74</td>
<td>64</td>
</tr>
<tr>
<td>N-doped biomass-GC</td>
<td>1.6 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>20</td>
<td>180</td>
<td>0.53</td>
<td>66</td>
</tr>
<tr>
<td>Chitin-derived AC</td>
<td>0.1 M V$^{4+}$/0.1 M H$_2$SO$_4$</td>
<td>50</td>
<td>147</td>
<td>-</td>
<td>67</td>
</tr>
<tr>
<td>Corn protein CB-CF</td>
<td>0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>5</td>
<td>146</td>
<td>0.87</td>
<td>68</td>
</tr>
<tr>
<td>Corn protein C nanorods</td>
<td>0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>10</td>
<td>280</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Cocoon-derived carbon</td>
<td>1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>5</td>
<td>166</td>
<td>0.8</td>
<td>70</td>
</tr>
<tr>
<td>Wood-based carbon</td>
<td>0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>20</td>
<td>540</td>
<td>-</td>
<td>71</td>
</tr>
</tbody>
</table>

3.3 Metal Oxides

In addition to nanostructured carbon materials, non-noble transition metal oxides have extensively been investigated (Table 3.3) given their low cost, in comparison to metal-based catalysts, which is critical for large-scale VRFB systems. Transition metal cations often have variable oxidations states, allowing them to easily undergo oxidation/reduction during catalysis. In this section, a few papers on different metal oxides will be reviewed, with more focus on WO$_3$.

3.3.1 Non-noble Transition Metal Oxides

H. Zhou et al. suggested that CeO$_2$ provides many oxygen vacancies that would be beneficial for promoting the VO$_{2}^+/VO_2^+$ redox reaction. A smaller $\Delta E_p$ of 260 mV was obtained
(308 mV for GF), owing to the enhanced wettability and oxygen content. The same group also investigated the possible role of ZrO$_2$ in improving VO$_{2^+}$/VO$_2^+$ and V$^{3+}$/V$^{2+}$ reactions.$^{74}$ The incorporation of ZrO$_2$ NPs into GF increased the oxygen functional groups, as well as the wettability leading to a $\Delta E_p$ of 224 mV and 223 mV, compared to 308 mV and 291 mV, for the VO$_{2^+}$/VO$_2^+$ and V$^{3+}$/V$^{2+}$ redox reactions, respectively. Both studies provided a reaction mechanism, similar to the one proposed earlier by W. Li et al. (Figure 3.1).$^{16,33}$ That is, vanadium ions attach to oxygen functional groups on the surface of the oxide. However, GF was thermally treated in both studies before the addition of the metal oxide, making it difficult to assign the improved activity solely to the metal oxide. In another study, L. Cao et al. modified CP with MoO$_3$ micro flakes for the positive and negative electrodes.$^{75}$ Enhanced kinetics were obtained, specifically for the V$^{3+}$/V$^{2+}$ reaction with a $\Delta E_p$ value of 171 mV, compared to 306 mV for thermally treated CP. As for the positive reaction, the $\Delta E_p$ slightly decreased from 144 mV to 130 mV. More recently, Zeng et al. modified CC electrodes with Mn$_3$O$_4$ aiming to enhance the kinetics of the VO$_{2^+}$/VO$_2^+$ and V$^{3+}$/V$^{2+}$ redox reactions.$^{76}$ The polarization overpotential was found to decrease significantly when Mn$_3$O$_4$-CC was used for V$^{3+}$/V$^{2+}$ ($\Delta E_p$ from 402 mV to 82 mV) while only a very slight change was obtained for the VO$_{2^+}$/VO$_2^+$ reaction, even though it was previously reported that Mn$_3$O$_4$ enhances the VO$_{2^+}$/VO$_2^+$ reversibility. This could be a result of the different preparation methods. Even though Mn$_3$O$_4$ looks like a very promising candidate, it promotes the parasitic HER which is a massive drawback.

Hou et al. used TiO$_2$ particles to decorate the CP electrode for V$^{3+}$/V$^{2+}$ electrocatalysis.$^{77}$ This modification improved the wettability of the electrode resulting in a $\Delta E_p$ reduction from 425 mV to 327 mV. This increase in reaction kinetics is however not massive, and its origin is not well understood. N. Yun et al. used NiO-GF as an electrocatalyst for both half redox reactions.$^{78}$ The
electrode exhibited high surface area and hydrophilicity, as well as oxygen functional groups, that decreased the overpotential towards vanadium electrochemical reactions, specifically the negative side. The $\Delta E_p$ noticeably decreased from 905 mV to 163 mV for $V^{3+}/V^{2+}$, and from 470 mV to 253 mV for the positive side. However, the stability of NiO in highly acidic media is questionable. S. Mehboob et al. investigated the performance of SnO$_2$-CF material for the negative and positive electrodes.\textsuperscript{79} Enhancement of the VO$^{2+}$/VO$^{2+}$ reversibility was acquired with a $\Delta E_p$ reduction from 919 mV to 766 mV. Even though the authors claimed the higher reversibility towards the negative electrode using SnO$_2$, CV results did not show any improvement. Also, HER was promoted but this was not discussed in the paper. Cr$_2$O$_3$ was also utilized by Y. Xiang et al. for the VO$^{2+}$/VO$^{2+}$ reaction.\textsuperscript{80} They achieved improved kinetics as indicated by the $\Delta E_p$ value of 280 mV, compared to 410 mV for GF. This could be attributed to the higher hydrophilicity and surface area. Nevertheless, the reason for the enhancement was not very clear.

### Table 3.3: Summary of $\Delta E_p$ values from the above studies on metal oxides towards both VO$^{2+}$/VO$^{2+}$ and V$^{2+}$/V$^{3+}$ half-reactions.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Electrolyte</th>
<th>$v$ (mV s$^{-1}$)</th>
<th>$\Delta E_p$ (mV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$-CF</td>
<td>Positive: 0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>1</td>
<td>260</td>
<td>73</td>
</tr>
<tr>
<td>ZrO$_2$-CF</td>
<td>Positive: 0.1 M V$^{4+}$/2 M H$_2$SO$_4$</td>
<td>1</td>
<td>224</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Negative: 0.1 M V$^{3+}$/2 M H$_2$SO$_4$</td>
<td>1</td>
<td>223</td>
<td></td>
</tr>
<tr>
<td>MoO$_3$-CP</td>
<td>Positive: 1 M V$^{4+}$/2.62 M H$_2$SO$_4$</td>
<td>10</td>
<td>130</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Negative: 1 M V$^{4+}$/2.62 M H$_2$SO$_4$</td>
<td>10</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>Mn$_3$O$_4$-CC</td>
<td>Negative: 0.1 M V$^{3+}$/3 M H$_2$SO$_4$</td>
<td>5</td>
<td>82</td>
<td>76</td>
</tr>
<tr>
<td>TiO$_2$-CP</td>
<td>Negative: 1 M V$^{3+}$/3 M H$_2$SO$_4$</td>
<td>4</td>
<td>327</td>
<td>77</td>
</tr>
<tr>
<td>NiO-CF</td>
<td>Positive: 0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>5</td>
<td>253</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Negative: 0.1 M V$^{3+}$/3 M H$_2$SO$_4$</td>
<td>5</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>SnO$_2$-CF</td>
<td>Positive: 0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>10</td>
<td>766</td>
<td>79</td>
</tr>
<tr>
<td>Cr$_2$O$_3$-GF</td>
<td>Positive: 0.1 M V$^{4+}$/3 M H$_2$SO$_4$</td>
<td>2.5</td>
<td>280</td>
<td>80</td>
</tr>
</tbody>
</table>

#### 3.3.2 Tungsten Oxide

Among all metal oxides mentioned above, tungsten oxide (WO$_3$) nanostructures are specifically attractive candidates for electrochemical applications given their suitable phase...
Chapter 3: Electrode Advancements in VRFBs

structure for rapid ion intercalation, multiple oxidation states, chemical stability, non-toxic nature, and low cost.\(^{29}\) They have shown excellent results in supercapacitor experiments.\(^{81}\) They have also been used as electrode material in VRFBs (Table 3.4) showing promising results due to their stability in acidic media and the already-mentioned superior electrochemical performance, specifically owing to the W\(^{6+}\)=O catalyzing functional groups.\(^{82}\)

![Figure 3.3](image)

**Figure 3.3:** Schematic illustration of (a) VO\(_2^+\)/VO\(_2^+\) and (b) V\(^{2+}\)/V\(^{3+}\) electrochemical reaction mechanisms on WO\(_3\), as proposed by C. Yao *et al.*\(^{82}\) Adapted from ref. 82.

C. Yao and co-workers were the first to use WO\(_3\) for VRFBs, along with super activated carbon (SAC) to increase the conductivity of the electrode.\(^{82}\) The synergistic effect, as a result of the increased number of active sites from unsaturated carbon atoms and W\(^{6+}\)=O groups, decreased the \(\Delta E_p\) from 311 mV (CP) and 151 mV (CP-SAC) to 106 mV for the positive electrode. As for the V\(^{3+}\)/V\(^{2+}\) reaction, \(\Delta E_p = 110\) mV was achieved, compared to zero activity using plain CP. They also proposed a mechanism for both reactions via W\(^{6+}\)=O bonds, as shown in Figure 3.3. Following this, Shen *et al.* reported \(R_{CT}\) values of 23 \(\Omega\) and 25.8 \(\Omega\) for WO\(_3\)-GF and bare GF, respectively for the VO\(^{2+}\)/VO\(_2^+\) redox couple, claiming that WO\(_3\) enhanced the activity of the electrode.\(^{83}\) However, \(\Delta E_p\) of WO\(_3\)-GF was larger than that of GF, indicating slower kinetics at the surface of WO\(_3\). Not enough characterization was employed to understand the potential cause of
the electrode’s activity. D. Kabtamu et al. used Nb-doped WO$_3$ nanowires on CF for the VO$^{2+}$/VO$_2^+$ redox reaction. The $\Delta E_p$ values decreased from 810 mV for CF and 720 mV for WO$_3$-GF to 620 mV for Nb-doped electrode. The enhanced activity was attributed to the oxygen vacancies induced by Nb incorporation that could act as active sites for vanadium ions.

In more recent work, M.G. Hosseini et al. achieved a 2-fold increase in power density for N-WO$_3$ incorporated CF electrodes because of the decreased $\Delta E_p$ from 249 mV (plain) to 137 mV. This was attributed to the synergistic effect between highly electronegative nitrogen and WO$_3$ active sites, which improved electron and oxygen transfer. It should be noted, however, that N-doping played a more important role in the kinetics by looking closely at the EIS data. In other words, N-CF exhibited a much lower $R_{CT}$ than WO$_3$-CF. W. Lee et al. synthesized mesoporous tungsten oxynitride as an electrocatalyst for the $V^{3+}/V^{2+}$ redox reaction and found that the $\Delta E_p$ and $R_{CT}$ values were 207 mV and 4.3 $\Omega$, compared to 219 mV and 7 $\Omega$ for mesoporous WO$_3$. Even though the researchers incorporated nitrogen within the structure to increase the conductivity of WO$_3$, hence the reactivity, the electrocatalytic enhancement was very little. As the commercial WO$_3$ NPs did not display any activity, the porosity of the mesoporous WO$_3$ or tungsten oxynitride was the main reason for the catalytic activity. As for the positive reaction, catalytic activity was negligible and oxygen evolution was observed. To compare materials, they also used mesoporous carbon and found that it enhanced the reversibility of the positive reaction, but inhibited the negative reaction, unlike WO$_3$.

M. Faraji et al. fabricated WO$_3$/CNTs-graphite electrode for the VO$^{2+}$/VO$_2^+$ reaction in a qualitative study. While CNTs did not improve the kinetics of the electrode, the WO$_3$ electrode exhibited a higher reversibility, opposing W. Lee’s research. The WO$_3$/CNTs-graphite electrode displayed the best kinetics, but oxygen evolution, as well as other side reactions, were observed in
the CV results, which were not discussed by the authors. In a more recent study, they prepared a porous film electrode using the same materials, and improved VO\(^{2+}/\text{VO}_2^+\) kinetics (ΔE\(_p\) = 360 mV), and lowered the ohmic resistance.\(^{88}\) This was solely due to the high porosity of the film, hence improved wettability, as the equivalent non-porous structure did not display a reduction peak in the CV results. The same porous structure without WO\(_3\) exhibited a value of ΔE\(_p\) = 630 mV. However, the same structure without CNTs did not exhibit any redox peaks. This shows that carbon structures are necessary for the activity of the positive electrode, which contradicts their previous paper\(^{87}\) but confirms W. Lee’s study\(^{86}\). The researchers did not explain this discrepancy.

