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New Conductive Support Materials for Fuel Cell Catalyst Layers
by
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Declaration

This thesis is submitted to the University of Warwick in support of my application for the degree of Doctor of Philosophy. It has been composed by myself and has not been submitted in any previous application for any degree.
Abstract

New mixed-metal manganese ruthenium oxides have been synthesised hydrothermally in aqueous acid at 200 °C. The resulting materials Mn_{1-x}Ru_xO_2 (x<0.6) show a rutile type structure with the $P4_2/mnm$ space group in which the manganese is reduced below the +4 oxidation state and the ruthenium is oxidised above +4. These materials were characterised by a range of diffraction, spectroscopic and other analytical techniques to confirm their structures, metal oxidation states, surface areas and powder conductivities. The materials have been shown to have some stability in aqueous sulfuric acid but are degraded under more harsh conditions.

Niobium, titanium and niobium titanium carbonitrides, Nb_{1-q}Ti_qC_{1-p}N_p (0≤q≤1, p<1), were made via a new low temperature synthesis using nitrogen gas flow from a guanidine carbonate precursor. The resulting materials offer higher surface areas than conventional synthesis techniques. These materials have been characterised using a range of diffraction, spectroscopic and other analytical techniques. Neutron diffraction allows the C:N ratio to be determined and analysis of total scattering shows that at higher temperatures of synthesis the amount of amorphous carbon contaminant is minimised. The materials have been shown to have good conductivity and surface areas making them good candidates as catalyst supports in proton exchange membrane fuel cells. The niobium and niobium titanium carbonitrides show good stability in sulfuric acid and have shown stability whilst under electrochemical potential in acid. Preliminary tests of iridium loaded niobium carbonitrides suggest that the materials provide useful electrochemical activities for practical applications.

The synthesis of various other materials has been explored for use as catalyst supports, including titanium niobium oxides, tantalum carbonitrides, tantalum titanium carbonitride, tantalum niobium carbonitride, iron carbide, vanadium carbonitrides, molybdenum carbonitrides and tungsten carbonitrides. These materials have all been synthesised via a new low temperature synthesis under nitrogen gas flow. They have been analysed by a range of techniques including X-ray diffraction and spectroscopy. Electrochemical testing of the conducting titanium niobium oxide (Ti_{0.89}Nb_{0.11}O_2) showed good stability under electrochemical potential whilst in acid.
Chapter 1 – Introduction

In a world of ever increasing energy consumption finding ways in which to produce electricity sustainably is becoming an increasing problem. The use of fossil fuels and their impact on the environment and increasing public awareness of this problem has led to research focusing on how to solve the world energy crisis. Renewable energy sources such as wind turbines, photovoltaics and fuel cells all have a role in increasing our renewable energy production. Table 1.1 shows a comparison of different electricity production techniques. Fuel cells show high efficiency and although they have high costs, they also have zero emissions, offer scalability and quick installation.\(^1\) This can help solve problems associated with the use of fossil fuels such as finite resources, air pollution, and greenhouse gas emissions leading to global warming.\(^2\)

\textit{Table 1.1: Comparison of different electricity generation systems reproduced from Kirubakaran et al.}\(^1\)

<table>
<thead>
<tr>
<th></th>
<th>Reciprocating engine: diesel</th>
<th>Turbine generator</th>
<th>Photovoltaics</th>
<th>Wind turbine</th>
<th>Fuel cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity range</td>
<td>500 kW – 5 MW</td>
<td>500 kW – 25 MW</td>
<td>1 kW – 1 MW</td>
<td>10 kW – 1 MW</td>
<td>2000 kW – 2 MW</td>
</tr>
<tr>
<td>Efficiency</td>
<td>35 %</td>
<td>29-42 %</td>
<td>6-19 %</td>
<td>25 %</td>
<td>40-60 %</td>
</tr>
<tr>
<td>Capital cost / $/kW</td>
<td>200-350</td>
<td>450-870</td>
<td>6600</td>
<td>1000</td>
<td>1500-3000</td>
</tr>
</tbody>
</table>

There are 6 common types of fuel cells available for generation of electrical power: proton exchange membrane fuel cell (PEMFC), solid-oxide fuel cell (SOFC), alkaline fuel cell (AFC), direct methanol fuel cell (DMFC), phosphoric acid fuel cell (PAFC) and molten carbonate fuel cell (MCFC).\(^3\)\(\text{-}^6\) The power ratings and advantages of these fuel cells are summarised in Figure 1.1. PEMFCs have advantages for the use of grid applications such as high power rating and quick start up, but their drawback is the high cost platinum catalysts used to activate the hydrogen.\(^3\)

PEMFCs have the potential to revolutionise the energy market, by alleviating the problems associated with the powering of our society. Fuel cells use hydrogen as the source of fuel with oxygen as the oxidant and the only by product is water.\(^2\) PEMFCs
are being developed for uses such as electrical power sources in vehicles and portable applications.\textsuperscript{7–10} Their use is hindered by two main problems, production costs and poor durability/reliability.\textsuperscript{11}

![Diagram of fuel cell types and power ratings](image)

**Figure 1.1:** Fuel cell types used in grid connection according to power ratings and fuel cell types, reproduced from Inci et al.\textsuperscript{3}

### 1.1 Proton exchange membrane fuel cell (PEMFC)

PEMFCs consist of a cathode, an anode and a separating proton exchange membrane.\textsuperscript{2} Each electrode has a gas diffusion layer (GDL) and an electrocatalyst layer as shown in Figure 1.2, forming the membrane electrode assembly (MEA). At the anode hydrogen oxidation reaction (HOR) takes place, where hydrogen is delivered to the anode of the MEA and divides into protons and electrons. The protons are carried across the proton exchange membrane to the cathode, where the oxygen reduction reaction (ORR) takes place.\textsuperscript{12} This process can be summarised by the equations shown in Equation 1.1.

Anode (HOR): $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ \hspace{1cm} ($E^o = 0 \text{ V}_{RHE}$)

Cathode (ORR): $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2\text{O}$ \hspace{1cm} ($E^o = 1.229 \text{ V}_{RHE}$)

The overall reaction: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ \hspace{1cm} ($E^o_{\text{cell}} = 1.229 \text{ V}_{RHE}$)

*Equation 1.1*
Figure 1.2: Schematic diagram of proton exchange membrane fuel cell (PEMFC).

The proton exchange membrane is a defining characteristic of the PEMFC, the most commonly used membrane being Nafion™, a sulfonated tetrafluoroethylene based fluoropolymer-copolymer shown in Figure 1.3. The membrane needs to be able to conduct protons efficiently without conducting electrons, otherwise the fuel cell would short circuit.

Figure 1.3: Structure of Nafion™ a perfluorocarbonsulfonic acid.

1.2 Thermodynamic considerations

The PEMFC is an energy conversion device, therefore its conversion efficiency is important. When the fuel cell is operating in ideal conditions, at constant temperature
and pressure, the maximum electrical work \( W_{ele} \) that can be obtained is given by the Gibbs free energy \( \Delta G \) of the electrochemical reaction.\(^{13}\)

\[
W_{ele} = \Delta G = -nF E_{theor}
\]

\textit{Equation 1.2}

Where \( n \) is the number of electrons, \( F \) is the Faraday constant \( (96485 \text{ C mol}^{-1}) \) and \( E_{theor} \) is the reference potential (in volts).

The Gibbs free energy change can be calculated using Equation 1.3.

\[
\Delta G = \Delta H - T \Delta S
\]

\textit{Equation 1.3}

Where \( \Delta H \) is the enthalpy change and \( \Delta S \) is the entropy change.

The Gibbs free energy change of the reaction is given by Equation 1.4.

\[
\Delta G = \Delta G^0 - RT \ln \left( \frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}} \right)
\]

\textit{Equation 1.4}

Where \( \Delta G^0 \) is the Gibbs free energy change of reaction under standard conditions \( (1 \text{ atm, 298 K}) \), \( R \) is the gas constant \( (8.3145 \text{ J mol}^{-1}) \), \( a_{H_2} \) is the activity of hydrogen inside the stack, \( a_{O_2} \) is the activity of oxygen in the stack and \( a_{H_2O} \) the activity for water in the stack.

Equation 1.2, Equation 1.3 and Equation 1.4 can be combined to give the Nernst equation shown in Equation 1.5.

\[
E_{cell} = E^0 + \frac{RT}{nF} \ln \left( \frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}} \right)
\]

\textit{Equation 1.5}

Where \( E^0 \) is the standard cell potential \( (1 \text{ atm, 298 K}) \), \( n \) is number of electrons and \( E_{cell} \) is the potential at the temperature of interest.

This gives the ideal potential of 1.23 V with the liquid water product as shown in Equation 1.1 and 1.18 V for the gaseous water product.\(^{13,14}\) The maximum theoretical
efficiency of a fuel cell working at standard operating conditions is given by the ratio of the Gibbs free energy to the enthalpy change of the overall reaction. This gives a maximum theoretical efficiency of 83%. This is temperature dependent and decreases with increasing temperature of operation.\textsuperscript{14}

During the actual electrochemical process within fuel cells many losses including kinetic losses, ohmic losses and mass transport losses occur.\textsuperscript{13} Kinetic loss is caused by slow reactions at the electrode surfaces, in order to force the electrons to the electrodes through the chemical reaction, some potential is lost. Ohmic losses are caused by the resistance of the polymer membrane, the contact resistance between the membrane and electrodes and the resistance of the electrodes. Mass transport losses are caused by the mass diffusion from the flow channels to the active sites, which can cause concentration gradients during the reaction process.\textsuperscript{13,15} These losses lead to an actual efficiency of less than the theoretical efficiency.

During the fuel cell operation any collection of charges such as hydrogen ions in the electrolyte and electrons in the electrode will generate an electrical voltage. When this layer of charges forms it represents a store of electrical charges. This is known as the double layer charging effect. When the current changes the charge will change only during a certain time and the voltage will not immediately follow the current changes, unlike with ohmic voltage drop. This results in an instant voltage change after any current change due to internal resistance and then the voltage will slowly change to its final value.\textsuperscript{13}

### 1.3 PEMFC reactions

The oxygen reduction reaction (ORR) shown in Equation 1.6, has slow kinetics and the reaction is complicated. This is mainly due to many intermediates being formed, which depends on the electrolyte, the composition and the structure of the electrode materials.\textsuperscript{12,16}

\[
\text{Cathode (ORR): } \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2\text{O} \quad (E^\circ = 1.229 \text{ V}_{\text{RHE}})
\]

\textit{Equation 1.6}

The ORR process on Pt catalysts includes several individual reactions: one is the production of water through a four electron pathway, and another is production of hydrogen peroxide through a two electron pathway. Incomplete reduction of oxygen
to hydrogen peroxide leads to low energy conversion efficiency and produces a reactive intermediate, which can further convert to harmful free radical species.\textsuperscript{12} This is summarised in Figure 1.4. In fuel cells the four electron pathway is preferable due to no formation of the peroxide species. However, the reaction involves the O$_2$ being dissociated at the surface of the catalyst and then recombining with H$^+$ to form H$_2$O, which is a slow reaction.\textsuperscript{16}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{oxygen_reduction_mechanism.png}
\caption{Oxygen reduction mechanism on noble catalysts adapted from Yuan et al.\textsuperscript{12}}
\end{figure}

At the anode the HOR occurs, the hydrogen is stripped of its electrons and becomes protons and electrons, as shown in Equation 1.7.

Anode (HOR): \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \) \hspace{1cm} \( E^o = 0 \text{V}_{RHE} \) \hspace{1cm} \textit{Equation 1.7}

This occurs by a reaction mechanism involving several steps as shown in Equation 1.8 for a platinum catalyst.\textsuperscript{12}

\[
\begin{align*}
\text{H}_2 + 2\text{Pt} & \rightarrow 2\text{H}_{\text{ads}} - \text{Pt} \quad \text{(Tafel reaction)} \\
\text{H}_2 + \text{Pt} & \rightarrow \text{H}_{\text{ads}} - \text{Pt} + \text{H}^+ + \text{e}^- \quad \text{(Heyrovsky reaction)} \\
\text{H}_{\text{ads}} - \text{Pt} & \rightarrow \text{Pt} + \text{H}^+ + \text{e}^- \quad \text{(Volmer reaction)}
\end{align*}
\]

\textit{Equation 1.8}

Where H$_{\text{ads}}$ is the adsorbed hydrogen atom as an adatom.

The dissociative adsorption of a hydrogen molecule is followed by two separate one electron oxidations of the H$_{\text{ads}}$ in the Tafel-Volmer pathway. The Heyrovsky-Volmer
pathway consists of two one electron oxidations: the first one is held simultaneously with chemisorption and the second one is the oxidation of H$_{ads}$.$^{16,17}$

The HOR reaction most commonly uses platinum catalysts, which are expensive, and therefore research to reduce the Pt loading or finding new active and CO tolerant catalysts are important. More than 80 % of the hydrogen produced for fuel cell use has been produced from partial oxidation or steam reforming of hydrocarbons. This can lead to the hydrogen fuel containing traces of CO and CO$_2$. CO can strongly adsorb onto the Pt active sites and greatly decreases the activity of the Pt anode in fuel cells.$^{16}$

CO$_2$ can have significant poisoning effects on the fuel cell performance.$^{18-20}$ This CO$_2$ poisoning effect is due to the in-situ production of CO from CO$_2$ on the platinum surface through either the reverse water-gas shift reaction or the electrochemical reduction of CO$_2$, as shown in Equation 1.9. The adsorption of produced CO on the active platinum sites could block the reaction sites for hydrogen oxidation causing a performance drop.$^{20}$

\[
\begin{align*}
CO_2 + 2Pt - H_{ads} &\rightarrow Pt - CO_{ads} + H_2O + Pt \quad \text{(reverse water-gas shift reaction)} \\
2Pt + CO_2 + H^+ + e^- &\rightarrow Pt - CO_{ads} + Pt - OH_{ads} \quad \text{(electrochemical reduction)}
\end{align*}
\]

Equation 1.9

Two approaches are known to oxidise the CO molecule on the Pt electrode: apply a high potential or modify the structure and the composition of the Pt in order to oxidise the CO at very low potential.$^{16}$

1.4 PEMFC MEA degradation

To reduce the costs of using expensive platinum group metal catalysts the loading must be decreased while maintaining or improving the performance of the MEA.$^{21}$ For the durability of the PEMFCs to be improved problems such as instability of alloyed catalysts, Pt sintering, Pt dissolution, carbon support corrosion and membrane degradation need to be overcome.$^7$

In the case of carbon supported catalysts carbon oxidation reactions (COR) can occur as shown in Equation 1.10.
C + 2H₂O → CO₂ + 4H⁺ + 4e⁻ \hspace{1cm} (E^o = 0.207 \text{ } V_{RHE})

C + H₂O → CO + 2H⁺ + 2e⁻ \hspace{1cm} (E^o = 0.518 \text{ } V_{RHE})

Equation 1.10

This leads to the formation of either carbon monoxide or carbon dioxide.\textsuperscript{22-24} Under the normal PEMFC operating conditions carbon is quite stable due to the corrosion/oxidation of the carbon kinetics being slow. However, upon fuel starvation or gas switching conditions during the start-up and shutdown protocols, the cathode potential can exceed 1.2 \text{ } V_{RHE}. This is caused by voltage reversal caused by a sudden change in fuel demand, pressured drop variations between cells and poor water management.