Likewise, D. Kabtamu et al. fabricated a 3D WO\(_3\)/GO foam and obtained ΔE\(_p\) values of 113 mV for VO\(^{2+}/\text{VO}_2^+\) and 122 mV for V\(^{3+}/\text{V}^2+\) redox reactions, owing to the synergistic effects.\(^{89}\) Enhancement was much more pronounced on the negative side, in comparison with pure GO, than the positive side upon the addition of WO\(_3\). As for the positive side, GO exhibited nearly the same electrocatalytic activity as WO\(_3\)/GO, while WO\(_3\) showed poor kinetics. These findings confirm Lee’s and Faraji’s studies; that is, carbon structures usually enhance the kinetics of the positive reaction but inhibit that of the negative reaction, as opposed to WO\(_3\).\(^{86,88,89}\)

However, the low conductivity of WO\(_3\) limits its performance towards the electrochemical reactions of vanadium ions.\(^{90}\) One way to overcome this is to create oxygen vacancies, which would decrease the bandgap of the material by introducing shallow donors. A recent paper by A. W. Bayeh et al. studied the electrocatalytic activity of W\(_{18}\)O\(_{49}\) (WO\(_{2.72}\)) nanowires on VO\(^{2+}/\text{VO}_2^+\) reversibility.\(^{91}\) They found that the ΔE\(_p\) decreased from 900 mV (CF) to 717 mV, ascribed to the improved conductivity and oxygen vacancies created upon reduction, which would act as active sites towards vanadium ions. Unfortunately, no direct comparison with WO\(_3\) was made to confirm their hypothesis. Therefore, it is worth searching for the difference in electrocatalytic activity
between stoichiometric and non-stoichiometric tungsten oxide as electrode materials in an electrochemical application as the VRFB literature lacks this information. One study in a supercapacitor application, by Jung and Kim, found that the $R_{CT}$ of WO$_{2.72}$ in acidic media was improved, compared to that of WO$_3$, due to the fast kinetics and ease of ion diffusion.\(^9^0\)

**Table 3.4:** Summary of all the studies on WO$_3$ for both half redox reactions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte</th>
<th>$v$ (mV s$^{-1}$)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$I_{pc}/I_{pa}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$-SAC-CP</td>
<td>Positive: 0.05 M V$^{4+}$ + 0.05 M V$^{3+}$ / 3 M H$_2$SO$_4$</td>
<td>10</td>
<td>106</td>
<td>0.97</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Negative: 0.05 M V$^{2+}$ + 0.05 M V$^{3+}$ / 3 M H$_2$SO$_4$</td>
<td>10</td>
<td>110</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>WO$_3$ -GF</td>
<td>Positive: 0.05 M V$^{4+}$ / 2 M H$_2$SO$_4$</td>
<td>5</td>
<td>720</td>
<td>0.97</td>
<td>83</td>
</tr>
<tr>
<td>Nb-WO$_3$-GF</td>
<td>Positive: 0.05 M V$^{4+}$ / 2 M H$_2$SO$_4$</td>
<td>5</td>
<td>620</td>
<td>0.85</td>
<td>84</td>
</tr>
<tr>
<td>WO$_3$-CF</td>
<td>Positive: 0.05 M V$^{4+}$ / 1 M H$_2$SO$_4$</td>
<td>1</td>
<td>230</td>
<td>0.68</td>
<td>85</td>
</tr>
<tr>
<td>N-WO$_3$-CF</td>
<td>Positive: 0.05 M V$^{4+}$/ 1 M H$_2$SO$_4$</td>
<td>1</td>
<td>137</td>
<td>0.76</td>
<td>85</td>
</tr>
<tr>
<td>Mesoporous WO$_3$-GC</td>
<td>Negative: 0.15 M V$^{4+}$ / 2 M H$_2$SO$_4$</td>
<td>10</td>
<td>219</td>
<td>0.9</td>
<td>86</td>
</tr>
<tr>
<td>Mesoporous N-WO$_3$-GC</td>
<td>Negative: 0.15 M V$^{4+}$ / 2 M H$_2$SO$_4$</td>
<td>10</td>
<td>207</td>
<td>0.93</td>
<td>86</td>
</tr>
<tr>
<td>Porous WO$_3$-CNTs-graphite</td>
<td>Positive: 0.14 M V$^{4+}$ / 2 M H$_2$SO$_4$</td>
<td>20</td>
<td>360</td>
<td>0.83</td>
<td>88</td>
</tr>
<tr>
<td>WO$_3$-GO-GC</td>
<td>Positive: 1.6 M V$^{4+}$ / 2.5 M H$_2$SO$_4$</td>
<td>50</td>
<td>133</td>
<td>-</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>Negative: 1.6 M V$^{4+}$/ 2.5 M H$_2$SO$_4$</td>
<td>50</td>
<td>122</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>W$<em>{18}$O$</em>{49}$-GF</td>
<td>Positive: 0.05 M V$^{4+}$ / 2 M H$_2$SO$_4$</td>
<td>5</td>
<td>717</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>WO$_3$H$_2$O/WO$_2$.63  _CC</td>
<td>Negative: 0.1 M V$^{4+}$/ 1 M H$_2$SO$_4$</td>
<td>5</td>
<td>46.6</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WO$_3$H$_2$O/WO$<em>2$.63  _C$</em>{70}$-CC</td>
<td>Positive: 0.1 M V$^{4+}$/ 1 M H$_2$SO$_4$</td>
<td>5</td>
<td>176</td>
<td>0.71</td>
<td></td>
</tr>
</tbody>
</table>

Most of the research up to date has mainly focused on the positive reaction and ignored the negative reaction due to its overlap with HER, which makes it harder to study. Even though the positive reaction has been extensively studied, the observed kinetics are still not satisfactory for improved high energy and power densities, and ultimately low price for commercialization. Also, the electrochemical analysis performed to study the positive reaction was mainly based on equations for reversible reactions (Randles-Sevcik equation), despite that it is well-known to be a quasi-reversible reaction. Therefore, a more thorough analysis should be done to obtain accurate
results. It can also be noticed that all the studies on the electrode material were conducted in vanadium electrolyte containing only $\text{H}_2\text{SO}_4$, and none of the papers examined the performance of the electrode materials in a mixed acid electrolyte to imitate the 3rd generation (G3) VRFBs. Taking all these points into consideration, the focus of this work was to enhance the kinetics of both half-cell reactions in a mixed acid medium.

### 3.3 Hypothesis and Aims

This work aims to improve the electrocatalytic activity of carbon cloth (CC) electrodes towards $\text{VO}^{2+}/\text{VO}_2^+$ and $\text{V}^{3+}/\text{V}^{2+}$ redox reactions in a VRFB system, by incorporating fullerene $\text{C}_{76}$ particles and hydrated $\text{WO}_3\cdot\text{x}$ NPs. CC electrodes were chosen, instead of the commonly used carbon felt (CF) and graphite felt (GF), because of their lower resistance. Moreover, compared to carbon paper (CP), CC was shown to have a higher permeability towards vanadium ions, which would ultimately lead to a higher energy efficiency (EE). To activate the CC electrodes, thermal treatment was firstly employed, as it remains the standard method of activation, to incorporate oxygen functional groups and increase the wettability of the electrode. An attempt was made to optimize the conditions of CC oxidation to obtain the most stable and catalytic electrode. The mixed acid electrolyte was also used to imitate commercial G3 VRFBs and study the kinetics of the electrodes in the presence of HCl.

Despite the massive attention towards employing carbon nanostructures, the fullerene family has not yet been explored in VRFBs application. Fullerenes have a unique cage-like structure with high surface area and conductivity, which would allow for fast electron transfer (ET). The electronic cloud surrounding the fullerene molecule could also enhance the adsorption of vanadium ions onto its surface. Fullerene $\text{C}_{60}$ has been found to boost the performance of Li-ion batteries and supercapacitors by increasing the charge storage capacity.
Out of all the commercially available fullerenes (C_{60}, C_{70}, and C_{76}), C_{76} has the highest conductivity.\textsuperscript{95,97} Based on this background, the kinetics of both half-cell reactions were investigated using C_{76}-decorated CC electrodes, as it is anticipated that C_{76} would boost the reversibility of the electrodes. As already mentioned in Section 3.2, carbon nanostructures have shown more catalytic activity in the positive side than the negative side, so it is expected that C_{76} particles would work as a better catalyst towards the VO^{2+}/VO^{2+} redox reaction.

As discussed in Section 3.3.2., quite a few papers used WO_3 due to its low cost, stability, and high catalytic activity. However, stoichiometric WO_3 suffers from low conductivity. Therefore, using non-stoichiometric WO_{3-x} to create oxygen vacancies at the surface would increase the donor density and conductivity, as discussed in Kim’s paper.\textsuperscript{90} Oxygen vacancies would also act as active sites for chemisorption, and hence enhance the electrocatalytic activity of the electrode towards vanadium ions. Whereas WO_{2.72} has recently been used only for the positive electrode in VRFBs in Bayeh \textit{et al.}’s paper,\textsuperscript{91} the other reduced form W_{32}O_{84} (WO_{2.63}) has never been investigated. In fact, using WO_{3-x} in a VRFB system is expected to enhance the activity of the negative electrode more than the positive electrode. This is speculated based on the literature in Sections 3.3.1. and 3.3.2., that metal oxides usually work better at the negative side.

Hydrated tungsten oxide (WO_{3.x}H_2O) was also fabricated based on its advantages over anhydrous WO_3. Even though the use of WO_{3.x}H_2O as an electrocatalyst for vanadium ions in VRFBs has not been reported, it showed better electroactivity in the supercapacitor application compared to WO_3.\textsuperscript{98} The reported mechanism for WO_{3.5}H_2O was the following: going to more negative potential causes more cation adsorption and insertion due to the electrostatic attraction between positively charged ions and negatively charged electrode interface. This leads to a higher
double-layer capacitance in the negative potential range, as well as a faster cation diffusion. The layered structure of the hydrated oxide has also been proven to boost the intercalation of multivalent cations, which would otherwise slowly diffuse in the equivalent anhydrous structure. Another study also showed that the kinetics of WO$_3$.2H$_2$O was faster than that of WO$_3$, as indicated by the CV results, with higher capacity retention at high scan rates. However, in the VRFB application, the focus is more on the adsorption and diffusion of vanadium ions. Therefore, it is expected that WO$_3$.xH$_2$O would enhance the reversibility of vanadium ions, specifically V$^{2+}$/V$^{3+}$, due to the negatively charged electrode, which would enhance the adsorption process.

Herein, a WO$_3$.0.33H$_2$O/W$_{32}$O$_{84}$ (hydrated tungsten oxide, HWO) nanocomposite was synthesized to investigate its electrocatalytic effect on both VRFBs half-cell reactions. It is expected that this nanocomposite will be better used for the negative side, based on its catalytic activity mechanism mentioned above. Another reason is that most metal oxides have shown better electrocatalytic activity towards the V$^{3+}$/V$^{2+}$ reaction than VO$^{2+}$/VO$_2^+$, as reported by many papers in Section 3.3.2. Different ratios of HWO:C$_{76}$ were finally prepared to optimize the kinetics of both half-cell reactions. Before discussing the results obtained, the experimental work will first be presented in the next chapter.
Chapter 4: Materials and Methods

4.1 Materials

Vanadium (IV) sulfate oxide hydrate (VOSO₄, 99.9%, Alfa-Aesar), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), dimethylformamide (DMF, Sigma-Aldrich), polyvinylidene fluoride (PVDF, Sigma-Aldrich), sodium tungsten oxide dihydrate (Na₂WO₄, 99%, Sigma-Aldrich), oxalic acid (anhydrous, 98%, Alfa-Aesar). Carbon cloth (CC) and carbon felt (CF) were purchased from the Fuel Cell Store.

4.2 Thermal Treatment of CC

The as-received CC (untreated CC, UCC) electrodes were thermally treated in a tube furnace in the air at 450 °C for 1 h, 3 h, 10 h, 20 h, and 30 h at a heating rate of 15 °C min⁻¹. Treated CC electrodes (TCC) were named TCC (1h), TCC (3h), TCC (10h), TCC (20h), and TCC (30h), respectively. Untreated carbon felt (UCF) was also thermally treated for 10h to produce TCF (10h).

4.3 Synthesis of WO₃.₀₃₃H₂O/W₃₂O₈₄ NPs

WO₃.(H₂O)₀.₃₃₃/W₃₂O₈₄ (hydrated tungsten oxide, HWO) was fabricated by a hydrothermal (HT) reaction.¹⁰⁰ 2 g of Na₂WO₄ salt was dissolved in 12 mL H₂O under electromagnetic stirring giving a colorless solution. This was followed by the addition of 12 mL of 2 M HCl dropwise, resulting in a pale-yellow suspension. This suspension was placed in a Teflon-lined stainless autoclave in an oven at 180 °C for 3 h to undergo the HT reaction. For the preparation of WO₃, everything was the same except the addition of 12 mL oxalic acid after HCl.¹⁰¹ The residue was
taken by filtration, washing three times with ethanol and H₂O, drying in the oven at 70 °C for ~3 h, and grinding to obtain the grey-blue powder of HWO or yellow powder of WO₃. HWO was then further annealed under Ar and H₂ atmospheres at 450 °C for 2 h at a rate of 5 °C/min to produce HWO (Ar) and HWO (H₂), respectively. Powder samples were used for electrochemical and physicochemical characterization.