When the anode is starved of hydrogen, it requires an additional source of electrons and protons. This causes its voltage to increase relative to the cathode due to charging, until the cell voltage reverses and the anode voltage becomes sufficiently large enough to drive the oxygen evolution reaction (OER) and carbon oxidation.\textsuperscript{25} Although the carbon oxidation is thermodynamically Favoured at low potential, the kinetics are slow and therefore potentials greater than 1 V are required. The OER is favoured when the potential reached 1.23V or higher. It becomes the major reaction at the lower potential during cell reversal. However, after a short time the OER deactivates and carbon corrosion proceeds, which drives the anode potential even higher.\textsuperscript{25}

At above 1.2 \text{ } V_{RHE} carbon oxidises at reaction rates high enough to cause significant structural degradation.\textsuperscript{22,26} The cell voltage reversal can lead to significant heat generation, which can create pin holes in the membrane causing the MEA to become electrically shorted.\textsuperscript{25} The carbon lost reduces the effective platinum surface area and weakens the catalyst layer. This reduces the number of active sites and can cause catalyst agglomeration.\textsuperscript{27} If enough CO and CO₂ are lost the catalyst layer collapses leaving only Nafion™ ionomer and unsupported platinum.\textsuperscript{22} As mentioned previously, CO poisons the platinum catalyst.\textsuperscript{24} This is because CO can strongly adsorb on to the Pt catalyst and blocks catalytically active area.\textsuperscript{12}

Cell failure can only be prevented by either stopping or delaying the rise in anode cell voltage by system control methods, such as voltage and gas exhaust monitoring or
flushing of the anode compartment to remove excess water. An alternative method is to catalyse the OER so it occurs preferentially instead of COR reactions during start and shutdown procedures. This removes the water content from the gas flows and therefore prevents or restricts COR reactions from occurring. These reactions are summarised in Figure 1.5. Catalysts which have good OER activity and have been considered for this purpose include IrO$_2$, RuO$_2$, and IrRu$_4$, but these materials are expensive. These catalysts can be added to the Pt catalysts as a cocatalyst or if the HOR activity is high enough they could be used instead of Pt, or the support could be made as a OER active support. In work by You et al. IrRu$_4$ was tested as a bifunctional catalyst for both HOR and OER reactions at the anode, as shown in Figure 1.6.

![Chemical equations and diagrams](image)

**Figure 1.5:** Carbon corrosion diagram of a PEMFC adapted from You et al. This shows the conditions within the PEMFC under normal operation, startup/shutdown and in cell reversal.

9
Figure 1.6: Carbon corrosion diagram of a PEMFC adapted from You et al.\textsuperscript{33} This shows the conditions within the PEMFC under normal operation, startup/shutdown and in cell reversal with an anode catalyst of IrRu\textsubscript{4} with both OER and HOR activity.\textsuperscript{33}

The catalyst support plays a critical role in the cell performance and durability, as it provides the stable loading sites for the catalytic nanoparticles, as well as providing pathways for both electron and mass transfer by forming porous channels.\textsuperscript{27} Electrocatalysts of PEMFCs often undergo degradation which includes dissolution, agglomeration and detachment of catalytic nanoparticles as shown in Figure 1.7.\textsuperscript{27,36} Corrosion of the catalyst supports accelerates the electrocatalyst degradation by damaging the loading sites and weakening the interaction between the support and nanoparticles.\textsuperscript{27}
The support materials need to give a high dispersion and a narrow distribution of the nanoparticle catalyst, to provide a conductive layer to coat electrodes, and support the active catalyst materials. A high surface area is necessary to improve the dispersion. A conductivity of at least 0.1 S cm$^{-1}$ is required for catalyst supports. Catalyst supports also need to be stable under the conditions found in PEMFCs, where aqueous acid electrolytes are used at temperatures of 60-100 °C. As mentioned previously, carbon supports (e.g. Vulcan XC-72 carbon black or Ketjen) undergo corrosion under these intense conditions, particularly on the cathode side where the ORR takes place. The carbon support can also be oxidised by fuel starvation of the hydrogen, which can lead to loss of activity of the MEA, as shown previously in Figure 1.5. Some of the different degradation processes of PEMFCs are shown in Figure 1.8.
1.5 Materials for catalyst supports

Carbon is the most commonly used support in PEMFCs, due to its high electrical conductivity, high surface area and high chemical and electrochemical stability. Carbon supports are also cheap and readily available and exist in many forms. However, as mentioned previously they undergo corrosion under the stop and start protocols of the PEMFC. A dramatic decrease in the thickness of the cathode catalyst layer was observed during accelerated degradation tests (ADT) of the Pt/Vulcan XC-72 carbon black. An ADT by the U.S. Drive Partnership involves holding the electrode at 1.2 V for 400 hrs.

Due to the poor corrosion resistance of Vulcan XC-72 carbon black, other carbon based materials have been investigated for the use as catalyst supports including carbon nanotubes, graphene, graphitised carbon, porous carbon, carbon nanocomposites and nitrogen doped carbon materials.
Highly graphitised carbon materials show an improvement on stability in comparison to carbon black, however these materials often have lower surface area meaning fewer nucleation sites of metal nanoparticle deposition. Work by Tamiki et al. found that the degree of graphitisation of the carbon used corresponds with a tolerance to carbon corrosion. In order to improve the activity or number of active sites, functionalisation of the surfaces can be used to produce functional groups and defects. This can include nitrogen doping, which can also improve the stability.

Previously various metal oxides have been studied as catalyst supports including indium tin oxide, TiO$_x$, WO$_x$, IrO$_2$, SnO$_2$ and RuO$_2$. These metal oxides have shown promising effects on catalytic activity and durability of the PEM fuel cell catalysts. However, in general, they have low surface area, low conductivity and can be unstable in acid. Ir and Ru oxides are currently the only known active and relatively acid stable oxygen evolution catalysts, but costs and abundance make them impractical for wide scale applications.

Manganese oxides have previously been studied for use as oxygen evolution catalysts, and have been shown to have stability in highly acidic electrolytes. Manganese oxides have also been shown to be active for ORR in alkaline conditions, where Mn$^{3+}$ was found to have a critical part in the ORR and incorporation of Mn$^{4+}$ improved charge transfer to adsorbed oxygen and promoted the catalysis. Chan et al. found that activity of MnO$_2$ was enhanced by the presence of Mn$^{3+}$. Electrodeposited manganese oxide films have already been used to catalyse OER in acidic conditions. Huynh et al. proposed that δ – MnO$_2$ can be “activated” by potential cycling protocols, producing a current density 2 orders of magnitude higher than that of the original manganese oxide film.

Wen et al. claims to have made mixed metal Mn$_{1-x}$Ru$_x$O$_y$ as a potential electrode material, and shows that ruthenium substitution improves the electrochemical properties of the material. Browne et al. suggests a high activity for OER of manganese ruthenium oxide electrocatalysts in alkaline media. However, these examples provided little evidence of a solid solution.

Metal oxides can be formed using high temperature solid-solid reactions, where separate metal oxide precursors are mixed and then heated to temperatures often exceeding 1000 °C. The materials are subsequently reground to ensure homogeneity.
The high temperatures and pressures often used in these syntheses form highly crystalline materials with limited control of the crystal form, and only the most thermodynamically stable phases are formed. Therefore, soft chemical methods have been developed including hydrothermal or solvothermal synthesis. This consists of a mixture of solid and liquid reagents, which are heated in a sealed vessel close to or above the boiling point of the solvent. Materials such as perovskites, pyrochlores, ruthenium oxide materials and other transition metal oxides have been made via this method to help control the final product and its crystallinity.

Manganese oxides can be made by hydrothermal synthesis and this can help to tune the crystallite sizes and phases of manganese oxides formed. Hydrothermal synthesis can be used to control the precipitation through closed system heating and the formation of solid phase from the transformation of the supersaturated state to the saturated state of solution. This transformation includes processes such as nucleation, aggregation, coalescence and growth of particles. After nucleation the aggregation of particles takes place on the nucleation centres, and the coalescence of aggregated particles occurs through Ostwald ripening mechanism. This causes dissolution of the small crystallites to provide more solution species to add to the larger crystals. Therefore, the crystallinity of the product is expected to increase with reaction time. This, as well as changing the reaction conditions, such as temperature and pH, allows tunability of the crystallites formed by hydrothermal synthesis. Hydrothermal synthesis is used in this thesis to help manipulate the properties such as crystallite size and surface area of the manganese oxides and manganese ruthenium oxides formed in Chapter 3.

Huang et al. showed that mesoporous TiO$_2$ has promise as a catalyst support. Pt/TiO$_2$ showed similar activity to Pt/C and increased durability. This suggests that making metal oxides with high surface area can improve their activity for this application. However, it was found that although it demonstrated good performance in a half-cell test it failed to reach that performance in a MEA test. RuO$_2$ on TiO$_2$ has shown good stability in both half cell and MEA tests, showing excellent stability in comparison to Pt on carbon. One of the main issues with using TiO$_2$ as a support is its low conductivity, however this can be improved by generating oxygen vacancies in the TiO$_2$. Substoichiometric titanium oxide has shown stability up to 1.5 V, however synthesis requires high temperatures resulting in agglomeration and low surface
Another solution to the low conductivity is to substitute some of the titanium with a metal cation with a different d-electron count so to introduce electrons or holes for electronic conduction. Substitution of TiO$_2$ with 3 % niobium replacing Ti$_4^+$ resulted in materials with a million fold increase in conductivity. These materials have shown high conductivity (1.11 S cm$^{-1}$) and high electrochemical stability. Pt/Ti$_{1-x}$Nb$_x$O$_2$ showed nearly 10 fold higher ORR activity when compared to Pt/C. Fuel cell testing of Pt/Ti$_{1-x}$Nb$_x$O$_2$ based MEA showed only a small voltage loss after 3000 cycles, whereas Pt/C showed no activity after 1000 cycles. This is discussed further in Chapter 5.

Metal carbides have been suggested as an alternative to carbon catalyst supports. Group 4-6 transition metal carbides have been shown to be chemically stable and only degrade in concentrated acid or base. Metal carbides can form a range of stoichiometries including MC, MC$_{1-x}$, M$_2$C and M$_3$C. Liu et al. suggests that WC and Mo$_2$C show promise for use as catalyst supports in PEMFCs. TiC has superior corrosion resistance and has shown promise as a catalyst support in ORR, Pt/TiC shows activity of 6 times that of Pt/C. Regmi et al. tested nine different carbides including WC, TaC, HfC, Mo$_2$C, Nb$_4$C$_3$, ZrC, Cr$_3$C$_2$, V$_8$C$_7$ and TiC, and found all had improved ORR activities in comparison to glassy carbon. These transition metal carbides were shown to enhance the HER and ORR activities as a catalyst support as opposed to Pt/C.

Transition metal nitrides are thermodynamically more stable and more catalytically active than their parent metals. Transition metal nitrides are similar to their carbide counterparts and have similar compositions. Similar to carbides, the transition metal nitrides are known to have high chemical stability whilst under potential, and therefore should be considered for use as potential catalyst supports. It was found that titanium nitride nanoparticles can act as catalyst supports for PEMFCs and showed better activities than conventional platinised carbon electrocatalysts in acidic and alkaline media.

The synthesis of transition metal carbide and nitride materials are usually formed using high temperature synthesis with reactive gas flow, which can give them low surface area and make the synthesis to dangerous for large scale production. In this thesis lower temperature syntheses by using guanidine carbonate and ammonium metal...
oxalate to form transition metal carbide and nitrides are explored in Chapters 4-5. It was hoped that by using lower temperatures of synthesis and developing reactions under nitrogen gas flow, the materials would have an increased surface area and be less dangerous to produce on a mass scale.

1.6 Aims of this work and Organisation of the Thesis

The work presented herein is concerned with the synthesis and characterisation of new materials for use as catalyst supports for PEMFCs. These materials need to be conductive (>0.1 S cm⁻¹) and stable under the acidic conditions found within a fuel cell. The materials need have a high surface area to disperse the Pt catalyst on. It would be beneficial if the materials also had some OER activity in order to prevent reactions such as carbon corrosion. If the materials contain carbon then another OER catalyst such as IrO₂ would also need to be dispersed on the support, to prevent the corrosion of the carbon. Electrochemical tests will be used to test the effectiveness of the materials as supports, including their stability and activity for OER. Hydrothermal synthesis and lower temperature synthesis routes for forming transition metal carbides and nitrides are used in order to produce materials with a high surface area.

Chapter 2 discusses the techniques and characterisation used in this thesis. In Chapter 3 hydrothermal synthesis in acidic conditions was utilised to make oxide materials with high surface area and to attempt to make manganese oxide materials more conducting by introducing more conducting metals such as ruthenium. In Chapters 4 – 5 synthesis based on decomposition of solid precursors was utilised to make materials under nitrogen with high surface area by using a guanidine carbonate method. This enabled materials such as transition metal carbides, carbonitrides and nitrides to be made via a lower temperature method than conventional methods. Chapter 6 details the acid resilience and electrochemical properties of the materials made in Chapters 3 – 5. Each chapter will start with an introduction section that provides more background to the specific materials being studied. The final chapter, Chapter 7 gives conclusions of all of this work and possible future work.

1.7 References


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Chapter 2 – Experimental

2.1 Synthesis

2.1.1 Hydrothermal Synthesis

All hydrothermal synthesis was carried out using Teflon®-lined stainless steel autoclaves as shown in Figure 2.1. The internal volume was 23 ml. In order to prevent bursting due to pressurisation the fill of reaction mixture was limited to 50 % of the internal volume. Reaction mixtures were stirred in the Teflon® liners before sealing them inside the autoclave and placing them in a pre-heated fan oven at the desired temperature (between 100-240 °C). Once the required time was elapsed the autoclaves were removed from the oven and left to cool to room temperature before opening them. Products were then collected either by vacuum filtration or centrifugation dependent on particle size. The materials were subsequently washed with deionised water to remove any surface sulfuric acid or sulfate groups, then the materials were dried at 70 °C in a drying oven overnight.