4.4 Preparation of Electrodes

UCC and TCC were cut into ~ 1.5 cm width x 7 cm length electrodes. C₇₆, HWO, HWO-10% C₇₆, HWO-30% C₇₆, HWO-50% C₇₆, and WO₃ suspensions were prepared by the following method: 20 mg of the active material powder and 10 wt% (~2.22 mg) PVDF binder were dissolved in ~ 1 mL DMF and sonicated for 1 h for homogeneity. Subsequent deposition of different C₇₆ loadings (1 mg, 2 mg, 3 mg and 5 mg) on UCC and TCC electrodes (area ~ 1.5 cm²) took place. As for WO₃, HWO, and HWO-C₇₆ composites, 2 mg of the material was loaded onto an active electrode area of ~1.5 cm². Casting deposition was achieved by taking the required volume from the suspension (100 µL for 2 mg loading) by a micropipette, followed by brushing for more homogeneity. All electrodes were then oven-dried at 60 °C overnight. Electrodes were measured before and after to ensure accurate mass loading. To prevent the vanadium electrolyte from going up the electrode by capillary effect, a thin layer of wax was applied on top of the active material.

4.5 Electrochemical Characterization

A Biologic SP 300 workstation was employed for all electrochemical measurements. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to study the kinetics and diffusion processes of VO²⁺/VO²⁺ and V²⁺/V³⁺ redox reactions. A three-electrode
cell (Figure 4.1) was used for both techniques with an electrolyte concentration of 0.1 M VOSO$_4$ ($V^{4+}$) in 1 M H$_2$SO$_4$, or 1 M H$_2$SO$_4$ + 1 M HCl (mixed acids). The reference electrode was saturated calomel electrode (SCE, +0.242 V vs. standard hydrogen electrode, SHE), the counter electrode was platinum (Pt) coil, and the working electrode was the material under study (Section 4.4). For CV, scan rates ($\nu$) of 5, 10, 20, and 50 mV s$^{-1}$ were applied for each electrode material, at a potential window of (0 to 1) V for VO$_2^+$/VO$_2^{2+}$ and (-0.2 to -0.7) V for V$^{2+}$/V$^{3+}$ vs. SCE. IR correction was applied to avoid taking into account any ohmic losses. All cyclic voltammograms (CVs) were then corrected to the SHE scale when plotted. To investigate the activity retention of the electrodes, repetitive cycling CVs were conducted at $\nu$ of 5 mV s$^{-1}$ for UCC, TCC, UCC-C$_{76}$, UCC-HWO, and UCC-HWO-50% C$_{76}$. As for EIS, tests were performed over a frequency range of 0.01-10$^5$ Hz with a voltage perturbation of 10 mV, at the open-circuit voltage (OCV) for VO$_2^+$/VO$_2^{2+}$ and with a -0.5 V bias vs. SCE for V$^{2+}$/V$^{3+}$. Nyquist plots were analyzed for each material. Each experiment was repeated 2-3 times to ensure consistency of the results. However, some of the produced Nyquist plots for the V$^{2+}$/V$^{3+}$ redox reactions did not have reasonable shapes even when repeated, so these results will not be displayed here. This could be due to the $V^{4+}$ solution used. However, the heterogeneous rate constants ($k^0$) were obtained by Nicholson’s method (Section 5.4).$^{101,102}$
4.6 Physicochemical Characterization

The surface morphologies and structure of UCC and TCC were observed using Field Emission Scanning Electron Microscopy (FESEM, Zeiss SEM Ultra 60, 5 kV) to observe the roughness of the structure upon treatment. FESEM was also employed for C_{76}, HWO, and WO_{3} to determine their shape, as well as their distribution on CC electrodes. Energy-Dispersive X-ray spectroscopy equipped within the FESEM (EDX, Zeiss Inc.) was used for elemental mapping of HWO-C_{76} on CC electrodes.

A high-resolution transmission electron microscope (HR-TEM, JOEL JEM-2100), operating at an accelerating voltage of 200 kV, was used to provide higher resolution imaging of C_{76} and HWO particles. For HWO, the lattice planes could be visualized with the d-spacing...
providing. The diffraction ring pattern of HWO was also revealed. Crystallographic Tool Box (CrysTBox) software was used to analyze the diffraction ring pattern of HWO using the ringGUI feature, and the results were compared with the XRD pattern.\textsuperscript{103}

The structure and graphitization of UCC and TCC were analyzed by X-ray diffraction (XRD) at a scan rate of 2.4° min\textsuperscript{-1} from 5°-70° with Cu K\textsubscript{a} (λ = 1.54060 Å), using Panalytical X-ray diffractometer (model 3600). The crystal structure and phase of HWO and annealed HWO samples were also revealed by XRD. PANalytical X’Pert HighScore software was utilized to match the peaks of HWO and annealed HWO samples with the tungsten oxide cards available in the database.\textsuperscript{104} Results for HWO were compared with TEM results.

The chemical composition and state were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, ThermoScientific). The surface chemistry of UCC, TCC, C\textsubscript{76}, and HWO, and their functional groups were revealed. The oxidation state of tungsten in HWO was also obtained. CasaXPS software was used to deconvolute the peaks and hence analyze the data.\textsuperscript{105}

Fourier transform infrared spectroscopy (FTIR, Perkin Elmer spectrometer using KBr FTIR grade) measurements were carried out to determine the surface functional groups of UCC, TCC, C\textsubscript{76}, and HWO. Results were compared with XPS results.

Raman spectroscopy (ProRaman-Lanalyzer, with an excitation laser beam wavelength of 532 nm) was used to estimate the defects and conductivity of UCC, TCC, and C\textsubscript{76}. Contact angle measurements (KRUSS DSA25) were also used to characterize the wettability of the electrodes.
Chapter 5: Results and Discussion

In this chapter, four main topics on the electrode material for vanadium ions in a VRFB system are tackled. The first section provides a quick comparison between the activity of carbon cloth (CC) and carbon felt (CF) electrodes, as well as an overview of the thermal oxidation of CC electrodes. In the second section, the incorporation of C76 particles to untreated CC (UCC) and the optimized treated CC (TCC) electrodes in H2SO4 and mixed acid electrolytes (1 M H2SO4 + 1 M HCl), and their electrocatalytic activity towards VO2+/VO2+ are thoroughly discussed. This is followed by the effect of WO3⋅(H2O)0.333/W32O84 (hydrated tungsten oxide, HWO) NPs and HWO-annealed samples on the kinetics of both half-cell reactions. Finally, the electrochemical activity of C76/HWO nanocomposites, in comparison with C76 and HWO, is investigated to achieve the best electrode material for VO2+/VO2+ and V2+/V3+ redox reactions.

5.1 Optimizing the Thermal Treatment of CC Electrodes

Many of the previous studies investigated the treatment of the as-received carbon-based electrodes (CF, GF, CP, or CC) before incorporating any catalytic activity enhancing materials. Therefore, thermal oxidation of UCC was employed to form thermally-treated CC (TCC) electrodes, as thermal oxidation is one of the most effective and safest treatment methods. This was done to incorporate oxygen functional groups onto the surface of the electrodes, which are known to serve as active sites for the vanadium redox reactions; thereby, increasing the rate of the reaction. This also means that the electrodes would become more hydrophilic, allowing more electrolyte penetration for enhanced electron transfer (ET).

The carbon cloth was thermally treated in air and at a constant temperature of 450 °C. The effect of the oxidation duration, from 1 h to 30 h, on the CC activity and stability was studied. The
Chapter 5: Results and Discussion

TCC (1h), TCC (3h), TCC (10h), TCC (20h), and TCC (30h) electrodes were tested. The 450 °C was chosen based on a similar work that addressed the thermal oxidation of CP.\textsuperscript{37} In the case of CP, the thermal oxidation at 450 °C for 30 h exhibited the best kinetics for the VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} redox reaction. However, due to the long period reported in the literature (30 h), optimizing the timing was explored in this research. This was done by examining the kinetics of all TCC electrodes towards VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} in H\textsubscript{2}SO\textsubscript{4} and mixed acid electrolytes. CV curves (Figure 5.1a and 5.1c) in both electrolytes show that the TCC (10h) exhibits the fastest kinetics, based on its lowest peak separation, ΔE\textsubscript{p}, value (Table 5.1). As depicted in Figure 5.1b and 5.1d, electrochemical impedance spectroscopy (EIS) graphs of TCC (10h) shows the smallest semi-circle, hence the lowest charge transfer resistance (R\textsubscript{CT}) value, compared to other TCC electrodes (Table 5.1). In addition, it can also be seen that the Warburg slope of the TCC (10h) electrode is the steepest, which means higher diffusion of vanadium ions though the electrode.\textsuperscript{19} The combination of fast kinetics and rapid diffusion rendered TCC (10h) electrode the most efficient electrode, among all other TCC electrodes, ultimately leading to the highest energy efficiency (EE) in a VRFB system.

**Table 5.1**: Summary of the ΔE\textsubscript{p} and R\textsubscript{CT} values as obtained from Figure 5.1.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>0.1 V\textsuperscript{4+}/H\textsubscript{2}SO\textsubscript{4} electrolyte</th>
<th>0.1 V\textsuperscript{4+}/mixed acid electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE\textsubscript{p} (mV)</td>
<td>R\textsubscript{CT} (Ω)</td>
</tr>
<tr>
<td>UCC</td>
<td>423</td>
<td>751</td>
</tr>
<tr>
<td>TCC (1h)</td>
<td>349</td>
<td>218</td>
</tr>
<tr>
<td>TCC (3h)</td>
<td>341</td>
<td>194</td>
</tr>
<tr>
<td>TCC (10h)</td>
<td>259</td>
<td>98</td>
</tr>
<tr>
<td>TCC (20h)</td>
<td>324</td>
<td>110</td>
</tr>
<tr>
<td>TCC (30h)</td>
<td>388</td>
<td>196</td>
</tr>
</tbody>
</table>
XRD analysis was performed to better understand the reason behind each electrode’s electrocatalytic activity, especially TCC (10h), towards the VO\(^{2+}/\text{VO}_2^+\) redox reaction. As shown in Figure 5.2a, the XRD pattern of the UCC electrode exhibits two broad and weak diffraction peaks at about 26° and 43.6°, which correspond to the reflection in the (002) and (100) planes of graphite aromatic layers, respectively. After thermal treatment, the (002) and (100) peaks became sharper and more intense, which indicates that the stacking structure of the aromatic layers in TCC electrodes was enhanced. That is, the number of parallel carbon layers increased, and the aromatic carbon grid layer became orderly arranged. Only in the XRD pattern of TCC (10h) that a peak around 53° emerged, corresponding to the (004) plane in graphitic carbon. Also, the TCC (10h)
electrode displays the most intense and narrowest peaks, rendering it the highest graphitization degree among all other TCC electrodes, as indicated by the Scherrer analysis (Equation 5.1 and Table 5.2). Beyond the 10 h treatment, the full width half maximum (β_{1/2}) of the (002) and (001) peaks became larger, indicating that at higher temperatures the structure became more unstable and its graphitization decreased again. Therefore, the high electrocatalytic activity of TCC (10h) should be attributed to its high graphitization degree (Table 5.2) and conductivity, as supported by previous studies in which higher graphitization led to better VO^{2+}/VO_{2}^{+} kinetics.\textsuperscript{47,48,52,55,60,61,65}

To get an insight into the morphology change due to treatment, SEM imaging was employed for the UCC (Figure 5.2b) and TCC (Figure 5.2c) electrodes. The SEM images clearly show that the roughness of CC electrodes increased upon thermal oxidation. This could be another reason for the enhanced activity as more roughness means more active sites and a higher surface area for vanadium redox reactions.\textsuperscript{43,45} In addition, a rougher surface accompanied by oxygenated active sites usually exhibits better electrolyte accessibility. Based on these results, TCC (10h) was chosen for all subsequent experiments and named TCC for short hereafter.
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Table 5.2: Crystallite size (CS) of all CC electrodes based on Figure 5.2a and Equation 5.1.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$\beta_{1/2}$ (°)</th>
<th>CS (Å)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCC</td>
<td>0.94</td>
<td>90.6</td>
<td>Graphitization decreases going up the table from TCC (3h) to UCC as the crystallite size decreases.</td>
</tr>
<tr>
<td>TCC (1h)</td>
<td>0.79</td>
<td>107.8</td>
<td>As the duration of oxidation increases so does the graphitization</td>
</tr>
<tr>
<td>TCC (3h)</td>
<td>0.63</td>
<td>135.0</td>
<td>Largest crystallite size = Highest crystallization and graphitization</td>
</tr>
<tr>
<td>TCC (10h)</td>
<td>0.47</td>
<td>181.1</td>
<td></td>
</tr>
<tr>
<td>TCC (20h)</td>
<td>1.57</td>
<td>54.3</td>
<td>Lowest crystallite size values = Lowest crystallization and graphitization degrees</td>
</tr>
<tr>
<td>TCC (30h)</td>
<td>1.42</td>
<td>59.9</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5.2:** The (a) XRD analysis for the UCC and all TCC electrodes, (b) SEM image of UCC, and (c) SEM image of TCC.