Figure 2.1: Schematic of an autoclave.

2.1.2 Solid-State Synthesis

The solid-state synthesis was performed in a horizontal split tube furnace from Lenton Furnaces (CSC 12/90/300H 1200 °C) with an impervious aluminous porcelain work tube with an outer diameter of 100 mm. The setup is shown in Figure 2.2. The ceramic insulation plugs were used to create a more even temperature profile across the length
of the tube furnace. This enabled multiple reactions to take place in different ceramic crucibles / boats during the same reaction at the same temperature. Dry nitrogen was required from a gas cylinder at a pressure of 1 bar with a flow rate of 100 ml min\(^{-1}\), which was monitored by a flow meter before the tube furnace. The outflow of the tube was passed into an empty bubbler before going through a second bubbler containing oil, to ensure any leaks could easily be detected. The empty bubbler prevented any suck back of oil into the furnace. The final gas output was released into an extractor hood. The gas tight ends and any tubing were regularly checked for any leaks, particularly due to the air sensitive nature of the materials. The temperature control system (Lenton 3216P1) allowed for a program with 8 different ramp and dwell settings. This was used to set the furnace at 30 °C for 2 hours to degas the system with nitrogen gas, before heating at 10 °C min\(^{-1}\) to the required temperature and dwell time and then cooling the furnace to 30 °C. Once the furnace was cooled the gas tight seals were loosened before leaving the nitrogen flowing for 1 hour, then the nitrogen was turned off and the seals loosened further before waiting for another hour. The materials could then be removed from the furnace. Caution had to be taken with this step due to the pyrophoric nature of the materials.

![Figure 2.2: Schematic of the tube furnace set up.](image)

2.2 Characterisation

2.2.1 Introduction to crystallography

All crystalline materials have a regular distribution of atoms or ions in space. The simplest portion of the structure that can be repeated is defined as the unit cell. The basic unit cell has 3 lengths defined as \(a\), \(b\), and \(c\). The angle between \(a\) and \(b\) is \(\gamma\),
between \( b \) and \( c \) is \( \alpha \) and between \( a \) and \( c \) is \( \beta \). There are 7 different crystal systems summarised in Table 2.1.

**Table 2.1:** The crystal systems and allowed centring. *The primitive description of the rhombohedral lattice is normally given the symbol \( R \).*

<table>
<thead>
<tr>
<th>Unit cell dimensions</th>
<th>Crystal system</th>
<th>Allowed centring</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a = b = c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
<td>Cubic</td>
<td>( P, I, F )</td>
</tr>
<tr>
<td>( a = b \neq c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
<td>Tetragonal</td>
<td>( P, I )</td>
</tr>
<tr>
<td>( a \neq b \neq c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
<td>Orthorhombic</td>
<td>( P, C, I, F )</td>
</tr>
<tr>
<td>( a \neq b \neq c ) ( \alpha = \beta = 90^\circ \gamma \neq 90^\circ )</td>
<td>Monoclinic</td>
<td>( P, C )</td>
</tr>
<tr>
<td>( a \neq b \neq c ) ( \alpha \neq \beta \neq \gamma \neq 90^\circ )</td>
<td>Triclinic</td>
<td>( P )</td>
</tr>
<tr>
<td>( a = b \neq c ) ( \alpha = \beta = 90^\circ \gamma = 120^\circ )</td>
<td>Hexagonal</td>
<td>( P )</td>
</tr>
<tr>
<td>( a = b = c ) ( \alpha = \beta = \gamma \neq 90^\circ )</td>
<td>Trigonal/Rhombohedral</td>
<td>( P(R) )*</td>
</tr>
</tbody>
</table>

A lattice is defined as an array of equivalent points in one, two or three dimensions. The centring of a lattice can be primitive (\( P \)), body-centred (\( I \)), base-centred (\( C \)) or face-centred (\( F \)), as shown in Figure 2.3. The four lattice types can be combined with the seven different crystal classes to give fourteen unique possibilities, as summarised in Table 2.1.\(^1\)\(^2\) The lattice points form an array in three dimensions showing the translational symmetry of the structure.

![Figure 2.3: The four types of lattice centring.](image)

Planes within a structure are a useful way to locate atoms and electron density. These planes are labelled using Miller indices. The Miller indices are written \( (h,k,l) \), where \( h, k \) and \( l \) are integers. Each plane is a representative member of a parallel set of planes.
The perpendicular distance between the planes is denoted $d_{hkl}$ (d-spacing). The expressions for d-spacing for several different crystal systems are shown in Table 2.2.

Table 2.2: Expression for d-spacings for three different crystal systems.\(^1\)

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Expression for $d_{hkl}$ in terms of lattice parameters and Miller indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$</td>
</tr>
</tbody>
</table>

2.2.2 Powder X-ray Diffraction

In X-ray diffraction the reflection of two parallel rays of the same wavelength by two adjacent planes of a lattice are considered in Figure 2.4. One ray strikes a point on the upper plane and the other ray must travel further, distance AB before striking the second plane. The reflected rays will differ in path length by a distance of BC. The net path length is shown in Equation 2.1.

$$AB + BC = 2d \sin \theta$$

*Equation 2.1*

Where $\theta$ is the incident angle.

For many glancing angles the path length difference is not an integer of wavelength and the waves interfere destructively. However, when the pathlength difference is an integer number of wavelengths, $AB + BC = n\lambda$, the reflected waves are in phase and interfere constructively. A reflection should be observed when the glancing angle satisfies Bragg’s law shown in *Equation 2.2.*\(^3\)

$$n\lambda = 2d \sin \theta$$

*Equation 2.2*

Reflections with $n = 2, 3, \ldots$ correspond to path length difference of 2, 3, … wavelengths. Because all higher $n$ values have an equivalent $n = 1$ for another $hkl$, therefore $n$ is equal to 1.
Figure 2.4: Derivation of Bragg’s law.

The Bragg’s law is used to determine the spacing between the layers in the lattice. This is because the angle $\theta$ corresponding to a reflection has been determined, so $d$ can be calculated.

The scattering of X-rays is caused by oscillations, which an incoming electromagnetic wave generates in the electrons of the atoms. Therefore, heavier atoms with more electron density give rise to stronger scattering than lighter atoms.²

Information regarding crystallite size can be obtained by using the Scherrer equation, shown in Equation 2.3, where $\tau$ is crystallite size, $\kappa$ is the shape factor typically 0.9, $\theta$ is the Bragg angle and $\beta$ in radians is the Bragg broadening, which is the full width half maxima (FWHM) of the peak corrected for instrumental broadening.⁴

$$\tau = \frac{\kappa \lambda}{\beta \cos \theta}$$

Equation 2.3

Powder X-ray diffraction (XRD) data were collected on either a Siemens D5000 or a Bruker D8 Advance X-ray diffractometer which operates using a Cu Kα₁/₂ radiation source ($\lambda = 1.5418$ Å). Most samples were studied using short scans for 55 minutes from 5-70 ° or 5-90 ° 2θ, with a 0.02 ° step size. Aluminium sample holders were occasionally used and these led to peaks at 38.4, 44.6 and 65.2 °.
Further XRD data were collected for higher resolution using a Panalytical X’Pert Pro MPD, equipped with a monochromatic Cu Kα1 radiation (λ=1.54056 Å) and a PIXcel solid state detector.

For the refinement of the unit cell of a material from powder XRD, Pawley refinements were performed using TOPAS software implemented with jedit.5,6 The Pawley method involves a least squares analysis of a powder diffraction pattern, where the variables are peak position parameters, peak shape parameters and peak areas. This means no structural model is required. Rietveld refinements also include parameters that determine the peak areas, including atomic coordinates, anisotropic displacement parameters, and absorption and extinction parameters, meaning Rietveld refinement requires a structural model. Pawley refinements only require a space group and unit cell.7

2.2.3 Powder Neutron Diffraction

Neutrons can be generated in a nuclear reactor and are slowed to thermal velocities that have wavelengths similar to those of X-rays. Nuclear reactors are “continuous white light” neutron sources, so they generate all wavelengths at all times continuously and thus need monochromators in order to be a useful well defined probe. Spallation source facilities such as ISIS Neutron and Muon source are a different sort of neutron generation, no nuclear reactor involved, neutrons are produced in short bursts as focused bunches of protons are made to hit the target periodically. The finite timing of neutron generation allows you to separate the neutron ‘wavelengths’ by time of flight (TOF) by knowing when they were generated, when they were detected and the path length.8

Neutron diffraction differs from XRD in two main aspects. The scattering of neutrons is a nuclear phenomenon, where neutrons pass through the electrons of atoms and interact with the nuclei. The intensity that neutrons are scattered is therefore independent of the number of electrons and neighbouring elements in the Periodic Table may scatter neutrons with largely different intensities.2 Neutrons have mass but effectively no charge which is why they have very weak interactions with electromagnetic fields such as electron clouds. This can be seen in Figure 2.5, where coherent scattering length differs widely and does not depend on atomic number.
Secondly, neutrons possess a magnetic moment due to their spin and this can couple to the magnetic fields of atoms or ions in a crystal, and modify the diffraction pattern.\(^2\)

Another difference is that the form factor of X-rays originates from the size of the electron cloud around the nucleus, whereas in neutron diffraction the neutron wave is of a similar size to the nucleus. This means that the drop off in intensity at low d-spacing and high angles seen in XRD does not affect neutron diffraction.

![Figure 2.5: Coherent scattering lengths for neutron diffraction.\(^9,10\)](image)

The difference in the coherent scattering length between carbon (6.6460 fm) and nitrogen (9.36 fm) makes this technique particularly useful in the analysis of carbonitride materials, as will be seen in Chapter 4.

TOF neutron diffraction measurements were recorded using intense pulses of neutrons produced by a spallation source, at ISIS Neutron and Muon Source in the UK. As the neutrons travel away from the target they are separated by wavelength due to their different velocities. The neutrons diffracted off the sample hit the detector and TOF data is recorded. The time of flight is related to the Bragg equation and the de Broglie equation by Equation 2.4, where \(\lambda\) is wavelength, \(d\) is the interplanar separation, \(h\) is Plank constant, \(\theta\) is the angle of diffraction, \(v\) is the velocity of the neutron, \(t\) is the time taken and \(L\) is the distance the neutron travels from the sample to the detector.
\[
\lambda = 2d \sin \theta \\
\lambda = \frac{h}{mv} \left( = \frac{ht}{mL} \right) \\
t = \left( \frac{2mLd}{h} \right) \sin \theta
\]

Equation 2.4

This gives the theoretical time of flight and is referred to as parameter DIFC in GSAS, which can be refined for the different banks apart from the highest resolution bank, in a multiple bank refinement. The neutron absorption cross-section is wavelength dependent, therefore short wavelength neutrons are absorbed less than longer wavelength neutrons. Therefore, the total flight path will vary with neutron wavelength. This means that the observed time of flight reflections may be different from the expected time of flight. A correction for this of parameter DIFA in GSAS, is used and refined. A zero parameter, which is an instrument dependent parameter and accounts for differences between various timing signals in the accelerator and the instrument acquisition time and should not be refined.

The real time of flight is a function of these three parameters shown in Equation 2.5, where time of flight \(t\) is related to \(d\) – spacing \(d\) of a reflection.

\[
t = DIFC \ d + DIFA \ d^2 + ZERO
\]

Equation 2.5

All powder neutron diffraction data were collected on the Polaris instrument at ISIS Neutron and Muon Source, UK. The samples were loaded into vanadium cans of 6 or 8 mm diameter, which are essentially invisible to neutrons due to its very low scattering cross section, 0.0184 barns. These cans were then placed inside a chamber which was then evacuated. The vacuum vessel has 6 detector banks, which collect data at different angles as detailed in Table 2.3.
Table 2.3: Polaris detector banks angle range.

<table>
<thead>
<tr>
<th>Detector Bank</th>
<th>2θ range / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>very low angle</td>
<td>6 – 14</td>
</tr>
<tr>
<td>low angles</td>
<td>19 – 34</td>
</tr>
<tr>
<td></td>
<td>40 – 67</td>
</tr>
<tr>
<td>90 degrees</td>
<td>75 – 113</td>
</tr>
<tr>
<td>back- scattering</td>
<td>135 – 143</td>
</tr>
<tr>
<td></td>
<td>146 – 168</td>
</tr>
</tbody>
</table>

Rietveld refinements were performed on the neutron diffraction data using the software GSAS,\(^1\) which was visualised using the EXPGUI interface.\(^2\)

2.2.4 Total scattering

Total scattering experiments take into account both the diffuse and Bragg scattering. Bragg scattering typically has intense sharp peaks, whereas diffuse scattering has features which are much broader and less intense. They are related to short and medium range order and can reveal deviations from the ideal crystal structure. Typically, diffuse scattering is treated as the background in Rietveld refinements. To get data with statistics high quality enough for total scattering analysis around 1200-1350 μA worth of data was collected per sample. Data were also collected for a vanadium rod, the empty sample container and the empty instrument. This was so the data could be normalised and the background removed. Typically, each of these data sets was recorded for 150 μA worth of data. The data from the vanadium rod were used to normalise the data. The empty instrument and empty container were recorded for the background subtraction. The corrected data were calculated using Equation 2.6.

\[
\text{Total scattering data} = \frac{\text{Sample} - \text{Empty container}}{\text{Vanadium rod} - \text{Empty instrument}}
\]

Equation 2.6

These datasets were recorded as accurately as possible to avoid introducing errors into the final data. It is also important to measure the mass and the height of the sample in its container accurately. This allows calculation of the number of atoms in the beam.
2.2.5 PDF analysis
The reciprocal space i(Q), the total scattering data, is converted by Fourier transform into the differential correlation function, D(r), which is a real space distribution of interatomic distances. This correlation function is also known as the pair distribution function (PDF). Information such as the nearest neighbour distances can be taken from these data. Further analysis can be done by taking a model crystal structure and calculating its PDF, which can then be compared to the data. This can be helpful at identifying unknown phases or peaks. The data can also be fitted in a similar way to Rietveld refinement, using small box modelling, where a model is taken and refined until the difference between the model and the data is minimised. This method is known as PDF analysis, and the software used in this thesis was PDFfit2/PDFgui.\textsuperscript{13}

The PDFs in this thesis were fitted by Aron Summer (university of Warwick) with the help of Helen Playford (ISIS Neutron and Muon Source).