$$CS = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta} \quad (5.1)^{22}$$
In addition to the XRD results, XPS analysis was conducted for the UCC (Figure 5.3a and 5.3b) and TCC (Figure 5.3c and 5.3d) electrodes to study the surface composition of each electrode, and hence understand their difference in activity towards the VO$^{2+}$/VO$_2^+$ redox reaction. Even though the XPS survey showed similar O/C ratios of 6.48% and 6.59% for UCC and TCC, respectively, the narrow scan XPS spectra of the C 1s and O 1s for both electrodes revealed a few differences. The narrow scan of the C 1s core level of UCC (Figure 5.3a) was deconvoluted into four peaks at binding energies 284.5, 284.8, 286.6, and 288.3 eV ascribed to C=C sp$^2$, C-C sp$^3$, C-OH, and C=O bonds, respectively. The corresponding atomic percentages were 26%, 56.2%, 3.6% and 14.2% respectively. The narrow scan of O 1s of UCC (Figure 5.3b) confirmed the presence of C=O (63.3%) and C-OH (36.7%) bonds at 531.8 and 532.8 eV, respectively. Upon treatment, the atomic percentage of graphitized C=C sp$^2$ increased from 26% to 43%, while the defective C-C bonds decreased from 56.2% to 33.1%, as shown in Figure 5.3c, indicating higher graphitization and conductivity, confirming XRD results in Figure 5.2a. Figure 5.3c also revealed that COOH functional groups, at a binding energy of 289.7 eV, were incorporated into TCC’s structure, which is known to enhance the hydrophilicity (Figure 5.6a and 5.6b in Section 5.2) and act as active sites for VO$^{2+}$/VO$_2^+$. This was also confirmed by the O 1s high-resolution spectrum of TCC (Figure 5.3d), which showed that C-OH bonds increased from 36.8% to 80% upon thermal treatment. Therefore, it was concluded that CC oxidation increased C=C and COOH relative to C-C and C=O, respectively. Because the UCC and TCC electrodes had nearly the same O/C content, it can be deduced that COOH has more activity towards VO$^{2+}$/VO$_2^+$ than C=O, which supports previous studies.$^{34,42,43,45}$
To confirm the better activity of CC electrodes over the commonly used carbon felt (CF) ones, CV scans for the untreated and thermally-treated CF (10h) samples were also conducted. Even though the CF has a significantly higher real area per geometric area than CC, Figure 5.4a shows that the CV of the untreated CF (UCF) did not exhibit a reduction peak, and its oxidation peak was at far positive potential due to the high overpotential. For the treated samples (Figure 5.4b), thermally-treated CF (TCF) had a much higher ΔE_p value of 476 mV, compared to 259 mV for TCC. It can also be seen that the peaks of TCF were still not well-defined even after treatment and that the oxidation-current density had a much higher value than that of the reduction-current density. A possible explanation could be that the adsorption tendency of vanadium ions towards

Figure 5.3: High-resolution XPS spectra of (a) UCC C 1s, (b) UCC O 1s, (c) TCC C 1s and (d) TCC O 1s.
CF was less than that of CC. That is, much of the produced VO$_2^+$ ions diffused back to the bulk electrolyte rather than became adsorbed onto the surface of the CF electrode. This adsorption tendency, however, improved with thermal treatment.

**Figure 5.4:** The cyclic voltammetry (CV) curves at $\nu = 5$ mV s$^{-1}$ in 0.1 M V$^{4+}$/1 M H$_2$SO$_4$ for (a) untreated samples of CC and CF and (b) thermally treated samples.
5.2 Electrocatalytic Activity of C\textsubscript{76} Particles Towards VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+}

The C\textsubscript{76} particles were used to further boost the kinetics of the positive redox reaction in a VRFB system. This was studied using UCC and TCC electrodes in H\textsubscript2}SO\textsubscript{4} and mixed acid electrolytes to imitate the first and third generations (G1 and G3) of the VRFBs for more practicality. The microstructure and morphology of C\textsubscript{76} were investigated using SEM and TEM, as shown in Figure 5.5a and inset of Figure 5.5b, respectively. As the diameter of the C\textsubscript{76} buckyball structure is about 0.79 nm, only aggregates of C\textsubscript{76} particles could be observed by TEM imaging given its limited resolution.\textsuperscript{106}

![Figure 5.5:](image)

Figure 5.5: (a) SEM image of C\textsubscript{76} particles. (b) C\textsubscript{1s} core-level XPS spectrum of C\textsubscript{76} with TEM image of C\textsubscript{76} particles as inset. (c) FTIR spectra and (d) Raman spectra of the three electrodes UCC, TCC, and C\textsubscript{76}.
The surface chemistry of C\textsubscript{76} was examined by XPS. The C 1s spectrum of the C\textsubscript{76} in Figure 5.5b shows four peaks at 284.3, 284.7, 286.3, and 290.0 eV, corresponding to the binding energies of sp\textsuperscript{2} C=C (45.5%), sp\textsuperscript{3} C-C (24.3%), C-OH (20.0%), and COOH (10.2%) bonds, respectively.\textsuperscript{34,60} This indicated that the major hybridization in C\textsubscript{76} is sp\textsuperscript{2} as expected as each carbon atom in C\textsubscript{76} forms three bonds with its three sp\textsuperscript{2} hybrid orbitals, whereas the sp\textsuperscript{3} hybridization is due to the single bonds in pentagons. The existence of C-OH and COOH bonds reveals that the surface of C\textsubscript{76} is oxygen-functionalized, allowing it to be hydrophilic (Figure 5.6) and more efficient for electrolyte utilization (EU).\textsuperscript{34}

These functional groups were also identified using FTIR and compared with UCC and TCC electrodes. As shown in Figure 5.5c, the O-H, C=O, and C-O stretching vibrations are observed around 3410 cm\textsuperscript{-1}, 1638 cm\textsuperscript{-1}, and 1150 cm\textsuperscript{-1}, respectively, for all electrodes. For only the TCC and C\textsubscript{76} electrodes, the C≡C stretch vibration, C=C stretching and bending vibrations, and C=O stretch vibration appeared at about 2030 cm\textsuperscript{-1}, 1618 cm\textsuperscript{-1}, 620 cm\textsuperscript{-1}, and 1775 cm\textsuperscript{-1}.\textsuperscript{47} The presence of C≡C and C=C bonds indicate the material’s high conductivity, leading to better electron transfer (ET) at the electrode/electrolyte interface.\textsuperscript{55} While the presence of C=O functionalization implies improved electrode wettability (Figure 5.6), and more oxygen active sites for vanadium ions, compared to UCC. The peak at 1050 cm\textsuperscript{-1} for UCC could be attributed to C-F impurity.

To get a better insight on the ordering and conductivity of the electrodes, Raman spectroscopy was conducted to estimate the defects of the electrodes from the ratio of the D band, \~ 1350 cm\textsuperscript{-1}, to G band, \~ 1590 cm\textsuperscript{-1}, (I\textsubscript{D}/I\textsubscript{G}), as depicted in Figure 5.5d.\textsuperscript{25,50} The D band corresponding to the breathing mode of A\textsubscript{1g} symmetry represents the disorder in carbon materials, resulting from the functional groups, defects, and grain boundaries. Specific to
graphitic carbon is the G band which arises from the in-plane bond stretching of sp$^2$ crystalline domains of E$_{2g}$ symmetry in carbon fibers of UCC and TCC, as well as the hexagons and pentagons of C$_{76}$. The calculated I$_D$/I$_G$ for UCC, TCC, and C$_{76}$ is 1.05, 1.21, and 0.93, respectively. In addition, the Raman spectrum of TCC exhibited a shoulder D’ at 1612 cm$^{-1}$, which is a defect-induced band.$^{25,50}$ This showed the increase in the number of defects upon treatment in TCC, compared to UCC, probably due to the presence of more oxygen functional groups and increased roughness. Even though C$_{76}$ was functionalized, it seems that its sp$^2$ character dominated, indicating the high ordering of the carbon atoms in its structure. The 2D (overtone of D band) and the combinational D+G bands at ~ 2950 cm$^{-1}$ and ~ 2675 cm$^{-1}$ were indicative of crystalline structure,$^{25,50}$ which should be consistent with good electrical conductivity and hence good electrochemical activity.

Contact angle measurements were also employed to compare the wettability of the UCC, TCC, and C$_{76}$ electrodes. Figure 5.6a shows that the water droplet would not attach to the surface of the UCC electrode, showing its high hydrophobicity. Upon thermal treatment, the hydrophilicity of the TCC electrode dramatically increased, as depicted in Figure 5.6b that the water droplet was immediately absorbed. This could be attributed to the COOH functional groups (Figure 5.3) found on the surface of TCC, as well as the increased number of defects (Figure 5.5d) that could act as sites for oxygen functional groups when placed in solution.$^{34,36,39,40}$ The C$_{76}$ electrode shows intermediate wettability, but the water droplet gets completely absorbed after 57 seconds. Also, C$_{76}$ might get oxidized in the first CV cycle due to the high oxidation potential and the presence of H$_2$SO$_4$. The intermediate hydrophilicity of C$_{76}$ is in line with the XPS results. The atomic
percentage of COOH in C76 and TCC is 10.2% and 20.7%, respectively, while UCC does not exhibit any COOH functional groups.

![Images of SEM images and water contact angle measurements for UCC, TCC, and C76.](image_url)

**Figure 5.6:** The SEM images and water contact angle measurements of (a) UCC, (b) TCC, and (c) C76.

C76 incorporation with different loadings on UCC and TCC in H2SO4 (G1) and mixed acid (G3) electrolytes was investigated and compared to plain TCC electrodes. As could be seen in Figures 5.7 and 5.8, TCC is shown to significantly decrease the values of ΔE_p and R_CT from (403 ± 8) mV to (230 ± 7) mV, and from (730 ± 22) Ω to (133 ± 23) Ω, respectively, as well as achieving an I_pc/I_pa ratio of 0.5 (0.2 for UCC) indicating faster electrode kinetics and enhanced reversibility.

This could be attributed to the addition of COOH groups (Figure 5.3) that increased hydrophilicity (Figure 5.6), and would also act as active sites for the adsorption of vanadium ions, as suggested by previous studies.16,34,36,41,42 More specifically, this enhancement was probably due to the increase in the defect density as indicated by the higher I_D/I_G ratio as found in the literature,36,39,52,53,60 as well as the appearance of the D' band (Figure 5.5d).
The enhancement effect of the C$_{76}$ is found to increase in both 1 M H$_2$SO$_4$ and mixed acids electrolytes upon increasing C$_{76}$ loading from 1 mg to 5 mg, with ∆E$_{p}$ and R$_{CT}$ values gone from (204 ± 8) mV to (109 ± 3) mV, and from (50 ± 5) Ω to (4 ± 1) Ω, respectively. The enhanced activity was also manifested in the increase of the I$_{pc}$/I$_{pa}$ ratio from 0.6 ± 0.05 to 0.75 ± 0.01. Hence, 5 mg loading on UCC and TCC electrodes was chosen for all subsequent measurements to be compared with plain UCC and TCC electrodes. According to the previous results, the ∆E$_{p}$ values decreased in the order UCC > TCC > UCC-C$_{76}$ ~ TCC-C$_{76}$, the cathodic peak became more well-developed leading to the higher I$_{pc}$/I$_{pa}$ value, and the R$_{CT}$ values decreased in the order UCC > TCC > UCC-C$_{76}$ ~ TCC-C$_{76}$, supporting the CV results. At high loading of C$_{76}$ (>2 mg), UCC-C$_{76}$ and TCC-C$_{76}$ were shown to have the same activity towards vanadium ions, as evinced by the same ∆E$_{p}$ and R$_{CT}$ values, and hence the substrate effect became negligible. Accordingly, unlike most previous studies, it is unnecessary to treat CC before adding the desired electrocatalyst (C$_{76}$ here), which would not only eliminate one of the preparation steps while enhancing the reaction rate but also save energy. More importantly, the parasitic chlorine gas evolution was considerably inhibited by UCC-C$_{76}$ compared to TCC and TCC-C$_{76}$, which might otherwise corrode the electrode at high positive potentials, and impede the performance of the cell due to the reduced charge efficiency.
Figure 5.7: The electrochemical behavior of UCC, TCC, UCC-C\textsubscript{76}, and TCC-C\textsubscript{76}. (a, c) CVs and (b, d) Nyquist plots in (a,b) 0.1 M VOSO\textsubscript{4}/1 M H\textsubscript{2}SO\textsubscript{4} and in (c, d) 0.1 M VOSO\textsubscript{4}/mixed acid electrolytes. CVs at \( \nu = 5 \text{ mV s}^{-1} \) and EIS at OCV.

Figure 5.8: The effect of C\textsubscript{76} loadings on the kinetics of VO\textsuperscript{2+}/VO\textsuperscript{2+} in the G1 and G3 of VRFBs, with (a) showing the \( \Delta E_p \) (obtained from CVs at \( \nu = 5 \text{ mV s}^{-1} \)) and (b) showing the \( R_{CT} \) (obtained from EIS at OCV).
Besides the surface functionalization, the superior electrochemical improvement caused by the C76 could be attributed to two other factors. The dominant sp² character, as revealed by the XPS and Raman spectra (Figure 5.5b and 5.5d), reflected the high conductivity of C76, which would facilitate ET between vanadium ions and the electrode. Secondly, the delocalization of π electrons around C76 could enhance the adsorption of the positively-charged VO²⁺ and VO₂⁺ ions by strong electrostatic attractions. This might also be the reason why chlorine evolution was less in comparison to TCC. That is, negatively-charged chloride ions had less tendency to get adsorbed onto the surface of negatively-charged C76 than they would on the surface of TCC. Thus, UCC-C76 was chosen to be the best electrode material in both electrolytes.

To address the diffusion process of the VO₂⁺/VO₂⁺ redox reaction, the Randles-Sevcik method (Equation 5.2) is usually used by researchers in VRFB applications to calculate diffusion coefficients from the slope of Ip against ν⁻¹/². A higher slope of the linear relation between Ip and ν⁻¹/² means a higher diffusion coefficient. Using Equation 5.2, it was found that the slope increases in the order UCC-C76 ~ TCC-C76 > TCC > UCC as shown in Figure 5.9, indicating fast diffusion of vanadium ions to the C76 electrode. Equation 5.3 could also be used, where Ip vs ν⁻¹/² linear relation depends on the diffusion coefficient, as well as the reaction mechanism, α, giving a more accurate representation.

\[ I_p = (2.69 \times 10^5) n^2 AC \sigma ν^{1/2} \]  
\[ I_p = (2.99 \times 10^5) n^2 AC (D\alpha)^{1/2} ν^{1/2} \]

However, Randles-Sevcik and Equation 5.3 are strictly for reversible and irreversible reactions, respectively, while this is not the case for VO₂⁺/VO₂⁺, which is a quasi-reversible redox reaction. Besides, it is hard to separate the contributions from D and α in Equation 5.3, but EIS
could help in separating them. While these equations could still provide good qualitative results for comparison, more accurate results could be obtained from EIS measurements. The Nyquist plots in Figure 5.7b and 5.7d exhibited a linear Warburg response at low frequencies that could only be related to the diffusion of vanadium ions. The slope of these Warburg lines is inversely proportional to the diffusion resistance, and hence a higher slope means better diffusion of ions.\(^{19}\)

It was found that the slope of the Warburg lines increased in the order UCC-C\(_{76}\) ~ TCC-C\(_{76}\) > TCC > UCC (Table 5.3), implying that C\(_{76}\) facilitated the diffusion of vanadium ions, compared to UCC and TCC.

![Figure 5.9: Relationship between \(I_p\) and \(v^{1/2}\) using Equation 5.2 and data from Figure 5.7a.](image)

**Table 5.3:** Warburg (W) slopes calculated from the Nyquist plots in Figure 5.7.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Warburg (W) slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H(_2)SO(_4)</td>
<td>UCC 0.259</td>
</tr>
<tr>
<td>UCC</td>
<td></td>
<td>TCC 1.226</td>
</tr>
<tr>
<td>TCC</td>
<td>Mixed acid</td>
<td>UCC-5 mg C(_{76}) 1.641</td>
</tr>
<tr>
<td>C(_{76})</td>
<td></td>
<td>UCC-5 mg C(_{76}) 1.71</td>
</tr>
</tbody>
</table>
To investigate the stability of C\textsubscript{76}, 100 cycles of repetitive CVs at $v = 5 \text{ mV s}^{-1}$ in H\textsubscript{2}SO\textsubscript{4} (Figure 5.10a) and mixed acid (Figure 5.10b) were conducted for the best-chosen UCC-C\textsubscript{76} electrode and compared it to plain UCC. A very slight peak shift was observed for UCC-C\textsubscript{76} when compared to UCC in both electrolytes. The degradation rates of UCC-C\textsubscript{76} were 190 $\mu$V/cycle and 140 $\mu$V/cycle, compared to 610 $\mu$V/cycle and 510 $\mu$V/cycle for UCC in H\textsubscript{2}SO\textsubscript{4} and mixed acid, respectively. Even though chlorine evolution occurred only on UCC-C\textsubscript{76}, it was still remarkably achieving better stability than UCC, suggesting that C\textsubscript{76} was corrosion resistive. This could also be attributed to the excellent $R_{CT}$ value, which is believed to suppress fading capacity upon cycling. In fact, both electrodes were slightly more stable in mixed acid than in pure H\textsubscript{2}SO\textsubscript{4}, which could be ascribed to the higher stability of vanadium ions upon cycling when HCl is added.

Figure 5.10: The stability of UCC-C\textsubscript{76} compared to UCC in (a) H\textsubscript{2}SO\textsubscript{4} and (b) mixed acids after 100 cycles of repetitive CVs. Peak shift values are written on each curve.

5.3 Electrocatalytic Activity of Hydrated Tungsten Oxide (HWO) NPs

Given the fact that C\textsubscript{76} particles only worked for the positive electrode, another material was required to enhance the kinetics of the negative electrode, while also inhibiting the overlapping hydrogen evolution reaction (HER). As discussed in Chapter 3, metal oxides have previously
shown better results than carbon materials towards the V\textsuperscript{2+}/V\textsuperscript{3+} redox reaction.\textsuperscript{75,76,78,82,83,86-89} WO\textsubscript{3-x}H\textsubscript{2}O and WO\textsubscript{3-x} are expected to exhibit higher kinetics, compared to the previously used anhydrous WO\textsubscript{3}, as mentioned in Section 3.4.\textsuperscript{90,98,99} While W\textsubscript{18}O\textsubscript{49} (WO\textsubscript{2.72}) has very recently been used for the positive electrode,\textsuperscript{91} W\textsubscript{32}O\textsubscript{84} (WO\textsubscript{2.63}) has never been used as an electrode material for VRFBs, in addition to WO\textsubscript{3-x}H\textsubscript{2}O as well. Therefore, hydrated tungsten oxide (HWO), WO\textsubscript{3-0.33}H\textsubscript{2}O/WO\textsubscript{2.63}, was synthesized via facile hydrothermal (HT) methods to investigate its activity towards the electrochemical reactions at both half-cells. A loading of ~ 2 mg cm\textsuperscript{-2} was used for all the experiments based on the above results that ΔE\textsubscript{p} and R\textsubscript{CT} values sharply decreased and leveled off at this optimum and moderate loading (Figure 5.8). Besides, all experiments were only conducted in the mixed acid electrolyte to imitate the G3 VRFB for more practicality, and to investigate the effect of electrode material on chlorine evolution. It was shown in the last section that the thermal treatment is not necessary when C\textsubscript{76} was used at high loading. Therefore, UCC electrodes were also employed in this investigation without further modifications. The as-synthesized HWO was further annealed under Ar (HWO-Ar) and H\textsubscript{2} (HWO-H\textsubscript{2}) atmospheres at 450 °C to investigate the effect of annealing on the kinetics of vanadium ions. Whereas H\textsubscript{2} annealing was employed to further reduce HWO and create more oxygen vacancies, Ar annealing was done for further crystallization of the HWO structure. SEM imaging and XRD analysis were implemented to identify the phase of each HWO sample and reveal the morphology. This would help in comparing the relative electrocatalytic activity of each sample towards both vanadium redox reactions. SEM images in Figure 5.11, showed that all samples consisted of nanoparticles (NPs) in the 25-50 nm range. The small-sized particles are expected to provide a large surface area for vanadium redox reactions.
All HWO samples exhibited (001) and (002) peaks at ~ 23.5º and ~ 47.5º, respectively, characteristic of the non-stoichiometric W\textsubscript{32}O\textsubscript{84} (WO\textsubscript{2.63}) (PDF 077-0810, a = 21.4 Å, b = 17.8 Å, c = 3.8 Å, α = β = γ = 90º) consistent with their apparent blue color (Figure 5.11d).\textsuperscript{107,108} Other peaks at about 20.5º, 27.1º, 28.1º, 30.8º, 35.7º, 36.7º, and 52.7º are allocated to (140), (620), (350), (720), (740), (560) and (970) diffraction planes, of orthorhombic WO\textsubscript{2.63}, respectively.\textsuperscript{108} It is worth mentioning that some of these peaks also corresponded to planes of other non-stoichiometric tungsten oxides making it difficult to match. However, the most intense peaks of WO\textsubscript{2.63} matched the most intense peaks in the sample, in addition to WO\textsubscript{2.63} generally matching with more peaks than all other tungsten oxide phases. HWO-H\textsubscript{2} specifically exhibited the highest amount of WO\textsubscript{2.63}.

Figure 5.11: The SEM images of (a) HWO, (b) HWO-Ar, and (c) HWO-H\textsubscript{2}, besides the (d) XRD data of all HWO samples, indicating all the diffraction planes.

All HWO samples exhibited (001) and (002) peaks at ~ 23.5º and ~ 47.5º, respectively, characteristic of the non-stoichiometric W\textsubscript{32}O\textsubscript{84} (WO\textsubscript{2.63}) (PDF 077-0810, a = 21.4 Å, b = 17.8 Å, c = 3.8 Å, α = β = γ = 90º) consistent with their apparent blue color (Figure 5.11d).\textsuperscript{107,108} Other peaks at about 20.5º, 27.1º, 28.1º, 30.8º, 35.7º, 36.7º, and 52.7º are allocated to (140), (620), (350), (720), (740), (560) and (970) diffraction planes, of orthorhombic WO\textsubscript{2.63}, respectively.\textsuperscript{108} It is worth mentioning that some of these peaks also corresponded to planes of other non-stoichiometric tungsten oxides making it difficult to match. However, the most intense peaks of WO\textsubscript{2.63} matched the most intense peaks in the sample, in addition to WO\textsubscript{2.63} generally matching with more peaks than all other tungsten oxide phases. HWO-H\textsubscript{2} specifically exhibited the highest amount of WO\textsubscript{2.63}.

Figure 5.11: The SEM images of (a) HWO, (b) HWO-Ar, and (c) HWO-H\textsubscript{2}, besides the (d) XRD data of all HWO samples, indicating all the diffraction planes.
noticed by the shift in 2 theta values towards those of WO$_{2.63}$ in the database. This was expected as H$_2$ is a reducing agent, thereby creating more oxygen vacancies. The intensities of the peaks were, however, a bit difficult to interpret as another phase also existed in all samples. In the as-synthesized HWO, hydrated tungsten oxide (WO$_3$(H$_2$O)$_{0.333}$) (PDF 087-1203, a = 7.3 Å, b = 12.5 Å, c = 7.7 Å, $\alpha = \beta = \gamma = 90^\circ$) was also present. Peaks at around 18$^\circ$, 22.9$^\circ$, 27.1$^\circ$, 28.1$^\circ$, 36.7$^\circ$, 47.5$^\circ$, 52.7$^\circ$, and 55$^\circ$ correspond to (111), (002), (022), (220), (222), (004), (153) and (402) planes of orthorhombic WO$_3$(H$_2$O)$_{0.333}$, respectively.$^{100}$ These were ascribed to lattice spacings (d-spacings) of 4.90, 3.87, 3.30, 3.17, 2.45, 1.93, 1.75, and 1.66 Å, respectively. S. Songara et al. using the same synthesis method, obtained a white color product which is related to the existence of WO$_3$(H$_2$O)$_{0.333}$. However, in this work, a blue/white color product was obtained due to the different conditions, which indicates that the products containing both the WO$_3$(H$_2$O)$_{0.333}$ and the reduced form of tungsten oxide.