2.2.6 X-ray Absorption Fine Structure Spectroscopy
X-ray absorption fine structure (XAFS) spectroscopy is based on the X-ray photoelectric effect, in which an X-ray photon incident on an atom within a sample is absorbed and liberates an electron from an inner atomic orbital. The “photoelectron” wave is scattered from the atoms around the X-ray absorbing atom as shown in Figure 2.6. This creates interferences between the outgoing and scattered parts on the photoelectron wavefunction. These quantum interference effects cause an energy dependent variation in the X-ray absorption probability, which is proportional to the X-ray absorption coefficient. These modulations can provide information about the structure, atomic number, structural disorder and thermal motions of neighbouring atoms.\textsuperscript{14}
Figure 2.6: Photoelectron scattering, where $R_j$ is interatomic distance.

XAFS is made up of two components the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS), which is shown in Figure 2.7. XANES requires large signal, low concentrations and has fast acquisitions times. It has the benefits of quick semi-quantitative interpretation. The pre-edge can give information about the coordination geometry, from electronic transitions to empty bound states. The edge position can give the oxidation state, from the ionisation threshold. EXAFS requires longer acquisition times than XANES. The EXAFS can be interpreted by crude interpretation of the Fourier transform. This is similar to atomic radial distribution function, but is not the same, and information such as distance, number and type of atoms, as well as structural disorder can be obtained from it. Further analysis of EXAFS can be done using Artemis software, which enables the structure to be fitted to different models.\textsuperscript{15}
Figure 2.7: An X-ray absorption spectrum showing the XANES and EXAFS regions.

XANES can be used to analyse the oxidation state of metals, this involves recording the edge position or $E_0$ of these materials and a range of reference materials with known oxidation states. $E_0$ refers to the zero energy for the photoelectron, the choice of $E_0$ is arbitrary, here the position was chosen as halfway up the edge, but other choices include the first peak in the first derivative or the largest peak in the first derivative. The reference materials edge positions are then used to plot a trendline of oxidation state against edge position, and the unknown materials oxidation state can then be calculated. This method does involve error which is dependent on the reference materials coordination number, bond distances, symmetry and their purity.

EXAFS fitting was performed using the Artemis software, after normalisation using Athena software. Normalisation of the data includes rescaling the data so that the edge jump is 1 and plotting a smooth background function through the oscillatory part of the spectrum, the background is then subtracted to give $\chi(E)$. This can be converted to $\chi(k)$ by using Equation 2.7.
\[ k = \frac{1}{\hbar} \sqrt{2m_e(E - E_0)} \]

Equation 2.7

Where \( k \) is the photoelectron wavenumber, \( \hbar \) is Plank’s constant, \( m_e \) is the mass of an electron, \( E \) is the energy of the incident photon and \( E_0 \) is the zero energy of the photoelectron.

The EXAFS equation shown in Equation 2.8, causes \( \chi(k) \) to drop off in amplitude with \( k \). Therefore, \( \chi(k) \) is often multiplied by \( k \), \( k^2 \) or \( k^3 \), this is known as \( k \) – weighting and results in a plot with uniform amplitude.\(^{16}\)

\[
\chi(k) = \sum_j S_0^2 N_j f_j(k) \frac{2R_j}{kR_j^2} e^{-2k^2\sigma_j^2} e^{-2k^2\sigma_j^2} \sin \left( 2kN_j + \delta_j(k) \right)
\]

Equation 2.8

Where \( k \) is the photoelectron wavenumber, \( N_j \) is the coordination number, \( R_j \) is the interatomic distance, \( \sigma_j^2 \) is the mean square variation of distance of the \( j \)th shell, \( f_j(k) \) is the effective scattering amplitude, \( \delta_j(k) \) is the effective scattering phase shift, \( \lambda(k) \) is the mean free path, \( S_0^2 \) is an amplitude reduction factor accounting for the relaxation of the absorbing atom due to the presence of the empty core level and multiple electron excitations.

A FEFF calculation is usually done from a crystal information file, this calculates the theoretical multiple scattering pathways. FEFF does this by solving the Dirac-Fock equation, which is a relativistic cousin of the Schrödinger equation as applied to atoms.\(^{14}\) The software however does not allow for partial occupancy, which can make it difficult to simulate mixed metal oxides where substitution occurs. A method in how to do this involves editing the crystal information file to have approximately the right number of atoms substituted and correcting with the amplitude reduction factor. Another method, used in this project, involves using two different crystal information files one with no substitution, and one with substitution of all metal sites other than the central or scattering metal. When fitted each amplitude is multiplied by the substitution level. This method works well but does not allow for pathways involving multiple metal scattering paths.
Other fitting parameters used in Artemis include $N$ which is the coordination number. This has to be a pure number and cannot be a maths expression or variable, typically this is the path degeneracy. However, another way to account to coordination numbers is to make $N = 1$, and then have $S_0^2$ (the amplitude reduction factor) = amp*CN. The amplitude reduction factor should be less than or equal to 1.1, with the ideal range being 0.7-1. $\Delta E_0$ is the adjustment to the $E_0$ used to evaluate the wavenumber of the theory. It is the parameter which aligns the energy grids of the data. $\Delta R$ is the adjustment of the half path length of the path. For a single scattering path, it is the adjustment of the interatomic distance. $\sigma^2$ is the mean square variation in path length and this encapsulates both static and thermal disorder, this must be a positive value in fits and preferably small.

Mn, Ru, Ti and Nb K-edge XANES and EXAFS was measured on B18 at Diamond Light Source, UK, in transmission mode from samples diluted with appropriate amounts of polyethylene powder and pressed into pellets of 12 mm diameter and of a thickness (~1 mm) to optimise edge jump and minimise self-absorption. Spectra were normalised using Athena and analysed using Artemis.\textsuperscript{15}

For \textit{in-situ} heating XANES, the materials were mixed with boron nitride to dilute the samples and were loaded into quartz capillaries. The capillaries were glued into a stand to make them airtight, before a thermocouple was inserted into the capillary to monitor temperature. The stand was placed into the furnace, and the gastight ends were attached, and the gas flow (air) was added. The XANES were recorded every 50 °C in triplicate, and the heating ramp rate was set to 10 °C min\textsuperscript{-1}. The materials were heated to 700 °C in order to reach the oxidation shown in the TGA shown in Chapter 4.

\subsection*{2.2.7 X-ray photoelectron spectroscopy}

The X-ray photoelectron spectroscopy (XPS) data were collected at the Warwick Photoemission Facility, University of Warwick, by Dr Marc Walker. The samples investigated in this study were attached to electrically-conductive carbon tape, mounted on to a sample bar and loaded in to a Kratos Axis Ultra DLD spectrometer which possesses a base pressure below $1 \times 10^{-10}$ mbar.

XPS measurements were performed in the main analysis chamber, with the sample being illuminated using a monochromated Al K$\alpha$ X-ray source. The measurements were conducted at room temperature and at a take-off angle of 90° with respect to the
surface parallel. The core level spectra were recorded using a pass energy of 20 eV (resolution approx. 0.4 eV), from an analysis area of 300 microns x 700 microns. The spectrometer work function and binding energy scale of the spectrometer were calibrated using the Fermi edge and 3d$^{5/2}$ peak recorded from a polycrystalline Ag sample prior to the commencement of the experiments. In order to prevent surface charging the surface was flooded with a beam of low energy electrons throughout the experiment and this necessitated recalibration of the binding energy scale. To achieve this, the main C-C/C-H component of the C 1s spectrum was referenced to 284.8 eV. The data were analysed in the CasaXPS package, using Shirley backgrounds and mixed Gaussian-Lorentzian (Voigt) lineshapes. For compositional analysis, the analyser transmission function has been determined using clean metallic foils to determine the detection efficiency across the full binding energy range.

XPS is a surface sensitive technique, which can give information such as elemental composition, chemical state and electronic state of the elements that exist in a material. The sampling depths, although expected to be different for each element, are between 5-10 nm.

2.2.8 Scanning Electron Microscopy (SEM)
Scanning electron microscopy (SEM) data were collected using a Zeiss SUPRA 55VP FEGSEM instrument with energy dispersive X-ray analysis (EDXA) in order to establish crystal size and morphology. EDXA was used to record the metal ratios or percent within the structures.

2.2.9 Transmission Electron Microscopy (TEM)
TEM and element mapping were recorded by Reza J. Kashtiban, the structure and morphology of the samples were analysed using a JEOL 2100 microscope equipped with LaB$_6$ operating at 200 kV.

2.2.10 Fourier Transform Infrared Spectroscopy
Infrared spectroscopy (IR) was used to compare samples to analyse their chemical bonding. The spectra were obtained using a PerkinElmer 100 FTIR spectrometer.

2.2.11 Thermal Analysis
The analysis of mass change in a sample upon heating is known as thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) can be used to observe heatflow changes during heating, this enables endothermic and exothermic events to
be observed. Endothermic events result in downwards feature and exothermic events result in an upwards feature or peak. The TGA-DSC can be run using different gas flows.

TGA with differential scanning calorimetry (DSC) were performed using a Mettler Toledo TGA/DSC 1-600 instrument heating in air to 900 °C at 10 °C min⁻¹.

On selected experiments TGA-DSC was used in combination with mass spectroscopy, where the output gas flow was run through a mass spectrometer to monitor the exhaust gases. This enabled a more accurate description of the TGA-DSC mass changes.

The TGA data was collected by James Crosland and Katie Everden. The TGA-MS were collected with the help of David Hammond.

2.2.12 Surface Area Measurement
Surface area measurements were carried out using a Micromeritics Tristar 3000 porosimeter. Brunauer-Emmet-Teller (BET) theory provides a model to understand the physical adsorption of gas molecules on the surface of a solid, and therefore gives information about the surface area of a sample. The sample was degassed first under nitrogen at 200 °C to remove surface water and impurities. The nitrogen of the adsorption isotherm was then recorded and the surface area measurement obtained from a seven point linear fit.

2.2.13 Powder Conductivity Measurement
Powder conductivity was measured using a custom built piece of equipment at Johnson Matthey, Sonning Common. Powder samples were added to a cylinder and compressed using a piston between two gold plated electrode plates (1 cm², one on the piston and one at the bottom of the cylinder) at 2 bar pressure under inert gas. The thickness of the resulting pellets was measured and the conductivity derived from the resistivity measured from the slope of change in voltage with applied current using an Autolab potentiostat.

2.2.14 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)
Measurements were taken using a PerkinElmer 5300DV ICP-OES. Standard solutions were made using reference solutions from Fischer Chemical. Reference solutions were made of 2000, 1000, 500, 250, 125, and 25 ppb ruthenium and for Nb, Ti, Mn solutions
were made of 4000, 2000, 1000, 500, 250 and 50 ppb. The calibration was only used if the correlation coefficient was greater then 0.999.

2.2.15 CHN analysis
This was performed by MEDAC Ltd by combustion analysis on an elemental analyser. The original analytical method is based on the complete and instantaneous oxidation of the sample by dynamic flash combustion which converts all organic and inorganic substances into combustion products. The resulting combustion gases pass through a reduction furnace and swept into the chromatographic column by the He carrier gas. Here they are separated and eluted as nitrogen, carbon dioxide, water and sulfur dioxide, and detected by a thermal conductivity detector which gives an output signal proportional to the concentration of the individual components of the mixture. The instrument is calibrated with the analysis of known standard compounds.

2.3 References
10 V. M. Nield and D. A. Keen, *Diffuse Neutron Scattering from Crystalline


Chapter 3 – Manganese Ruthenium Oxides

3.1 Introduction and Scope of the Chapter

Manganese oxides have recently been studied for use as oxygen evolution catalysts,\textsuperscript{1–4} and have been shown to have stability in highly acidic electrolytes.\textsuperscript{1} Manganese oxide has multiple forms mainly due to manganese being one of a few elements with more than five stable oxidation states. Also, for a given composition there may be more than one polymorph. Manganese oxide octahedral molecular sieves (OMS) have been studied intensively due to their controllable structures, porosities, and catalytic selectivity in contrast to their tetrahedral counterparts.\textsuperscript{5} OMS materials are natural semiconductors and already have applications in catalysis, ion exchange, radioactive hazard separation, sensors and batteries.\textsuperscript{5–7} However, the reported catalytic activity of manganese oxide polymorphs varies widely in the literature, which has been proposed by Huynh \textit{et al.} to be due to different preparation methods.\textsuperscript{3}

OMS materials, octahedral layered (OL) materials and amorphous manganese oxide materials, are often a mixed valent system of Mn\textsuperscript{4+} and Mn\textsuperscript{3+}.\textsuperscript{5,6,8} In these materials MnO\textsubscript{6} octahedral building blocks are connected by vertices and edges, generating porous channelled structures.\textsuperscript{6,8,9} Positive ions are present inside the tunnels or interlayers to compensate for the negative charge caused by the mixed valency of Mn\textsuperscript{4+} and Mn\textsuperscript{3+}. Ion exchange of these ions is important for the application of these materials in catalysis, batteries and ion traps.\textsuperscript{5} Several examples of these structures and their compositions are shown in Figure 3.1 and Table 3.1.
Figure 3.1: Schematic of several common porous manganese oxides with manganese represented in teal, oxygen in red and potassium in green, potassium ions are only shown in OL-1. 10–15
Table 3.1: Compositions and structures of common OMS materials\(^5\)

<table>
<thead>
<tr>
<th>Material Names</th>
<th>Structure</th>
<th>Composition</th>
<th>Mineral Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMS-1</td>
<td>3 × 3</td>
<td>(\text{Mg}^{2+}<em>{1.9-1.94}\text{Mn}^{2+}</em>{0.9-1.4}\text{Mn}^{4+}<em>{4.4-4.5}\text{O}</em>{12} \cdot n\text{H}_2\text{O})</td>
<td>Todorokite</td>
</tr>
<tr>
<td>OMS-2 α – MnO(_2)</td>
<td>2 × 2</td>
<td>(K_x\text{MnO}_2 \cdot n\text{H}_2\text{O}) ((x = 0.125-0.1875))(^16)</td>
<td>Cryptomelane</td>
</tr>
<tr>
<td>OMS-4 R – MnO(_2)</td>
<td>2 × 1</td>
<td>(\text{MnO}_2)</td>
<td>Ramsdellite</td>
</tr>
<tr>
<td>OMS-6</td>
<td>2 × 3</td>
<td>((\text{Na},\text{H}_2\text{O})_x\text{Mn}<em>3\text{O}</em>{10})</td>
<td>Romanechite</td>
</tr>
<tr>
<td>OMS-7 β – MnO(_2)</td>
<td>1 × 1 (Rutile structure)</td>
<td>(\text{MnO}_2)</td>
<td>Pyrolusite</td>
</tr>
<tr>
<td>OL-1 δ – MnO(_2)</td>
<td>Layered Structure</td>
<td>(\text{K}_{0.25-0.45}\text{MnO}_2 \cdot n\text{H}_2\text{O})</td>
<td>Birnessite</td>
</tr>
</tbody>
</table>