Upon annealing, WO$_3$(H$_2$O)$_{0.333}$ formed monoclinic WO$_3$ (PDF 087-2385, a = 5.3 Å, b = 5.2 Å, c = 7.7 Å, $\alpha = \gamma = 90^\circ$, $\beta = 91.7^\circ$) in HWO-Ar and HWO-H$_2$. This is logical as thermal treatment at 450 ºC would convert a hydrated material to its anhydrous form. Peaks at around 20.5$^\circ$, 23$^\circ$, 27.5$^\circ$, 28.1$^\circ$, 36.7$^\circ$, and 47.5$^\circ$ correspond to (011), (002), (111), (021), and (004) diffraction planes of monoclinic WO$_3$. The peaks after annealing appeared to be narrower due to the higher crystallization degree of the sample. It could be observed that HWO-Ar matched more WO$_3$ peaks than HWO-H$_2$, and its higher peak intensities could be attributed to the higher amount of WO$_3$. This was confirmed by the semi-quantitative analysis done by the software, which displayed 25% WO$_3$: 75% WO$_{2.63}$ and 15% WO$_3$: 85% WO$_{2.63}$ for HWO-Ar and HWO-H$_2$, respectively. The HWO as-synthesized sample displayed 26% WO$_3$(H$_2$O)$_{0.333}$: 74% WO$_{2.63}$. 

CV and EIS results for both half redox reactions using HWO, HWO-Ar, and HWO-H₂ are shown in Figure 5.12 below. For the negative redox reaction (Figure 5.12a and 5.12c), all three samples showed extremely improved kinetics, relative to plain UCC, which was found to be completely inactive towards the V²⁺/V³⁺ reaction (inset of Figure 5.12a), as confirmed by a few previous studies.²⁸,³¹,³³,⁴⁷ Specifically, the as-synthesized HWO showed more defined redox peaks. Compared to the annealed samples, HWO did not only inhibit HER more efficiently but also maintained fast kinetics, as shown by the smaller ΔE_p (46 mV vs. 63 mV in Figure 5.12a) and R_CT in the Nyquist plots (Figure 5.12c). This would ultimately increase the voltage efficiency, and reduce capacity fading due to unwanted side reactions. Because all three HWO samples contain WO₂.₆₃, the enhanced activity of the as-synthesized HWO could be attributed to its hydrated structure. Also, the hydrated tungsten oxide could be more efficient in boosting the interaction of positive ions than its anhydrous form, as explained by J. B Mitchell et al.,⁹⁹ which are the positive vanadium ions here. A ΔE_p less than 59 mV for one-electron transfer (ET) reaction observed in the as-synthesized sample indicates that the bulk diffusion is not the only controller of the reaction kinetics but also the consumption/diffusion of the reactants in the pores and interlayers within the WO₃(H₂O)₀.₃₃₃/WO₂.₆₃ mixture (thin-layer behavior). The superior electrocatalytic activity could also be ascribed to the synergistic effect between the hydrated form of tungsten oxide, as well as the higher conductivity and oxygen vacancies provided by the reduced form (WO₂.₆₃).

As for the positive electrode (Figure 5.12b and 5.12d), all HWO samples showed sluggish kinetics (ΔE_p > 350 mV), comparable with the plain UCC electrodes (inset of Figure 5.12b). Yet, it was interesting to realize that they suppressed chlorine evolution, which is desirable for a high coulombic efficiency and lower electrode corrosion. The slow ET was expected as it has been reported by a few previous studies that metal oxides do not act as good catalysts in the positive
Chapter 5: Results and Discussion

half-cell reaction.\textsuperscript{75,76,78,82,83,86,88,89} While the reason was not mentioned, it is reasonable to say that the VO\textsuperscript{2+/3+} redox reaction usually requires high conductivity, as discussed in Section 5.2, for improved kinetics.\textsuperscript{47,48,52,55,56,60} In other words, it might be that the C=C sites are essential for the VO\textsuperscript{2+/3+} reaction, as proposed by S. Liu et al. (mechanism in Figure 3.2).\textsuperscript{55} This, however, does not seem like a major issue for the negative redox reaction. Figure 5.12d showed that the as-synthesized HWO still displays better results as indicated by the relatively reduced $R_{CT}$ in the Nyquist plot. Based on these electrochemical results, the as-synthesized HWO was chosen for the subsequent experiments discussed in the next Section 5.4.

\textbf{Figure 5.12:} CVs at $\nu = 5$ mV s\textsuperscript{-1} (a, b) and the Nyquist plots of EIS at $-0.3$ V (c) and OCV (d) of all HWO samples for V\textsuperscript{2+/3+} (a and c) and VO\textsuperscript{2+/3+} (b and d) reactions in 0.1 M VOSO\textsubscript{4}/1 M H\textsubscript{2}SO\textsubscript{4} + 1 M HCl electrolyte. Insets of (a and b) show the electrochemical behavior of UCC and UCC-PVDF towards the reaction in the same solution used for the CVs. $\Delta E_p$ and $R_{CT}$ values are shown.
To validate that WO$_{2.63}$ would work as a better catalyst than WO$_3$, it was worth conducting CV and EIS experiments to show the difference between their electrocatalytic activity (Figure 5.13). This was also done to confirm Bayeh et al.’s hypothesis that the reduced form of tungsten oxide is a better catalyst than its stoichiometric form, even though they never made an experimental comparison. For synthesizing the stoichiometric tungsten oxide (WO$_3$.xH$_2$O) the same hydrothermal method for preparing HWO was used, but only oxalic acid was added, as a source of oxygen, as in Hosseini et al.’s experiment. The color of the produced WO$_3$ was bright yellow, indicating the presence of stoichiometric WO$_3$.

The morphology of WO$_3$ was found to be nanoplates (thickness = 40-70 nm), as shown in Figure 5.13a, unlike HWO’s nanoparticle morphology (Figure 5.11a). XRD analysis was conducted to study and compare the phases of both samples (Figure 5.13b). The stoichiometric tungsten oxide sample was shown to contain monoclinic WO$_3$ (PDF 087-2385, a = 5.3 Å, b = 5.2 Å, c = 7.7 Å, α = γ = 90°, β = 91.7°) and orthorhombic WO$_3$(H$_2$O)$_{0.333}$ (PDF 087-1203, a = 7.3 Å, b = 12.5 Å, c = 7.7 Å, α = β = γ = 90°) phases, which indicates that oxalic acid converted WO$_{2.63}$ to WO$_3$, but the hydrated structure was still present in the sample. HWO exhibited lower Δ$E_p$ and $R_{CT}$ values for both half-cell redox reactions as depicted in Figure 5.11c, 5.11d, 5.11e, and 5.11f. In the case of the V$^{2+}$/V$^{3+}$ reaction, the presence of defects in WO$_{2.63}$ seems to not significantly enhance its catalytic activity or suppress the HER. According to these results, it is the presence of the hydrated structure (WO$_3$(H$_2$O)$_{0.333}$) that is crucial for inhibiting the parasitic HER. In contrast, in the case of the VO$^{2+}$/VO$_2^+$ reaction, the presence of defects in the WO$_{2.63}$ plays a significant role in enhancing its catalytic activity, as evinced by the large difference in $R_{CT}$ values (Figure 5.11f). Besides the presence of oxygen vacancies that would act as active sites for VO$^{2+}$/VO$_2^+$ reaction, the high electrical conductivity of the deficient WO$_{2.63}$ material may play an
important role. Since the morphology of both samples was different, this could have also played a role in the activity of each electrode, indicating that NPs might have been more favorable than nanoplates for vanadium redox reactions.

**Figure 5.13:** (a) SEM image of WO$_3$/WO$_3$(H$_2$O)$_{0.333}$. (b) XRD of HWO and WO$_3$/WO$_3$(H$_2$O)$_{0.333}$. The cyclic voltammetry behavior ($v = 5$ mV s$^{-1}$) for (c) V$^{2+}$/V$^{3+}$ and (e) VO$^{2+}$/VO$_2^+$ and the Nyquist plots for (d) V$^{2+}$/V$^{3+}$ ($V = -0.3$) and (f) VO$^{2+}$/VO$_2^+$ (OCV) in 0.1 M VOSO$_4$/1 M H$_2$SO$_4$ + 1 M HCl electrolyte. $\Delta E_p$ and $R_{CT}$ values are shown for comparison.
Because the as-synthesized HWO showed the best electrocatalytic activity towards \( \text{VO}^{2+}/\text{VO}_2^+ \) and \( \text{V}^{2+}/\text{V}^{3+} \) electrochemical reactions among all other tungsten oxide samples, HR-TEM analysis was conducted for HWO to provide high magnification imaging of the NPs and crystallographic planes (Figure 5.14). As can be seen in Figure 5.14a, TEM imaging provided a better-quality image of HWO, than SEM imaging, and showed that its morphology was nanocubes. Zooming onto the nanocubes for selected area diffraction, the lattice structure, and the diffraction planes satisfying Bragg’s law could be visualized as depicted in Figure 5.14c, confirming the crystallinity of the material. The inset of Figure 5.14c shows a d-spacing of 3.3 Å, corresponding to the (022) and (620) diffraction planes found in \( \text{WO}_3(\text{H}_2\text{O})_{0.333} \) and \( \text{WO}_{2.63} \) phases in HWO, respectively.\(^{100,103,108}\) This is consistent with the above XRD analysis (shown again in Figure 5.14d), as the d-spacing of the observed lattice plane (Figure 5.14c) corresponds to the most intense XRD peak in the HWO sample. Accordingly, the (002) plane is the preferred orientation of the HWO crystallites.

The ring pattern is also displayed in Figure 5.14b with each ring corresponding to a different plane. \( \text{WO}_3(\text{H}_2\text{O})_{0.333} \) and \( \text{WO}_{2.63} \) planes are written in white and blue, respectively, with their respective XRD peaks also depicted in Figure 5.14d. The first ring shown in the ring pattern corresponds to the first marked peak in the XRD pattern of the diffraction plane (022) or (620). Going to larger diameter rings is the same as going right on the XRD graph, with decreasing d-spacing. From (022) to (402) rings, the d-spacing values were found to be 3.30, 3.17, 2.38, 1.93, and 1.69 Å, which are consistent with the XRD values of 3.30, 3.17, 2.45, 1.93, and 1.66 Å, respectively, mentioned above.\(^{103,104}\)
In addition to XRD and TEM, XPS analysis was also employed for the HWO sample to determine its surface chemistry and the oxidation state of tungsten (W). The narrow scan spectra of W 4f and O 1s core levels are shown in Figure 5.15a and 5.15b, respectively. The W 4f spectrum was separated into two spin-orbit doublet peaks corresponding to the binding energies of W oxidation states. Whereas the W 4f$_{5/2}$ and W 4f$_{7/2}$ peaks located at binding energies of 37.8 and 35.6 eV are ascribed to W$^{6+}$, the W 4f$_{5/2}$ and W 4f$_{7/2}$ peaks at 36.6 and 34.9 eV are characteristic of the W$^{4+}$ state, respectively. The presence of a lower oxidation state (W$^{4+}$) further confirms the

Figure 5.14: (a) The HR-TEM image of the HWO, with the inset showing a magnified image, (b) the ring pattern of the HWO showing the planes associated with WO$_3$(H$_2$O)$_{0.333}$ and WO$_{2.63}$ phases, (c) an image of the lattice planes confirming the crystallinity of the samples, with the inset showing a magnified image of the planes and a d-spacing of 0.33 nm, corresponding to (002) and (620) planes, as depicted in (d).
formation of non-stoichiometric \( \text{WO}_{2.63} \), while the presence of \( W^{6+} \) indicates stoichiometric \( \text{WO}_3 \) attributed to \( \text{WO}_3(\text{H}_2\text{O})_{0.333} \). The fitting data reveal that the atomic percentages of \( W^{6+} \) and \( W^{4+} \) are 35.4% and 39.7%, and 4.6% and 8.9%, for \( 4f_{5/2} \) and \( W 4f_{7/2} \), respectively. The O 1s spectrum was deconvoluted into two peaks at 533 (22.2%) and 530.4 eV (77.8%). The former corresponds to O-H, while the latter is ascribed to the crystal lattice oxygen bond in W-O. The presence of the O-H functional group is consistent with the hydrated nature of HWO. According to these results, it seems that it is the W-OH functional groups that suppress the HER in HWO and \( \text{WO}_3/\text{WO}_3(\text{H}_2\text{O})_{0.333} \), rather than the oxygen vacancies in \( \text{WO}_{2.63} \), which are present in the annealed HWO samples that promoted HER.