A variety of manganese oxides were evaluated by Robinson et al. as catalysts for water oxidation, and it was found that oxides containing more Mn\(^{3+}\) and Mn\(^{2+}\) than Mn\(^{4+}\) exhibited the highest oxygen evolution reaction (OER) activities.\(^{17}\) Robinson found that the most active materials of Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\), are more active because they possess Mn\(^{3+}\) (d\(^4\)) in edge sharing octahedral with longer Mn – O bonds than Mn\(^{4+}\)(d\(^3\)), due to the Jahn-Teller distortion.\(^{17}\) They hypothesised that MnO\(_2\) polymorphs with shorter and stronger Mn – O bonds are more stable, but this makes them less active for catalysis of O\(_2\) formation.\(^{17}\) Chan et al. found that activity of MnO\(_2\) oxygen evolution catalysts was enhanced by the introduction of Mn\(^{3+}\). Mn\(^{3+}\) is kinetically stabilised in tetrahedral sites and its presence strains the metal oxide lattice. This leads to a favourable disposition of oxide-based and metal-based energy levels that favours enhanced OER activity.\(^4\)

Electrodeposited manganese oxide films have already been used to catalyse OER in acidic conditions.\(^{1,2}\) Huynh et al. proposed that δ – MnO\(_2\) can be “activated” by potential cycling protocols, producing a current density 2 orders of magnitude higher than that of the original manganese oxide film. It was hypothesized that δ – MnO\(_2\) undergoes a phase change to α – Mn\(_3\)O\(_4\), which under subsequent anodic conditioning produces a disordered δ – MnO\(_2\) phase.\(^3\) These results suggest that the widely varying oxygen evolution activities across the different manganese oxides are due to the different preparation methods, which may introduce different oxide compositions, polymorphs and degrees of crystallinity to the system.\(^3\)
Among the various manganese oxides, only two have previously been made under hydrothermal conditions in an acid media, $\alpha - \text{MnO}_2$ (cryptomelane, OMS-2) and $\beta - \text{MnO}_2$ (pyrolusite, OMS-7).\(^6\),\(^18\) $\alpha - \text{MnO}_2$ has a composition of $K_x\text{MnO}_2$, where $x$ varies (e.g. $x = 0.125\text{-}0.1875$)\(^16\), and a pore size of about 4.6 Å,\(^18\) whereas $\beta - \text{MnO}_2$ has a composition of $\text{MnO}_2$ with the rutile structure.\(^19\) The structures of these are shown in Figure 3.2, $\alpha - \text{MnO}_2$ has a hollandite type structure and has pores which can accommodate different cations, such as $K^+,$\(^20\) $\text{Na}^+,$\(^20\) $\text{Ba}^{2+},$\(^20\) $\text{Pb}^{2+},$\(^20\) $\text{Cu}^{2+},$\(^20\) or $\text{Li}^+$.\(^20\)

DeGuzman et al. synthesized $\alpha - \text{MnO}_2$ by oxidising $\text{Mn}^{2+}$ with $\text{KMnO}_4$ and then heating hydrothermally or refluxing in an acidic media at 100 °C.\(^18\) It was later proposed by Qiu et al. that temperature could be used to adjust the polymorph formed, with temperatures of 100-120 °C forming $\alpha - \text{MnO}_2$ and temperatures higher than 120 °C forming $\beta - \text{MnO}_2$. They also found that varying ratios of $\text{Mn}^{2+}/\text{KMnO}_4$ could change the product as could varying the acid type and pH of the solution.\(^21\)

For this synthesis two methods of formation have been suggested:

$$2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$\(^{22}\)

*Equation 3.1*

$$\text{KMnO}_4 + [(1-x+2y)/2] \text{H}_2\text{O} \rightarrow K_x\text{MnO}_2\cdot y\text{H}_2\text{O} + (1-x) \text{KOH} + [(3+x)/4]\text{O}_2$$\(^{23}\)

*Equation 3.2*
Equation 3.1 is a redox reaction (comproportionation) and Equation 3.2 is a redox decomposition reaction. Based on these reactions Wang et al.\textsuperscript{22} proposed a mechanism of formation and phase transformation.

1. MnO\textsubscript{x} units form under hydrothermal conditions, then through condensation δ – MnO\textsubscript{2} forms.
2. The layered structure of δ – MnO\textsubscript{2} tends to curl with elevated temperature and pressure.
3. If enough K\textsuperscript{+} cations are present δ – MnO\textsubscript{2} will keep its structure. However, if a moderate amount is present it will collapse into the 2 × 2 α – MnO\textsubscript{2} structure. This can then further collapse into the 1 × 1 β – MnO\textsubscript{2} structure.\textsuperscript{22}

Wang et al. proposed a synthesis of α – MnO\textsubscript{2} using hydrothermal treatment of a system based on MnSO\textsubscript{4} – K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} – K\textsubscript{2}SO\textsubscript{4} – H\textsubscript{2}SO\textsubscript{4}, where the variation of acids, temperatures, pH and lengths of synthesis can be used to adjust the polymorph and morphology of the product.\textsuperscript{24}

The aim of the work described in this chapter was to investigate whether these hydrothermal reactions could be adapted to produce mixed metal manganese ruthenium oxides by adding KRuO\textsubscript{4} as a reagent. RuO\textsubscript{2} is a good OER catalyst but has no long term stability\textsuperscript{25} so mixing Mn with Ru may produce an active and stable material. Wen et al. claims to have made mixed metal Mn\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y} as a potential electrode material, and shows that ruthenium substitution improves the electrochemical properties of the material.\textsuperscript{26} Browne et al. suggests a high activity for OER of manganese ruthenium oxide electrocatalysts in alkaline media.\textsuperscript{27} However, these examples provided little evidence of a solid solution.

### 3.2 Synthesis

Syntheses of α – K\textsubscript{y}Mn\textsubscript{(1-x)}Ru\textsubscript{x}O\textsubscript{2} and β – Mn\textsubscript{(1-x)}Ru\textsubscript{x}O\textsubscript{2} were adapted from the hydrothermal method of DeGuzman et al. used for manganese oxides.\textsuperscript{18} Equation 3.3 shows the reaction conditions for the synthesis of α-Mn\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{2} and Equation 3.4 shows the reaction conditions for the synthesis of β-Mn\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{2}. The ratios of reagents were chosen to give the final formal oxidation state of +4 for the rutile structure.

\begin{equation}
(0.4-x)KMnO\textsubscript{4} + xKRuO\textsubscript{4} + 0.6\text{MnSO}_4\cdot\text{H}_2\text{O} \rightarrow \alpha-K_y\text{Mn}_{(1-x)}\text{Ru}_x\text{O}_2 \text{ (100°C synthesis)}
\end{equation}
(0.4-x)KMnO₄ + xKRuO₄ + 0.6MnSO₄·H₂O → β-Mn₁₋ₓRuₓO₂ \hspace{1cm} (200 \degree C synthesis)

Equation 3.4

A solution of 0.2945 g (0.001864 moles) KMnO₄ in 5 mL of water, was added to a solution of 0.44 g (0.0026 moles) MnSO₄·H₂O in 1.5 mL of water and 0.7112 g concentrated H₂SO₄ was added to give a final concentration of 1 mol dm⁻³ H₂SO₄. Varying amounts of KRuO₄ were substituted for the KMnO₄. These solutions were then heated in 23 mL Teflon-lined Parr autoclave to 100 °C for α-KₓMn₁₋ₓRuₓO₂ and to 200 °C β-Mn₁₋ₓRuₓO₂ for 24 hrs. The solid products were then recovered by centrifuge, washed with deionised water and dried at 80 °C in a drying oven.

3.3 Powder XRD and Pawley Fits

3.3.1 alpha

The powder XRD patterns of the α-KₓMn₁₋ₓRuₓO₂ (x≤0.2) materials prepared hydrothermally at 100 °C in 1 M H₂SO₄ are shown in Figure 3.3. The patterns show a broadening in the XRD patterns possibly indicating substitution of the ruthenium. However, this broadening may also indicate a decrease in crystal domain size. This substitution is shown by the Pawley XRD fits shown in Figure 3.3 and the fit parameters in Table 3.2, where an increase in the lattice parameters indicating the larger ion Ru⁴⁺ (0.67 Å) has been substituted for the smaller Mn²⁺ (0.60 Å). 28,29 However, it was found that a multi-phase Pawley fit including a rutile type phase (space group P4₂/mmm) of either β-MnO₂, RuO₂ or a mixture of β-Mn₁₋ₓRuₓO₂ and a hollandite phase (space group I4/m) α-KₓMn₁₋ₓRuₓO₂, fitted the data better. A broadening in the base of peak 29 ° indicative of the beta phase led to this discovery, as well as asymmetric peak shapes and the lower than expected intensity of the low angle alpha phase peaks. Table 3.2 summarizes the lattice parameters evaluated by the Pawley fits. In the alpha – only fits, it was found that α-KₓMnO₂ has a larger unit cell than both α-KₓMn₀.₀Ru₀.₁O₂ and α-KₓMn₀.₈Ru₀.₂O₂ as synthesized. Therefore, it seems unlikely that substitution has occurred due to ruthenium (+4) having a larger ionic radii, a larger unit cell would be expected. When a multiphase fit is used α-KₓMn₀.₀Ru₀.₁O₂ has smaller lattice parameters in comparison to α-KₓMn₀.₈Ru₀.₂O₂ for both the alpha and beta phase fits. Therefore, there is limited evidence of a solid solution, of the α-KₓMn₁₋ₓRuₓO₂ materials.
Figure 3.3: Pawley powder XRD fits of $\alpha$-$K_yMn_{1-x}Ru_xO_2$ samples, fitted to either alpha phase only or both alpha and beta phases.
Table 3.2: Pawley phase fit parameters from $\alpha\text{-Mn}_{1-x}\text{Ru}_x\text{O}_2$ samples fitted to either alpha phase only or both alpha and beta phases.

<table>
<thead>
<tr>
<th>Phases Fitted</th>
<th>Phases</th>
<th>Lattice Parameter $a$ / Å</th>
<th>Lattice Parameter $c$ / Å</th>
<th>Volume / Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha\text{-K MnO}_2$</td>
<td>alpha</td>
<td>9.838(5)</td>
<td>2.8604(11)</td>
<td>276.8(3)</td>
</tr>
<tr>
<td>$\alpha\text{-K}<em>{0.9}\text{Ru}</em>{0.1}\text{O}_2$</td>
<td>alpha</td>
<td>9.774(15)</td>
<td>2.856(2)</td>
<td>272.9(9)</td>
</tr>
<tr>
<td>$\alpha\text{-K MnO}<em>{0.9}\text{Ru}</em>{0.1}\text{O}_2$</td>
<td>beta</td>
<td>4.38(2)</td>
<td>2.945(12)</td>
<td>56.5(7)</td>
</tr>
<tr>
<td>$\alpha\text{-K MnO}<em>{0.9}\text{Ru}</em>{0.1}\text{O}_2$</td>
<td>alpha</td>
<td>9.8721(17)</td>
<td>2.855(4)</td>
<td>275(1)</td>
</tr>
<tr>
<td>$\alpha\text{-K MnO}<em>{0.8}\text{Ru}</em>{0.2}\text{O}_2$</td>
<td>alpha</td>
<td>9.888(8)</td>
<td>2.8684(11)</td>
<td>280.4(4)</td>
</tr>
<tr>
<td>$\alpha\text{-K MnO}<em>{0.8}\text{Ru}</em>{0.2}\text{O}_2$</td>
<td>beta</td>
<td>4.394(7)</td>
<td>2.958(8)</td>
<td>57.1(2)</td>
</tr>
<tr>
<td>Literature</td>
<td>$\beta\text{-MnO}_2^{28}$</td>
<td>4.40410(10)</td>
<td>2.87650(10)</td>
<td>55.793(4)</td>
</tr>
<tr>
<td></td>
<td>$\text{RuO}_2^{30}$</td>
<td>4.4919(8)</td>
<td>3.1066(7)</td>
<td>62.68(4)</td>
</tr>
<tr>
<td></td>
<td>$\alpha\text{-K}_{0.12}\text{MnO}_2^{10}$</td>
<td>9.866(3)</td>
<td>2.8720(10)</td>
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<tr>
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<td>$\alpha\text{-MnO}_2\cdot 0.154\text{H}_2\text{O}$</td>
<td>9.81359(10)</td>
<td>2.85077(2)</td>
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</tr>
</tbody>
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3.3.2 beta

The Pawley powder XRD refinements of the $\beta\text{-Mn}_{1-x}\text{Ru}_x\text{O}_2$ materials prepared hydrothermally at 200 °C in 1 M H₂SO₄ are shown in Figure 3.4. The peaks become broader with increasing substitution and show a shift to lower angles indicating an increase in lattice parameters. An increase in lattice parameters is indicative of substitution of the larger Ru⁺⁴ (0.67 Å) for Mn⁺⁴ (0.60 Å). The observed increase in broadness of the peaks possibly indicates a more disordered sample or may indicate smaller crystallite size. For the materials with less ruthenium substitution, two different peak FWHM are indicated by the broad base of the peaks and sharpness of the top of the peaks. It was found in SEM (shown later) that there were large particles amongst the smaller particles, confirming this suggestion. It was found by EDXA that when substituting in ruthenium, less manganese went into the structure than expected from the reagent ratios. The ratios quoted in Figure 3.4 are taken from EDXA.
Figure 3.4: Pawley refinements against powder XRD data ($\lambda = 1.54056 \text{ Å}$) of a range of $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ materials made hydrothermally at 200 °C, and $\text{RuO}_2$ made hydrothermally from $\text{KRUO}_4$ in 1 $M$ $\text{H}_2\text{SO}_4$ at 200 °C.
When the Pawley fitted unit cell parameters are plotted against percentage of ruthenium, as shown in Figure 3.5, an increase in lattice parameters $a$ and $c$ can be seen with increasing ruthenium content. The expected values for pure RuO$_2$ and pure β-MnO$_2$ were taken from Bolzan et al. and Boman.$^{28,30}$ It is found that the lattice parameter $a$ increased more than expected for the given ruthenium content and that lattice parameter $c$ increased less than expected. This could be due to the differences in the two pure end structures with β-MnO$_2$ having two long and four short bonds and RuO$_2$ having four long and two short bonds, as depicted in Figure 3.7. The $c/a$ ratio shown in Figure 3.6 shows that RuO$_2$ has a larger $c/a$ ratio than β-MnO$_2$. This is consistent with Bolzan et al. finding that a compressed arrangement is favoured for larger $c/a$ ratio.$^{29}$ It was also found that tetragonal distortion of the MO$_6$ octahedron is weakly dependent on the $c/a$ ratio of the rutile.$^{29}$ The volumes of the fitted unit cells increase in the trend expected by extrapolation of the pure end members, as shown in Figure 3.8. This suggests that the distortion is happening at a different ratio than expected but is averaged across the unit cell hence giving the expected volume change.

![Graph](image)

*Figure 3.5: Lattice parameters $a$ and $c$ calculated from the Pawley fits of β-Mn$_{1-x}$Ru$_x$O$_2$ materials in comparison with the values expected by extrapolation of the pure end members.$^{28,30}$ Error bars are fitted but are too small to see in most cases.*
Figure 3.6: Lattice parameters $c/a$ against ruthenium content of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials, showing how the tetragonal unit cell changes in comparison to the expected values from extrapolation of the pure end members. Error bars are fitted but are too small to see in most cases.

Figure 3.7: The unit cell structure of RuO$_2$ and $\beta$-MnO$_2$ with metals in black and oxygen in green, showing the longer bond lengths (blue) and the shorter bond lengths (red) of each structure.
Figure 3.8: Results from Pawley fits of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials unit cell volume in comparison to the value expected by extrapolation between the pure end members.$^{28,30}$

Crystallite size was calculated using the TOPAS crystallite size function using the Scherrer equation and is shown in Figure 3.9. The crystallite size decreases with increasing substitution of manganese with ruthenium. It is important to notice the large error bars for these calculations, but a trend is still visible. The error bars are particularly large for the lower ruthenium content materials, which are suspected of containing two different crystallite sizes.
Figure 3.9: Crystallite size of β-Mn₁₋ₓRuₓO₂ materials calculated using TOPAS crystallite size function with Scherrer’s equation.

### 3.4 SEM and TEM

SEM images of β-MnO₂ and the ruthenium substituted variants are shown in Figure 3.10. The images show morphology changes with an increase in ruthenium content. β-MnO₂ made in 0.36 M nitric acid contains shard particles with particle size of 1-8 μm in length. When acid type and concentration is changed to 1 M sulfuric acid the particle size is reduced and needles of ~1 μm in length form. When the structure is substituted with ruthenium the particles become smaller and form agglomerated clusters. The particle size matches the information found from powder XRD, showing that crystallite size decreases with increasing substitution, indicated by the broadening of Bragg peaks. Some larger particles were found in β-Mn₀.₈₇Ru₀.₁₃O₂, with the same elemental composition. These are thought to explain the peak shape found in the powder XRD.
Figure 3.10: SEM images of $\beta$-MnO$_2$ made in 0.36 M HNO$_3$, $\beta$-MnO$_2$ made in 1 M H$_2$SO$_4$, $\beta$-Mn$_{0.87}$Ru$_{0.13}$O$_2$, $\beta$-Mn$_{0.7}$Ru$_{0.3}$O$_2$, $\beta$-Mn$_{0.66}$Ru$_{0.34}$O$_2$ and $\beta$-Mn$_{0.6}$Ru$_{0.4}$O$_2$.

TEM imaging shown in Figure 3.11 and Figure 3.12 shows the different particle shapes across the $\beta$-Mn$_{0.925}$Ru$_{0.075}$O$_2$ and $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$ samples. $\beta$-Mn$_{0.925}$Ru$_{0.075}$O$_2$ shows needle like particles amongst much smaller particles. This confirms the powder XRD theory of two different crystallite sizes, affecting the Bragg peak broadness and shape. The more substituted material $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$ shows smaller particle sizes and a more well dispersed material. This matches the powder XRD where the peaks are broad suggesting smaller crystallite sizes.
Figure 3.11: TEM images of β-Mn$_{0.925}$Ru$_{0.075}$O$_2$.

Figure 3.12: TEM images of β-Mn$_{0.53}$Ru$_{0.47}$O$_2$.

3.5 ICP and EDXA

ICP and EDXA were used to calculate the relative amount of ruthenium and manganese in the samples. Figure 3.13 shows the differences between using EDXA and ICP for calculating the ruthenium content in β-Mn$_{1-x}$Ru$_x$O$_2$ compared with the
intended substitution level. It was found that EDXA and ICP agree with each other, and therefore EDXA could be used without needing to use ICP on each sample. The amount of ruthenium in the sample was always larger than expected. This can be explained by the manganese being more soluble in acid and therefore more manganese is left in solution. This was confirmed by ICP of the reaction solution.

![Graph](image_url)

*Figure 3.13: A comparison of the values from EDXA and ICP of the $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ materials with the expected amount from the synthesis reagent ratios.*

### 3.6 Thermal Stability

#### 3.6.1 Thermogravimetric analysis coupled with differential scanning calorimetry (TGA-DSC)

TGA-DSC was used to look at the stability of the different $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ materials, as seen in Figure 3.14. It was found that $\beta$-$\text{MnO}_2$ was stable until 550 °C, where it undergoes a phase change indicated by loss in mass and an endothermic feature in the heatflow. It undergoes a second phase change at 875 °C, where it loses mass and the heatflow also changes. This is because the $\beta$-$\text{MnO}_2$ reduces to $\text{Mn}_2\text{O}_3$ then to $\text{Mn}_3\text{O}_4$.\(^{31}\) The TGA indicates stability until 550-600 °C for the $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ samples. The second phase change only occurs in $\beta$-$\text{Mn}_{0.91}\text{Ru}_{0.09}\text{O}_2$ and $\beta$-$\text{Mn}_{0.69}\text{Ru}_{0.31}\text{O}_2$, this may be because otherwise the change is too small for the instrument to measure, or that
with increasing amounts of ruthenium the sample becomes more like RuO$_2$ and does not have this second phase change.

The initial mass loss in these samples until 500 °C, shown in Figure 3.14, indicates a loss of water from the sample. The more ruthenium substituted the larger the loss of water. This could be due to smaller particle size, hence more surface water. It may also indicate that the structure may change to incorporate water within the structure similar to some structures of hydrous ruthenium oxide observed by McKeown et al.\textsuperscript{32}

![Figure 3.14: TGA-DSC of a range of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ samples.](image-url)
3.6.2 Thermodiffractometry

Thermodiffractometry was used to assess the structure stability upon heating in air up to 900 °C. Figure 3.15 shows thermodiffractometry of β-MnO₂. The sample loses oxygen and is reduced to Mn₂O₃ at 550 °C and then reduces to Mn₃O₄ at 875 °C. This matches to the trends shown in the TGA-DSC, with an observed initial mass loss of 9.2% and a second mass loss of 3.1%.

The powder patterns of β-Mn₀.₈₇Ru₀.₁₃O₂ while heating are shown in Figure 3.16 and Figure 3.17. It shows that the structure is stable until 600 °C, where it changes into RuO₂ and Mn₂O₃, and the RuO₂ then becomes more crystalline shown by the sharpening of the peaks. From the TGA-DSC of samples β-Mn₀.₉₂Ru₀.₀₈O₂ and β-Mn₀.₆₉Ru₀.₃₁O₂, a further change was expected between 850-900 °C, for the Mn₂O₃ further reducing to Mn₃O₄, however no change is observed by XRD.

![Thermodiffractometry of β-MnO₂ heated from room temperature to 875 °C in air (in the initial XRD the sample holder peaks are greyed out). The pattern for Mn₂O₃ was simulated from Geller et al. and Mn₃O₄ was simulated from Bekheet et al.](image_url)
Figure 3.16: Thermodiffractometry of $\beta$-Mn$_{0.87}$Ru$_{0.13}$O$_2$ heated from room temperature to 900 °C in air. The pattern for Mn$_2$O$_3$ was simulated from Geller et al.$^{33}$ and the RuO$_2$ pattern was simulated from Boman et al.$^{30}$

Figure 3.17: Thermodiffractometry of $\beta$-Mn$_{0.87}$Ru$_{0.13}$O$_2$ heated from 400-650 °C in air compared to the $\beta$-Mn$_{0.87}$Ru$_{0.13}$O$_2$ at 30 °C, highlighting the change in phase occurring at 600 °C. The pattern for Mn$_2$O$_3$ was simulated from Geller et al.$^{33}$ and the RuO$_2$ pattern was simulated from Boman et al.$^{30}$
Samples with more ruthenium substituted have a broader XRD pattern to begin with and this makes it difficult to determine when the ruthenium oxide is formed. For example, in Figure 3.18 with sample $\beta$-Mn$_{0.82}$Ru$_{0.18}$O$_2$ the broadness of the peaks remains until 600 °C, which indicates stability until then. At 600 °C the peaks shift to the RuO$_2$ rutile phase and the manganese reduces to Mn$_2$O$_3$, as shown in Figure 3.19. Figure 3.20 shows the heating of the $\beta$-Mn$_{0.48}$Ru$_{0.52}$O$_2$ sample, with this higher substitution of ruthenium the ruthenium leaves the structure sooner at 300 °C, while Mn$_2$O$_3$ doesn’t form until 600 °C. There appears to be no visible shift in the sample peaks at 300 °C, this may indicate that the RuO$_2$ formed could come from an amorphous phase of hydrous ruthenium oxide, which crystallises at that temperature. In order to compare, a sample of RuO$_2$ was made via the same reaction conditions at 200 °C for 24 hours hydrothermally. This gives a broad powder XRD pattern as shown in Figure 3.21. On heating this sample increases in crystallinity at about 400 °C, and the crystallinity grows over time before forming a crystalline sample at about 850 °C. This is backed up by the TGA-DSC shown in Figure 3.14, where the sample continuously loses mass until 900 °C. This suggests a hydrated form of RuO$_2$ forms and therefore this was investigated further by TGA with mass spectroscopy.
Figure 3.18: Thermodiffactometry of $\beta$-$\text{Mn}_{0.81}\text{Ru}_{0.19}\text{O}_2$ heated from room temperature to 900 °C in air (in the initial XRD the sample holder peaks are greyed out). The pattern for $\text{Mn}_2\text{O}_3$ was simulated from Geller et al.\textsuperscript{33} and the $\text{RuO}_2$ pattern was simulated from Boman et al..\textsuperscript{30}

Figure 3.19: Thermodiffactometry of $\beta$-$\text{Mn}_{0.81}\text{Ru}_{0.19}\text{O}_2$ heated from 400-700 °C in air compared to the $\beta$-$\text{Mn}_{0.81}\text{Ru}_{0.19}\text{O}_2$ at 30 °C, highlighting the change in phase at 600 °C. The pattern for $\text{Mn}_2\text{O}_3$ was simulated from Geller et al.\textsuperscript{33} and the $\text{RuO}_2$ pattern was simulated from Boman et al..\textsuperscript{30}
Figure 3.20: Thermodiﬀractometry of $\beta$-Mn$_{0.48}$Ru$_{0.52}$O$_2$ heated from room temperature to 900 °C in air (in the initial XRD the sample holder peaks are greyed out). The pattern for Mn$_2$O$_3$ was simulated from Geller et al.$^{33}$ and the RuO$_2$ pattern was simulated from Boman et al..$^{30}$

Figure 3.21: Thermodiﬀractometry of RuO$_2$ made hydrothermally from KRuO$_4$ at 200 °C, heated from room temperature to 900 °C in air. RuO$_2$ pattern was simulated from Boman et al..$^{30}$
3.6.3 Thermogravimetric analysis with mass spectroscopy

Thermogravimetric analysis with mass spectroscopy (TGA-MS) was used to record mass changes and evolution of water mass (18), whilst heating to 120 °C and holding for 4 hours before heating to 1000 °C at 10 °C/min. Any mass loss heating to 120 °C and holding should be due to surface water. Any mass loss on further heating should show if any water of crystallisation exists. Figure 3.22 shows TGA-MS of hydrothermally made β-MnO₂. It shows an increase in water at 100 °C indicating the loss of surface water. The water evolution increases again when the sample is heated above 120 °C; this indicates water of crystallisation is leaving the structure. Other mass loses shown in the TGA indicate the manganese reducing to Mn₂O₃ and then further reduction to Mn₃O₄. Figure 3.23 shows the TGA-MS of β-Mn₀.₉₂Ru₀.₀₈O₂; this shows a similar trend to β-MnO₂ but shows more water of crystallisation coming off in the second phase of heating. The manganese shows similar reduction trends as the β-MnO₂ sample and the RuO₂ is expected to leave the structure at about 600 °C from the thermodiffactrometry of a similar material shown previously in Figure 3.16.

Figure 3.22: TGA-MS of hydrothermally made β-MnO₂, showing changes in mass 18 (H₂O) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.
Figure 3.23: TGA-MS of $\beta$-Mn$_{0.92}$Ru$_{0.08}$O$_2$, showing changes in mass 18 (H$_2$O) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.

The TGA-MS shown in Figure 3.24 shows $\beta$-Mn$_{0.8}$Ru$_{0.2}$O$_2$ water loss whilst being heated. The material loses more surface water in the first heating step to 120 °C than the previous sample and loses more mass overall after heating to 1000 °C suggesting more water of crystallisation loss as well. Figure 3.25 shows the TGA-MS for $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$, it again shows more water is lost overall and more water of crystallisation exists within the sample, this is shown by both the mass losses and the peaks in the mass spectrometry. A similar trend is seen in Figure 3.26 for $\beta$-Mn$_{0.41}$Ru$_{0.59}$O$_2$.  

\[ \text{Figure 3.23: TGA-MS of } \beta\text{-Mn}_{0.92}\text{Ru}_{0.08}\text{O}_2, \text{ showing changes in mass 18 (H}_2\text{O) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.} \]
Figure 3.24: TGA-MS of $\beta$-Mn$_{0.8}$Ru$_{0.2}$O$_2$, showing changes in mass 18 (H$_2$O) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.

Figure 3.25: TGA-MS of $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$, showing changes in mass 18 (H$_2$O) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.
Figure 3.26: TGA-MS of $\beta$-Mn$_{0.41}$Ru$_{0.59}$O$_2$, showing changes in mass 18 (H$_2$O) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.

Hydrothermally made RuO$_2$ TGA-MS is shown in Figure 3.27. It shows 3 main losses of mass, first after heating to 120 °C for surface water, second at 200 °C and third at 500 °C, both corresponding to more water loss as shown by the mass spectrometry. Figure 3.28 shows the TGA-MS for crystalline RuO$_2$, this material was made at high temperatures and therefore has little surface water, and the end mass is 99% at 1000 °C indicating only 1% of the material is water.
Figure 3.27: TGA-MS of hydrothermally made RuO$_2$, showing changes in mass 18 (H$_2$O) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.

Figure 3.28: TGA-MS of crystalline RuO$_2$, showing changes in mass 18 (H$_2$O) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.
The TGA-MS results for the $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials are summarised in Figure 3.29, giving the surface water, water of crystallisation and the total water content of these materials. The more ruthenium present in the samples the more water is present within the structure. This suggests that the materials are more complicated than simple rutile structures. Ruthenium oxides are known to have hydrous forms as is discussed by McKeown et al. and Donakowski et al.\textsuperscript{32,35} The crystalline RuO$_2$ shown for comparison in Figure 3.29, shows it is in the anhydrous form.