![Figure 5.15: XPS narrow scan spectra of (a) W 4f indicating the presence of \( W^{6+} \) and \( W^{4+} \), and (b) O 1s showing the presence of W-O bonds and O-H functional groups.](image)

5.4 The Electrochemical Activity of C76/HWO Nanocomposites

In the last two sections, \( \text{C}_{76} \) was shown to enhance the kinetics of the positive electrode due to its high conductivity and oxygen functional groups, and HWO was found to improve the kinetics of the negative electrode due to the hydrated structure and oxygen vacancies. Based on these results, it was interesting to prepare \( \text{C}_{76}/\text{HWO} \) samples with different ratios and investigate
their electrocatalytic effect on vanadium ions in both half-reactions. HWO suspensions with 10%, 30%, and 50% C\textsubscript{76} were prepared and deposited on UCC electrodes with a total loading of \(\sim 2\) mg cm\textsuperscript{-2}. The kinetics of \(V^{2+}/V^{3+}\) and \(VO^{2+}/VO_2^{+}\) was examined using CV and EIS in the mixed acid electrolyte as shown in Figure 5.16, along with SEM images and EDX mapping of the deposited HWO and HWO-C\textsubscript{76} particles. SEM imaging in Figure 5.16a shows the successful deposition of HWO and HWO-C\textsubscript{76} on and between the carbon fibers of UCC electrodes. EDX elemental mapping was also done to confirm the homogenous distribution of HWO-C\textsubscript{76} particles on UCC.

Figure 5.16b illustrated the effect of increasing the C\textsubscript{76}:HWO ratio on the kinetics of the \(V^{2+}/V^{3+}\) redox reaction. Going to higher C\textsubscript{76} loadings, \(V^{2+}/V^{3+}\) redox peaks became less defined due to the promotion of the HER. It is clear that no redox peaks were achieved when C\textsubscript{76} was used, and only HER was observed. On the other hand, using HWO without any C\textsubscript{76} content did not only render its superior \(V^{2+}/V^{3+}\) kinetics but also its HER inhibition. This is consistent with Lee’s study on mesoporous tungsten oxynitride.\textsuperscript{86} That is, while mesoporous WO\textsubscript{3} worked well for the negative reaction, mesoporous carbon showed no activity. \(\Delta E_p\) and \(I_{pa}/I_{pc}\) values were calculated from Figure 5.16b and summarized in Table 5.4 below. The results showed that HWO achieved the lowest \(\Delta E_p\) and highest \(I_{pa}/I_{pc}\) ratio, indicating excellent electrode kinetics. Seemingly, the HER was found to exhibit a high overpotential on the surface of HWO, but a low overpotential on C\textsubscript{76}. 
A reasonable explanation could be that the smaller H\(^+\) ions could more easily adsorb onto the surface of the negatively charged C\(_{76}\), by electrostatic attractions, than the V\(^{3+}\) ions. As explained in Section 3.3, the fast electron transfer (ET) and hence the enhanced activity of the V\(^{2+}/V^{3+}\) reaction on the surface of HWO is attributed to the hydrated structure of HWO, as well as the abundant oxygen vacancies that act as active sites. Compared to C\(_{76}\), HWO was found to have a much higher hydrophilic surface (Figure 5.17a) allowing for rapid diffusion of vanadium ions and a fast ET. In addition to the XPS results (Figure 5.15) that revealed the presence of W-O and O-H bonds on HWO, FTIR analysis (Figure 5.17b) also showed that HWO exhibited W-O bonds,
which could act as catalytic active sites for the V\(^{2+}/V^{3+}\) redox reaction. This is supported by previous studies on the catalytic activity of WO\(_3\) that W=O bonds could catalyze the V\(^{2+}/V^{3+}\) reaction.\(^{82,88}\) However, in this study, it is the W-OH rather than the W=O bonds that inhibit HER and enhance the kinetics of the V\(^{2+}/V^{3+}\) reaction.

**Table 5.4:** Summary of the results from the CVs and Nyquist plots in Figure 5.16 for each half-cell reaction using all samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>HWO</th>
<th>HWO-10% C(_{76})</th>
<th>HWO-30% C(_{76})</th>
<th>HWO-50% C(_{76})</th>
<th>C(_{76})</th>
</tr>
</thead>
<tbody>
<tr>
<td>v (mV s(^{-1}))</td>
<td>360 459 469</td>
<td>310 408 459</td>
<td>220 337 424</td>
<td>176 297 370</td>
<td>176 277 332</td>
</tr>
<tr>
<td>ΔE(_p) (mV)</td>
<td>0.46 0.51 0.64</td>
<td>0.71 0.82</td>
<td>103 85 35</td>
<td>9 14</td>
<td>0.13 0.9 1.04 1.32 0.94</td>
</tr>
<tr>
<td>I(<em>{pa})/I(</em>{pc})</td>
<td>0.59 0.47 0.30</td>
<td>0.32</td>
<td>- - -</td>
<td>-</td>
<td>- - -</td>
</tr>
</tbody>
</table>

**Figure 5.17:** The (a) Contact angle measurements of both samples, showing the highly wettable HWO surface and the more hydrophobic HWO-50% C\(_{76}\) surface, (b) FTIR analysis of HWO and HWO-50% C\(_{76}\), with the functional groups indicated on the graph at each wavenumber.
The opposite trend was observed for the VO$_2^+$/VO$_2^{2+}$ redox reaction (Figure 5.16c and 5.16d). Upon increasing the C$_{76}$ content, the electrochemical activity of the electrode was found to improve, as indicated by the reduced $\Delta E_p$ and increased $I_{pa}/I_{pc}$ ratio (Table 5.4). This was also confirmed by the R$_{CT}$ values (Table 5.4) extracted from the Nyquist plot in Figure 5.16d. These results were also consistent with Lee’s study that mesoporous WO$_3$ showed no activity towards VO$_2^+$/VO$_2^{2+}$, but mesoporous carbon displayed improved kinetics. This unraveled the fact that the positive reaction might be much more dependent on the conductivity (C=C bonds) of the electrode, unlike the negative reaction. It could also be that C$_{76}$ lowered the overpotential of the reaction by decreasing the organization energy due to the change in coordination geometry between [VO(H$_2$O)$_3$]$^{2+}$ and [VO$_2$(H$_2$O)$_4$]$^{2+}$. This, however, might not be achieved with the HWO electrode. In fact, HWO-50% C$_{76}$ and C$_{76}$ were found to exhibit nearly the same electrocatalytic activity towards the positive reaction. More interestingly, HWO-50% C$_{76}$ further inhibited the chlorine evolution, relative to C$_{76}$, as shown in Figure 5.14c, in addition to displaying a smaller semicircle (lower R$_{CT}$) in Figure 5.16d. This could be attributed to the synergistic effect between the negatively charged, highly conductive C$_{76}$ and the high wettability and W-O catalyzing functional group on HWO. Whereas less chlorine evolution would enhance the charge efficiency of the full cell, the enhanced kinetics would boost the full cell voltage efficiency. Apart from the kinetics of the redox reaction, the Warburg (W) slopes at low frequencies in the Nyquist plots (Fig. 14d) for all electrodes were calculated (Table 5.4) to compare the diffusion efficiency of each material. It was found that HWO-50% C$_{76}$ exhibited the highest slope; hence the fastest diffusion of vanadium ions, owing to the synergistic effects (also see Figure 5.18b). Meanwhile, C$_{76}$ showed a lower slope due to its lower wettability, hindering rapid diffusion of vanadium ions to the electrode’s surface and between the fibers. Based on these findings, it was evident that a good
balance between wettability, catalytic active sites and conductivity is essential for VO\textsuperscript{2+}/VO\textsubscript{2}+ fast kinetics and ET.

Since HWO and HWO-50% C\textsubscript{76} showed the best results for the negative and positive redox reactions, respectively, FTIR analysis was conducted for these two samples to study the presence of functional groups and the coordinated water molecules in the hydrated structure of HWO. As depicted in Figure 5.17b, both samples exhibited very strong broadband at ~710 cm\textsuperscript{-1} assigned to the O-W-O stretch vibration in the HWO lattice structure, an intense shoulder at ~ 840 cm\textsuperscript{-1} attributed to the W-O stretch vibration, a sharp band at ~ 1610 cm\textsuperscript{-1} referring to the O-H bending vibration and a broad absorption band at ~ 3400 cm\textsuperscript{-1} assigned to the O-H stretch vibration in hydroxyl groups.\textsuperscript{100} These results are consistent with the XPS spectra in the last section. W-O functional groups could provide active sites for vanadium redox reactions as mentioned above. As discussed in Section 5.1, the O-H groups could also catalyze both reactions, along with increasing the hydrophilicity of the electrode, hence facilitating diffusion and ET rate. The HWO-50% C\textsubscript{76} sample exhibited additional peaks for C\textsubscript{76}, as marked on the graph. Peaks at ~ 2905, 2375, 1705, 1607, and 1445 cm\textsuperscript{-1} could be assigned to C-H, O=C=O, C=O, C=C, and C-O stretch vibrations, respectively.\textsuperscript{47} As already known, C=O and C-O oxygen functional groups could act as active sites for vanadium redox reactions. It could be noticed that the intensity of the O-H peaks decreased upon C\textsubscript{76} addition, making it less hydrophilic (Figure 5.17a). Besides, the W-O bands were also less intense as a lower amount (half) of HWO was present in the HWO-50% C\textsubscript{76} sample. This perhaps means that the negative electrode is more dependent on the W-O-H sites than the positive electrode for fast ET. Besides, the W-O-H sites could be the reason behind inhibiting the HER. As in the case of the anhydrous WO\textsubscript{3} samples (HWO-Ar and HWO-H\textsubscript{2}), the HER rate was promoted
in comparison to the hydrated tungsten oxide, whether it was stoichiometric (WO3/WO3(H2O)0.333) or deficient (HWO, WO2.63/WO3(H2O)0.333).

To test and compare the wettability of both electrodes, contact angle measurements were employed as shown in Figure 5.17a. The HWO electrode immediately absorbed the water droplet, indicating super hydrophilicity because of the available O-H functional groups. The HWO-50% C76 was more hydrophobic with a contact angle ~ 135 ° after 10 s. In CV studies, however, the electrode became completely wet in less than a minute. This was consistent with the XPS and FTIR results that the more abundant O-H groups on the surface of HWO made it relatively more hydrophilic. It could be that, along with the catalytic W-OH bonds, the hydrophilicity of the electrode also affected the negative redox reaction more than the positive reaction, allowing for better diffusion and accessibility of vanadium ions within the electrode.

Additional post electrochemical analysis was conducted to reveal more information about the kinetics and diffusion of VO2+/VO2+ and V2+/V3+ redox reactions. For the diffusion process of vanadium ions, the Randles-Sevcik equation (see Section 5.2) was utilized, in which Ip was plotted against ν1/2 in Figure 5.18a and 5.18b for the negative and positive electrodes, respectively. From the slope of the graphs, the diffusion coefficient could be estimated. For V2+/V3+ (Figure 5.18a), HWO was found to have the highest anodic and cathodic slopes, indicative of rapid diffusion of ions to the electrode’s surface. Upon increasing the C76 concentration, diffusion of vanadium ions was slower due to the lower slopes. This was found to affect the reverse (anodic) reaction more than the forward reaction. That is, HWO enhanced the kinetics of the reverse reaction allowing for higher reversibility. This is consistent with the XPS, FTIR, and contact angle measurements that HWO had more O-H surface functionalization and higher wettability than HWO-C76. Consequently, superior electrode kinetics for HWO was obtained in Figure 5.16b above.
For the $\text{VO}^{2+}/\text{VO}^{2+}$ reaction (Figure 5.18b), $C_{76}$ displayed a steeper slope for the cathodic reaction than HWO-$C_{76}$. However, the more accurate diffusion results from EIS above showed that HWO-$C_{76}$ exhibited a steeper W slope (Table 5.4). As a result, HWO-$C_{76}$ was still chosen as a better electrocatalyst due to the synergism between the presence of HWO, the conductivity and oxygen bonds on $C_{76}$. Although this method has extensively been used in the VRFB field to calculate diffusion coefficient values, it should strictly be used for reversible or irreversible reactions, which is not the case for $\text{VO}^{2+}/\text{VO}_{2}^{+}$ and $V^{2+}/V^{3+}$ redox reactions. However, it could still give qualitative insights into the diffusion of ions though each electrode material for comparison.
To further analyze the reversibility of both half-cell reactions, Nicholson’s method for quasi-reversible reactions was used to determine the standard rate constant, \( k^0 \).\(^{101,102}\) This was done by plotting a dimensionless kinetic parameter, \( \Psi \), which is a function of \( \Delta E_p \), against \( \nu^{1/2} \) (Figure 5.18c and 5.18d). \( \Psi \) values were obtained by using the following equations:

\[
\Psi = \frac{-0.6288 + 0.0021(n \times \Delta E_p)}{1 - 0.017(n \times \Delta E_p)} \quad \text{for} \quad \Delta E_p < 200 \text{ mV} \quad (5.4)^{101}
\]

\[
\Psi = 2.18 \sqrt{\frac{\alpha}{\pi}} \exp \left( -\frac{\alpha^2Fn\Delta E_p}{RT} \right) \quad \text{for} \quad \Delta E_p > 200 \text{ mV} \quad (5.5)^{102}
\]

Where all parameters have their known definitions. \( \alpha \) was assumed to be 0.5 as it was found in Nicholson’s paper that the results were insensitive to the value of \( \alpha \). Table 5.5 shows the values of \( \Psi \) obtained for each electrode material for \( \text{VO}^{2+}/\text{VO}_2^+ \) and \( \text{V}^{2+}/\text{V}^{3+} \) reactions. The results were plotted (Figure 5.18c and 5.18d) to obtain \( k^0 \) from the slope of each graph, as written next to each line, by the following equation:

\[
\Psi = \left( \frac{D \alpha k^0}{D R} \right) \frac{\pi D_0 D R}{\sqrt{\pi D_0 n F v}} \quad (5.6)^{101,102}
\]

Where \( D_0 \) and \( D_R \) are the diffusion coefficients of the oxidant and reductant species; \( D (\text{V}^{2+}) = 6.85 \times 10^{-10} \), \( D (\text{V}^{3+}) = 9.5 \times 10^{-11} \), \( D (\text{V}^{4+}) = 4.22 \times 10^{-10} \), \( D (\text{V}^{5+}) = 4.03 \times 10^{-10} \) m\(^2\) s\(^{-1}\).\(^{109}\) \( k^0 \) values obtained in Table 5.5 were in the quasi-reversible range (10\(^{-1}\)-10\(^{-5}\) cm s\(^{-1}\)), confirming that both half-cell reactions are quasi-reversible. For \( \text{VO}^{2+}/\text{VO}_2^+ \), HWO-50% C\(_{76}\) was found to exhibit the highest slope, hence the highest \( k^0 \). This implied that this electrode achieved the fastest kinetics, in line with the CV and EIS results in Figure 5.16 and Table 5.4. Besides, \( k^0 \) values were
also obtained from the Nyquist plots (Figure 5.16d) using $R_{CT}$ values (Table 5.4) via the following equation:

$$k^0 = \frac{RT}{n^2F^2AR_{CT}C}$$  \hspace{1cm} (5.7)^{17}

These results of $k^0$ from EIS are summarized in Table 5.5, and also show that HWO-50% $C_{76}$ exhibited the highest ET rate, owing to the synergistic effects. Even though $k^0$ values were not the same due to the different derivations of each method, they still displayed the same order of magnitude and showed consistency. Regarding the $V^{2+}/V^{3+}$ reaction, HWO showed the highest value of $k^0$ as expected, which is consistent with the CV results (Figure 5.16b and Table 5.4).

Being a 1.5 ET reaction, the $\Delta E_p$ value was multiplied by 1.5 as the starting solution was $V^{4+}$.30

Table 5.5: Nicholson’s parameter, $\Psi$, as obtained by Equations 5.4 and 5.5. $k^0$ values were calculated using slopes in Figure 5.18c and d, and Equation 5.6. $k^0$ values from EIS data (Figure 5.16d) were obtained using Equation 5.7.

<table>
<thead>
<tr>
<th>Material</th>
<th>HWO</th>
<th>HWO/$C_{76}$ (10%)</th>
<th>HWO/$C_{76}$ (30%)</th>
<th>HWO/$C_{76}$ (50%)</th>
<th>$C_{76}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (mV s$^{-1}$)</td>
<td>5</td>
<td>20</td>
<td>5</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>$\Delta E_p$ (mV)</td>
<td>360</td>
<td>459</td>
<td>469</td>
<td>459</td>
<td>492</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>0.026</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>$k^0 \times 10^{-4}$ (cm s$^{-1}$)</td>
<td>0.421</td>
<td>0.774</td>
<td>2.08</td>
<td>2.5</td>
<td>2.28</td>
</tr>
<tr>
<td>EIS</td>
<td>0.216</td>
<td>0.26</td>
<td>0.627</td>
<td>2.47</td>
<td>1.58</td>
</tr>
<tr>
<td>$1.5 \times \Delta E_p$ (mV)</td>
<td>69</td>
<td>100</td>
<td>143</td>
<td>90</td>
<td>131</td>
</tr>
<tr>
<td>$\Psi$</td>
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<td>0.60</td>
<td>0.23</td>
<td>0.83</td>
<td>0.34</td>
</tr>
<tr>
<td>$k^0 \times 10^{-3}$ (cm s$^{-1}$)</td>
<td>6.87</td>
<td>5.55</td>
<td>1.79</td>
<td>1.79</td>
<td>-</td>
</tr>
</tbody>
</table>
Chapter 5: Results and Discussion

To have a complete picture of the achieved superior kinetics, it was important to compare the best electrode material for each redox reaction with bare UCC and TCC electrodes (Figure 5.19a and 5.19b). While UCC showed no activity towards $V^{2+}/V^{3+}$, TCC and HWO showed improved reversibility, with $\Delta E_p$ values equal to 58 and 46 mV, respectively (Figure 5.19a). Moreover, TCC suffered from a 20 mV-peak shift after the 10th cycle of CV, compared to only 2 mV for HWO, resulting in degradation rates of 2 mV/cycle and 0.2 mV/cycle, respectively. The HER also became pronounced after 27 cycles using HWO, but only after 10 cycles using TCC (Figure 5.19c). This was consistent with the hypothesis that W-O-H sites would hinder HER, thereby enhancing the stability of the electrode during cycling. The promoted HER upon cycling could be attributed to Pt particles being dissolved from the Pt counter electrode and redeposited on the surface of HWO, thereby catalyzing HER,\textsuperscript{110,111} which needs further investigation and confirmation using different counter electrodes. The electrochemical dissolution of Pt is also known to be enhanced upon cycling, especially in acidic solutions containing chloride ions.\textsuperscript{110} This, however, will not be a problem in full cell measurements. Another reason for the HER promotion upon repetitive cycling could be the formation of VO at high $V^{2+}$ surface concentration, which was computationally studied by J. Lee et al. to catalyze HER.\textsuperscript{112} Compared to TCC, HWO exhibited faster electrode kinetics, higher stability, and less HER, revealing the fact that thermal treatment was not needed and that HWO could merely be used with UCC. For the $VO^{2+}/VO_2^+$ electrochemical reaction, HWO-C\textsubscript{76} did not only display the lowest $\Delta E_p$ but also inhibit chlorine evolution relative to TCC by about seven times (Figure 5.19b).
As for the stability, HWO-50% C\textsubscript{76} showed a peak shift equal to 44 mV after 150 cycles (degradation rate 293 µV/cycle), in comparison with 50 mV for UCC. This might not be a massive difference, but the kinetics of UCC was very sluggish and tend to get worse with cycling, especially for the reverse reaction. Even though the reversibility of TCC was much better than that of UCC, TCC was found to have a large peak shift of 73 mV after 150 cycles. This could be attributed to the promotion of chlorine evolution, which might corrode and degrade the performance of the electrode.

\textbf{Figure 5.19:} A comparison between the best electrode materials relative to UCC for (a) V\textsuperscript{2+/3+} and (b) VO\textsuperscript{2+/3+} redox reactions. (c) and (d) are stability tests for V\textsuperscript{2+/3+} and VO\textsuperscript{2+/3+}, respectively. All CVs were at ν = 5 mV s\textsuperscript{-1} in 0.1 M VOSO\textsubscript{4}/1 M H\textsubscript{2}SO\textsubscript{4} + 1 M HCl electrolyte.
Chapter 6: Conclusion and Future Work

6.1 Conclusion

The widespread implementation of renewable energy requires suitable energy storage for a reliable and robust electrical grid. Among the current battery technologies, the VRFB exhibits a range of advantages such as decoupled power and energy densities, 100% depth of discharge, long cycle life, non-flammable chemistry, and low system maintenance cost, allowing it to be an excellent choice for long-term energy storage in grid-connected and off-grid applications. However, compared to other large scale battery technologies, its market penetration is still relatively small. This is due to its high capital cost, which primarily depends on cell stack price, and hence the performance of the electrode material at which the vanadium electrochemical reactions take place to store and release electrical energy. Therefore, to boost the economic appeal of this technology, enhancing and understanding the kinetics of vanadium redox reactions at both half-cells is extremely important to achieve high electrolyte utilization and energy efficiency. The objective of this study was to improve the kinetics of both redox reactions, VO$^{2+}$/VO$^{2+}$ at the positive side, and V$^{2+}$/V$^{3+}$ at the negative side.

In the first section of Chapter 5, the effect of thermal treatment of carbon cloth (CC) electrodes on the kinetics of VO$^{2+}$/VO$^{2+}$ was investigated. Charge transfer resistance was found to substantially decrease upon the thermal oxidation treatment, owing to the increased graphitization, roughness, COOH functional groups, wettability, as evidenced by XRD, SEM, XPS, and contact angle measurements, respectively. In Section 5.2, C$_{76}$ particles with different loadings were added to CC electrodes for further potential activation reduction for VO$^{2+}$/VO$^{2+}$. Increasing the loading up to 5 mg cm$^{-2}$ was found to decrease the peak separation, $\Delta E_p$, from $\sim$400 mV (UCC) and $\sim$250
mV (TCC) to \(~109\) mV in \(H_2SO_4\) and mixed acid electrolytes. Chlorine evolution was also inhibited on \(C_{76}\) in comparison to TCC electrodes, which showed that treatment was not required. The enhanced activity and stability of \(C_{76}\) was attributed to the high graphitization and conductivity, as well as C-OH and COOH groups, as indicated by the XPS and Raman results. In Section 5.3, \(WO_3.(H_2O)_{0.33}/WO_{2.63}\) (HWO) was fabricated and its electrocatalytic effect was investigated for both half-cell reactions. For \(VO^{2+}/VO_2^+\), no reversibility enhancement was observed, but chlorine evolution was inhibited in the mixed acids electrolyte. On the other hand, the kinetics of \(V^{2+}/V^{3+}\) was dramatically enhanced giving a \(\Delta E_p\) value of \(46\) mV while also inhibiting the HER at a \(2\) mg cm\(^{-2}\) loading, compared to no redox peaks and enhanced HER on UCC. Ar and H\(_2\) annealed samples of HWO resulted in \(WO_3/WO_{2.63}\) (higher \(WO_{2.63}/WO_3\) percentage for \(H_2\) annealing) and exhibited slightly worse kinetics than HWO, so further experiments were only done on HWO. The improved activity of HWO towards \(V^{2+}/V^{3+}\) was attributed to four factors: (1) hydrated structure providing O-H active sites, (2) reduced form of the oxide providing oxygen vacancies, which would also act as active sites, (3) enhancing the conductivity of the electrode relative to \(WO_3\), and (4) W-OH functional groups also acting as active sites and HER inhibitors. The reduced form and the O-H and W-O functional groups were evinced by XRD, XPS, and FTIR analysis.

To further investigate and optimize the kinetics of both redox reactions, different HWO: \(C_{76}\) ratios (2 mg cm\(^{-2}\) loading) were used in Section 5.4. Whereas increasing the \(C_{76}\) content to HWO reduced the reaction reversibility of \(V^{2+}/V^{3+}\) and increased the HER, it enhanced the kinetics of the \(VO^{2+}/VO_2^+\) reaction. Interestingly, HWO-50% \(C_{76}\) was the optimized material as it decreased the charge transfer resistance and further inhibited chlorine evolution relative to \(C_{76}\) and TCC. This was ascribed to the synergistic effects between C=C sp\(^2\) hybridization, O-H, and W-OH functional
groups. The degradation rate upon repetitive cycling for HWO-50% C\textsubscript{76} was found to be 0.29 mV/cycle, compared to 0.33 mV/cycle and 0.49 mV/cycle for UCC and TCC, respectively, rendering it its high stability in the mixed acids electrolyte. As for HWO’s stability, a degradation rate of 0.2 mV/cycle was achieved compared to 2 mV/cycle for TCC. The presented results successfully identified high-performance electrode materials for both half-cell reactions with fast kinetics and high stability. This would enhance the vanadium electrolyte utilization, increase the output voltage and hence the energy efficiency of VRFBs, thereby decreasing their cost for more future commercialization.

6.2 Future Work

Suggestions for further research directions include:

1) Full cell measurements using the optimized electrode materials for each redox reaction, with UCC and TCC being the control experiments. In fact, the cell setup is currently being optimized for the VRFB application.

2) More carbon morphologies could be compared with C\textsubscript{76}, as well as different nanocomposites containing C\textsubscript{76}. Other fullerenes could also be compared with C\textsubscript{76}.

3) Other reduced metal oxides could be utilized, such as reduced CeO\textsubscript{2}, especially for the negative electrode.

4) Tungsten-based oxides doped with other metal oxides that are known for HER inhibition should be tested.

5) To gain more understanding of the kinetics of both half-cell reactions, the rotating disc electrode could be utilized.
Bibliography


47. Han, P. *et al.* Graphene oxide nanoplatelets as excellent electrochemical active materials for