![Graph showing water content per mole of material](image)

*Figure 3.29: Calculated water content per mole of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ material, including the water of crystallisation and surface water, assuming all manganese reduces to Mn$_3$O$_4$ and ruthenium becomes RuO$_2$."

### 3.7 Mn K edge and Ru K edge XANES

Mn K edge and Ru K edge XANES were used to determine the oxidation states of the manganese and ruthenium in the manganese ruthenium oxides. Reference materials were measured with known oxidation states, and edge positions were determined and plotted against oxidation state. The linear trend from the reference materials was used to determine the average oxidation states of the metals of the manganese ruthenium oxides. Figure 3.30 shows the XANES of the Mn K edge reference materials and Figure 3.31 the XANES of the manganese ruthenium oxides. The edge positions were
taken at 0.5 $\chi_\mu(E)$, and these were plotted against average oxidation state in Figure 3.32. The linear trend from the reference materials was used to calculate the average manganese oxidation state of the manganese ruthenium oxides. The average manganese oxidation states shown in Figure 3.32 show a decrease in the average oxidation state of manganese with increasing ruthenium content of the manganese ruthenium oxides.

Figure 3.30: Mn K edge XANES data of the reference materials for manganese from B18 Diamond Light Source.
Figure 3.31: Mn K edge XANES data of $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ from B18 Diamond Light Source.

Figure 3.32: Calculated average manganese oxidation states for $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$, using a calibration curve from reference materials.
The XANES for the reference materials for ruthenium are shown in Figure 3.33 and for the manganese ruthenium oxides are shown in Figure 3.34. Here the edge was taken at $0.6 \chi_{\mu}(E)$, and the resulting values for the reference materials were plotted against the average oxidation state shown in Figure 3.35. A linear trendline was calculated and used to calculate the average oxidation states of the ruthenium in the manganese ruthenium oxides from the XANES shown in Figure 3.34. The average ruthenium oxidation states calculated in Figure 3.35 show an increase in oxidation state with increasing manganese content. This shows that by introducing ruthenium to the rutile manganese structure, the oxidation states are changing. The ruthenium increases in oxidation state while the manganese oxidation state decreases. The higher ruthenium content samples, $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$ and $\beta$-Mn$_{0.4}$Ru$_{0.6}$O$_2$, show a smaller increase in ruthenium oxidation state than the lower ruthenium content materials. This suggests a mixture of manganese ruthenium oxide and ruthenium oxide may have been formed or that Ru$_2$O$_3$ may have formed as has previously been suggested by Donakowski et al. at the surface. This could suggest that a Ru$_2$O$_3$ phase has formed a nanoshell surrounding the $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ core. A mixture of phases is also suggested by the thermodiffractometry shown in Figure 3.20, which shows a phase separation in the high ruthenium content sample at a lower temperature than that of the two lower substitution samples. This could suggest the shell oxidises at the lower temperature before the core breaks down at a higher temperature, which could explain the lack of shift in the main diffraction peaks of the $\beta$-Mn$_{0.48}$Ru$_{0.52}$O$_2$ phase.
Figure 3.33: Ru K edge XANES data of the reference materials for ruthenium from B18 Diamond Light Source.

Figure 3.34: Ru K edge XANES data of β-Mn$_{1-x}$Ru$_x$O$_2$ and reference RuO$_2$ from B18 Diamond Light Source.
Figure 3.35: Calculated average ruthenium oxidation states of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$, using a calibration curve from reference materials.

3.8 EXAFS

The Fourier transforms of the EXAFS of the Mn K edge of the manganese ruthenium oxides are shown in Figure 3.36. $\beta$-MnO$_2$, $\beta$-Mn$_{0.925}$Ru$_{0.075}$O$_2$ and $\beta$-Mn$_{0.8}$Ru$_{0.2}$O$_2$ all show similar features with the intensity decreasing with increasing amounts of ruthenium. However, the samples with more ruthenium substituted, $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$ and $\beta$-Mn$_{0.4}$Ru$_{0.6}$O$_2$, show slightly different peaks with an additional peak forming at 3.25 Å. The Fourier transforms of the Ru K edge EXAFS of the manganese ruthenium materials are shown in Figure 3.37. The $\beta$-Mn$_{0.925}$Ru$_{0.075}$O$_2$ and $\beta$-Mn$_{0.8}$Ru$_{0.2}$O$_2$ show similar features, while the $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$ and $\beta$-Mn$_{0.4}$Ru$_{0.6}$O$_2$ samples are similar to each other. The RuO$_2$ shows longer metal to metal distances than the other samples, due to the larger lattice size for RuO$_2$. The EXAFS of RuO$_2$ depends on the presence of hydrated phases, as has previously been described. This RuO$_2$ sample was made hydrothermally by heating K RUO$_4$ in 1M H$_2$SO$_4$ at 200 °C, so is a hydrated form of ruthenium oxide, as shown by the TGA-MS shown previously in Figure 3.29.
Figure 3.36: Fourier transform of Mn K edge EXAFS of $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ materials.

Figure 3.37: Fourier transform of Ru K edge EXAFS of $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ materials.
Fitting of EXAFS was carried out by normalising the data in Athena before fitting the k space in Artemis. The Mn and Ru K edge data were fitted simultaneously. The substitution of manganese for ruthenium was achieved by using the crystal structure of either manganese or ruthenium dioxide: this was used to create 4 Feff calculations of Mn-MnO₂, Mn-RuO₂, Ru-RuO₂ and Ru-MnO₂, where the first element is the element whose absorption is being studied and the rest of the Feff calculation is done assuming the rest of the structure is the second element. This was done due to Artemis and Feff calculations not being able to handle partial occupancy. The resulting pathways amplitude was multiplied by the occupancy for the element involved. The M – O pathways would usually give 2 M – O and 4 M – O distances depending on the Jahn-Teller distortion of the material. However, it was found in these materials that 6 M – O fitted better, due to the distances being too close to resolve.

Goodness of fit was determined by the R-factor, the smaller the number the better. The amplitude reduction factor should be less than or equal to 1.1, ideally between 0.7-1. The mean square variation in path length (σ²) encapsulates both static and thermal disorder, this should be positive and ideally small. E₀ should not be less than -10 eV or greater than 10 eV. The changes in path length were compared to the effective path length to determine if this change in path length was realistic for the incorporation of the amount of ruthenium thought to be within the sample.

Crystalline RuO₂ Ru K edge EXAFS is shown in Figure 3.38 and the resulting fit parameters are shown in Table 3.3. For the crystalline pure material, many pathways can be fitted to give a good fit. In order to compare the fits of the hydrothermally made materials, fewer parameters are fitted as there are more variables with the bonding due to the combination of manganese and ruthenium based pathways.
Figure 3.38: Crystalline RuO$_2$ EXAFS fitting in k-space and R-space, fitted to literature RuO$_2$.\textsuperscript{29}

Table 3.3: Fitting parameters for crystalline RuO$_2$ EXAFS data with R-factor=0.05736, $S_0^2=1.1(2)$ and $E_0=-4.7$ eV, where $R_{\text{eff}}$ is effective path length.

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</tr>
<tr>
<td>O1.2Ru1.5</td>
<td>16</td>
<td>0.005(3)</td>
<td>5.64350</td>
<td>5.63(3)</td>
</tr>
</tbody>
</table>
Hydrothermally made RuO$_2$ Ru K edge EXAFS data are shown in Figure 3.39. Three pathways are fitted: 6 Ru-O, 2 Ru-Ru and 8 Ru-Ru. These are summarised in Table 3.4, and show a good fit to the distances expected in RuO$_2$. Other pathways were ignored due to little contribution to the overall EXAFS data. However, this gives a larger R-factor compared to the crystalline RuO$_2$ due to using less parameters to fit the data.

![Hydrothermal RuO$_2$ EXAFS fitting in k space and R space, fitted to literature RuO$_2$.](image)

**Figure 3.39:** Hydrothermally made RuO$_2$ EXAFS fitting in k space and R space, fitted to literature RuO$_2$.

**Table 3.4:** Structural parameters fitted against the Ru K edge EXAFS of hydrothermal RuO$_2$, with R-factor=0.13086 $S_e^2=0.77(12)$ and $E_0=-3.9$ eV, where $R_{eff}$ is effective path length.

<table>
<thead>
<tr>
<th>Name</th>
<th>$N$</th>
<th>$\sigma^2$ / Å$^2$</th>
<th>$R_{eff}$ / Å</th>
<th>$R$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1.1</td>
<td>6</td>
<td>0.0045(12)</td>
<td>1.9713</td>
<td>1.971(10)</td>
</tr>
<tr>
<td>Ru1.1</td>
<td>2</td>
<td>0.0043(10)</td>
<td>3.1049</td>
<td>3.102(12)</td>
</tr>
<tr>
<td>Ru1.2</td>
<td>8</td>
<td>0.0058(8)</td>
<td>3.53850</td>
<td>3.548(10)</td>
</tr>
</tbody>
</table>

Hydrothermally made $\beta$-MnO$_2$ Mn K edge EXAFS data were fitted and are shown in Figure 3.40. Table 3.5 summarises the fitting parameters, similarly to RuO$_2$ three pathways are fitted and give a good fit.
Figure 3.40: Hydrothermally made $\beta$-MnO$_2$ Mn K edge EXAFS fitting in $k$ space and $R$ space, to literature $\beta$-MnO$_2$.\textsuperscript{28}

Table 3.5: Structural parameters fitted against the Mn K edge EXAFS of hydrothermal $\beta$-MnO$_2$, with R-factor=0.09786, $S_0^2=0.66(13)$ and $E_0=-6.0$ eV, where $R_{\text{eff}}$ is effective path length.

<table>
<thead>
<tr>
<th>Name</th>
<th>$N$</th>
<th>$\sigma^2 / \text{Å}^2$</th>
<th>$R_{\text{eff}} / \text{Å}$</th>
<th>$R / \text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1.1</td>
<td>6</td>
<td>0.0021(14)</td>
<td>1.88840</td>
<td>1.883(10)</td>
</tr>
<tr>
<td>Mn1.1</td>
<td>2</td>
<td>0.0018(16)</td>
<td>2.8765</td>
<td>2.880(16)</td>
</tr>
<tr>
<td>Mn1.2</td>
<td>8</td>
<td>0.0034(12)</td>
<td>3.4303</td>
<td>3.436(13)</td>
</tr>
</tbody>
</table>

For the mixed metal materials, both Mn K edge and Ru K edge were fitted simultaneously. This allows distances of single scattering pathways between Mn and Ru to equal the same, and therefore give a fit with fewer variables. Other methods were attempted but this was deemed to give the best fit.

$\beta$-Mn$_{0.41}$Ru$_{0.59}$O$_2$ EXAFS data from the Mn K edge and Ru K edge were fitted simultaneously to give the fits shown in Figure 3.41 and Figure 3.42. Three pathways were fitted as shown in Table 3.6. This gives a good fit.
Figure 3.41: $\beta$-$\text{Mn}_{0.41}\text{Ru}_{0.59}\text{O}_2$ Ru K edge EXAFS fitting in k space and R space, to modified literature RuO$_2$.$^{29}$

Figure 3.42: $\beta$-$\text{Mn}_{0.41}\text{Ru}_{0.59}\text{O}_2$ Mn K edge EXAFS fitting in k space and R space, to modified literature RuO$_2$.$^{29}$
Table 3.6: Structural parameters fitted against the Mn K edge and Ru K edge EXAFS of $\beta$-Mn$_{0.41}$Ru$_{0.59}$O$_2$ with an R-factor=0.07619, where $R_{\text{eff}}$ is effective path length.

<table>
<thead>
<tr>
<th>Name</th>
<th>$N$</th>
<th>$\sigma^2 / \text{Å}^2$</th>
<th>$R_{\text{eff}} / \text{Å}$</th>
<th>$R / \text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ru K edge</strong> ((S_0^2=0.82(8)) and (E_0=-1.48) eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-O</td>
<td>6</td>
<td>0.0046(8)</td>
<td>1.97130</td>
<td>1.972(7)</td>
</tr>
<tr>
<td>Ru-Ru</td>
<td>1.18</td>
<td>0.0049(12)</td>
<td>3.10490</td>
<td>3.067(16)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>0.82</td>
<td>0.0049(12)</td>
<td></td>
<td>2.99(3)</td>
</tr>
<tr>
<td>Ru-Ru</td>
<td>4.72</td>
<td>0.0062(11)</td>
<td>3.53850</td>
<td>3.535(8)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>3.28</td>
<td>0.0062(11)</td>
<td></td>
<td>3.512(17)</td>
</tr>
<tr>
<td><strong>Mn K edge</strong> ((S_0^2=0.62(18)) and (E_0=-4.73) eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-O</td>
<td>6</td>
<td>0.003(2)</td>
<td>(1.88840)</td>
<td>1.900(16)</td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>0.82</td>
<td>0.0049(12)</td>
<td>(2.87650)</td>
<td>2.94(8)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>1.18</td>
<td>0.0049(12)</td>
<td></td>
<td>2.99(3)</td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>3.28</td>
<td>0.0062(11)</td>
<td>(3.4303)</td>
<td>3.48(5)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>4.72</td>
<td>0.0062(11)</td>
<td></td>
<td>3.512(17)</td>
</tr>
</tbody>
</table>

$\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$ EXAFS Ru K edge and Mn K edge data were fitted and are shown in Figure 3.43 and Figure 3.44. This gives a good fit, and the fitted parameters are summarised in Table 3.7.
Figure 3.43: $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$ Ru K edge EXAFS fitting in k space and R space, to edited literature RuO$_2$.$^{29}$

Figure 3.44: $\beta$-Mn$_{0.53}$Ru$_{0.47}$O$_2$ Mn K edge EXAFS fitting in k space and R space, to edited literature RuO$_2$.$^{29}$
Table 3.7: Structural parameters fitted against the Mn K edge and Ru K edge EXAFS of $\beta$-$\text{Mn}_{0.53}\text{Ru}_{0.47}\text{O}_2$ with an $R$-factor=0.08564, where $R_{\text{eff}}$ is effective path length.

<table>
<thead>
<tr>
<th>Name</th>
<th>$N$</th>
<th>$\sigma^2 / \text{Å}^2$</th>
<th>$R_{\text{eff}} / \text{Å}$</th>
<th>$R / \text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru K edge ($S_0^2=0.78(9)$ and $E_0=-1.43$ eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-O</td>
<td>6</td>
<td>0.0048(9)</td>
<td>1.97130</td>
<td>1.979(8)</td>
</tr>
<tr>
<td>Ru-Ru</td>
<td>0.94</td>
<td>0.0052(11)</td>
<td>3.10490</td>
<td>3.06(2)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>1.06</td>
<td>0.0052(11)</td>
<td>2.983(19)</td>
<td></td>
</tr>
<tr>
<td>Ru-Ru</td>
<td>3.76</td>
<td>0.0066(12)</td>
<td>3.53850</td>
<td>3.529(13)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>4.24</td>
<td>0.0066(12)</td>
<td>3.511(11)</td>
<td></td>
</tr>
<tr>
<td>Mn K edge ($S_0^2=0.62(9)$ and $E_0=-7.08$ eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-O</td>
<td>6</td>
<td>0.0036(11)</td>
<td>(1.88840)</td>
<td>1.89591</td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>1.06</td>
<td>0.0052(11)</td>
<td>(2.87650)</td>
<td>2.90(3)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>0.94</td>
<td>0.0052(11)</td>
<td>2.983(19)</td>
<td></td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>4.24</td>
<td>0.0066(12)</td>
<td>(3.4303)</td>
<td>3.47(2)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>3.76</td>
<td>0.0066(12)</td>
<td>3.511(11)</td>
<td></td>
</tr>
</tbody>
</table>

The Ru K edge and Mn K edge EXAFS data for $\beta$-$\text{Mn}_{0.8}\text{Ru}_{0.2}\text{O}_2$ are shown in Figure 3.45 and Figure 3.46. The parameters give a good fit to the data shown in Table 3.8. The Ru K edge fits less well possibly due to little or no contribution from the first Ru-Ru pathway. This is also shown in Table 3.8 with the $R$ distance of 2.86(9) Å instead of the expected 3.10490 Å, it is also shorter than the expected Mn-Mn pathway of 2.87650 Å, therefore this is an unrealistic distance. This suggests that the ruthenium centre does not have ruthenium as its nearest metal neighbour due to the low ruthenium content of this sample.
Figure 3.45: $\beta$-Mn$_{0.8}$Ru$_{0.2}$O$_2$ Ru K edge EXAFS fitting in $k$ space and $R$ space, to edited literature $\beta$-MnO$_2$.$^{28}$

Figure 3.46: $\beta$-Mn$_{0.8}$Ru$_{0.2}$O$_2$ Mn K edge EXAFS fitting in $k$ space and $R$ space, to edited literature $\beta$-MnO$_2$.$^{28}$
Table 3.8: Structural parameters fitted against the Mn K edge and Ru K edge EXAFS of \(\beta\)-Mn\(_{0.8}\)Ru\(_{0.2}\)O\(_2\) with an R-factor=0.10094, where \(R_{\text{eff}}\) is effective path length.

<table>
<thead>
<tr>
<th>Name</th>
<th>(N)</th>
<th>(\sigma^2 / \text{Å}^2)</th>
<th>(R_{\text{eff}} / \text{Å})</th>
<th>(R / \text{Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru K edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-O</td>
<td>6</td>
<td>0.0025(8)</td>
<td>1.97130</td>
<td>1.954(6)</td>
</tr>
<tr>
<td>Ru-Ru</td>
<td>0.4</td>
<td>0.003(3)</td>
<td>3.10490</td>
<td>2.86(9)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>1.6</td>
<td>0.003(3)</td>
<td>2.926(15)</td>
<td></td>
</tr>
<tr>
<td>Ru-Ru</td>
<td>1.6</td>
<td>0.007(2)</td>
<td>3.53850</td>
<td>3.51(7)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>6.4</td>
<td>0.007(2)</td>
<td>3.481(12)</td>
<td></td>
</tr>
<tr>
<td>Mn K edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-O</td>
<td>6</td>
<td>0.003(2)</td>
<td>1.88840</td>
<td>1.89(2)</td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>1.6</td>
<td>0.003(3)</td>
<td>2.87650</td>
<td>2.89(4)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>0.4</td>
<td>0.003(3)</td>
<td>2.926(15)</td>
<td></td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>6.4</td>
<td>0.007(2)</td>
<td>3.4303</td>
<td>3.46(3)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>1.6</td>
<td>0.007(2)</td>
<td>3.481(12)</td>
<td></td>
</tr>
</tbody>
</table>

The Ru K edge and Mn K edge EXAFS data for \(\beta\)-Mn\(_{0.925}\)Ru\(_{0.075}\)O\(_2\) are shown in Figure 3.47 and Figure 3.48. The Mn data is fitted well and the resulting parameters are shown in Table 3.9. The Ru K edge fits less well, possibly due to little or no contribution from the first Ru – Ru pathway. This is also shown in Table 3.9 with the Ru – Ru pathway length of 2.48(9) Å instead of the expected 3.10490 Å. It is also shorter than the expected Mn – Mn pathway of 2.87650 Å, therefore this is an unrealistic distance. This suggests that at this low ruthenium content no ruthenium atoms are situated as next nearest metal sites.
Figure 3.47: $\beta\text{-Mn}_{0.925}\text{Ru}_{0.075}\text{O}_2$ Ru K edge EXAFS fitting in k space and R space, to edited literature $\beta\text{-MnO}_2$.\textsuperscript{28}

Figure 3.48: $\beta\text{-Mn}_{0.925}\text{Ru}_{0.075}\text{O}_2$ Mn K edge EXAFS fitting in k space and R space, to edited literature $\beta\text{-MnO}_2$.\textsuperscript{28}
Table 3.9: Structural parameters fitted against the Mn K edge and Ru K edge EXAFS of \(\beta\)-Mn\(_{0.925}\)Ru\(_{0.075}\)O\(_2\) with an R-factor=0.11774, where \(R_{\text{eff}}\) is effective path length.

<table>
<thead>
<tr>
<th>Name</th>
<th>(N)</th>
<th>(\sigma^2/\text{Å}^2)</th>
<th>(R_{\text{eff}}/\text{Å})</th>
<th>(R/\text{Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru K edge ((S_0^2=0.69) (10) and (E_0=-2.27) eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-O</td>
<td>6</td>
<td>0.0020(9)</td>
<td>(1.97130)</td>
<td>1.951(9)</td>
</tr>
<tr>
<td>Ru-Ru</td>
<td>0.15</td>
<td>0.0038(17)</td>
<td>(3.10490)</td>
<td>2.48(9)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>1.85</td>
<td>0.0038(17)</td>
<td></td>
<td>2.95(3)</td>
</tr>
<tr>
<td>Ru-Ru</td>
<td>0.6</td>
<td>0.0053(10)</td>
<td>(3.53850)</td>
<td>3.04(9)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>7.4</td>
<td>0.0053(10)</td>
<td></td>
<td>3.461(16)</td>
</tr>
<tr>
<td>Mn K edge ((S_0^2=0.78) (14) and (E_0=-6.21) eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-O</td>
<td>6</td>
<td>0.0034(16)</td>
<td>1.88840</td>
<td>1.88739</td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>1.85</td>
<td>0.0038(17)</td>
<td>2.87650</td>
<td>2.88(2)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>0.15</td>
<td>0.0038(17)</td>
<td></td>
<td>2.95(3)</td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>7.4</td>
<td>0.0053(10)</td>
<td>3.4303</td>
<td>3.438(17)</td>
</tr>
<tr>
<td>Mn-Ru</td>
<td>0.6</td>
<td>0.0053(10)</td>
<td></td>
<td>3.461(16)</td>
</tr>
</tbody>
</table>

The EXAFS data fitting of the M – O distance is summarised in Figure 3.49. It shows that the Ru – O and Mn – O distances increase with increasing ruthenium content of \(\beta\)-Mn\(_{1-x}\)Ru\(_x\)O\(_2\). This shows that the EXAFS matches the powder XRD data showing an increase in the unit cell parameters. The average M – O distance are shown in Figure 3.50. The as made end members were compared to the literature values and were found to be within the expected values.
Figure 3.49: Calculated values from EXAFS of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ of 6 M-O distances, compared with the literature values of the pure end members.$^{28,29}$

Figure 3.50: Average values from EXAFS of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ of 6 M – O distances compared with the literature values of the pure end members.$^{28,29}$
3.9 XPS

Manganese and ruthenium XPS data was used to observe the surface oxidation states of the $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials. Previous work by Morgan was used to help assign the ruthenium XPS,$^{36}$ and work by Biesinger $et$ $al.$ was used to help assign the manganese XPS.$^{37}$ The manganese XPS shown in Figure 3.51, shows that octahedral Mn$^{3+}$ exists in a similar environment to that seen in Mn$_2$O$_3$ at the surface of all of the $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials, including the as made $\beta$-MnO$_2$. This is unexpected as the XANES show an average oxidation state of +4 for manganese in $\beta$-MnO$_2$, therefore a small amount of Mn$^{3+}$ is only expected as a surface layer. The presence of Mn$^{3+}$ increases with increasing ruthenium content. This is consistent with the XANES, that showed more Mn$^{3+}$ was present with increasing ruthenium content.

The ruthenium XPS in Figure 3.52, showed a more complicated situation than manganese due to the overlapping of adventitious carbon signals. Following the work by Morgan, the RuO$_2$ peaks were assigned including satellite features and Ru(OH)$_3$. This could suggest that either Ru(OH)$_3$ is present at the surface of the samples or that a similar Ru$^{3+}$ environment exists. The hydrothermally made RuO$_2$ shows no presence of Ru(OH)$_3$ suggesting that this is a feature of the substituted $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ material.
Figure 3.51: Manganese 2p XPS of $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ materials.
Figure 3.52: Ruthenium 3d and carbon 1s XPS of β-Mn$_{1-x}$Ru$_x$O$_2$ materials compared to crystalline RuO$_2$. 
The manganese to ruthenium ratio calculated from XPS is compared to the EDXA results in Figure 3.53. It shows that at high ruthenium content the two techniques match reasonably well. But in the lower ruthenium content materials the EDAX gives a lower ruthenium content than the XPS. This suggests that more ruthenium is present at the surface than through the bulk of the material in samples $\beta$-Mn$_{0.925}$Ru$_{0.075}$O$_2$ and $\beta$-Mn$_{0.8}$Ru$_{0.2}$O$_2$.

![Graph showing Ru content by XPS vs EDXA](image)

*Figure 3.53: Percentage ruthenium to manganese content by EDXA compared to XPS.*

The XPS data are summarised in Figure 3.54 for the $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials. It shows the Ru$^{4+}$ content increasing with increasing substitution of the manganese. The Mn$^{4+}$ decreases with increasing substitution of ruthenium. A small amount of Ru$^{3+}$ is present at the surface of the $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials. A large amount of Mn$^{3+}$ is present at the surface.
Figure 3.54: Percentage content of Ru$^{4+}$, Ru$^{3+}$, Mn$^{3+}$ and Mn$^{4+}$ for β-Mn$_{1-x}$Ru$_x$O$_2$ materials, calculated from XPS.

3.10 Oxidation states

The XPS data matches the XANES data reasonably well as shown in Figure 3.55, but it is likely that the XPS shows more about the surface than the overall structure due to the surface sensitive nature of the technique. It is also possible that the surface of the materials by XPS could change due to the vacuum used during the measurements, which could change the surface water and possibly the oxidation states of the metals. The overlapping of the ruthenium region with the carbon region could also cause issues with the ruthenium assignment in the XPS.

The Ru in the β-Mn$_{1-x}$Ru$_x$O$_2$ materials is less than +4 by XPS analysis, but in the bulk from XANES analysis the average ruthenium oxidation state is slightly oxidised above +4. The XPS, which may be complicated by C, shows some reduced Ru$^{3+}$, which could be consistent with the ‘nanoskin Ru$_2$O$_3$’ proposition by Donakowski et al. As the Ru substitution is increased the Ru becomes more like RuO$_2$, which could be due to less manganese being present and therefore less Mn$^{3+}$ present.

The Mn is reduced below Mn$^{4+}$, especially at the surface. This balances the increase in Ru oxidation state, as shown in Figure 3.56, but gives an average metal oxidation state of slightly less than 4+, which suggests that the surface of the materials is more like 3+ and therefore could be consistent with a Mn$_2$Ru$_x$O$_3$ “nanoskin.”
Figure 3.55: Average oxidation states of manganese and ruthenium calculated from XPS compared with XANES.

Figure 3.56: Average metal oxidation states calculated from the Ru K edge and Mn K edge XANES.
3.11 Powder Conductivity

Powder conductivity measurements were made at Johnson Matthey using a custom built apparatus with two brass plates 17 mm diameter pressed together with the powder between using 3 bar pressure. The height of the powder was measured and resistance recorded across the plates, which was then converted to conductivity. It was found that conductivity increases with increasing substitution of the manganese with ruthenium, as shown in Figure 3.57. This increase corresponds well with what is expected. However, it is important to note that these powder conductivity measurements would be affected by surface effects due to the grain boundaries and these values are therefore expected to be lower than for a pellet or single crystal conductivity. Surface areas of the samples and surface water may also affect the conductivity measured by this method. This trend is as expected since $\beta$-MnO$_2$ is a semi-conductor$^{38}$ and RuO$_2$ is a metallic conductor.$^{39}$

![Graph showing conductivity vs. $x$ (β-Mn$_{1-x}$Ru$_x$O$_2$)](https://example.com/graph.png)

Figure 3.57: Powder conductivity of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$.

3.12 Surface Area

Surface area was recorded using a 7-point BET measurement. The results are plotted in Figure 3.58. It was found that with increasing amounts of ruthenium, the sample increased in surface area. This is consistent with the decrease in crystallinity in the
powder XRD patterns, showing that crystallite size has decreased, and the decrease in particle size seen by SEM.

![Figure 3.58: Surface area of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$.](image)

**3.13 Manganese ruthenium oxides conclusion**

Manganese ruthenium oxides with rutile structure have been successfully made for the first time. These materials were made under acidic hydrothermal conditions with the aim of crystallising materials that would be acid resilient. They have been analysed by XRD, SEM, TEM, ICP, EDXA, TGA-DSC, TGA-MS, thermodiffractometry, XANES, EXAFS, XPS, powder conductivity and BET surface area. The techniques combined analysis show a range of materials $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ ($x\leq 0.2$) that are stable to at least 600 °C, that have good electrical conductivity properties increasing with increasing ruthenium substitution and they show relatively high surface area. The EXAFS are fitted well to the proposed structures. They suggest that hydration of the samples is within the structure, and the hydration increases with increasing ruthenium substitution. This is backed up by evidence of increasing water of crystallisation shown in the TGA-MS. The XPS shows that the surface chemistry of these materials is interesting with different oxidation states at the surface than in the bulk shown by the XANES. This suggests that the surface water could affect these surface properties.
The materials show good conductivity for use as a catalyst support in PEMFCs with $x>0.29$ for $\beta$-Mn$_{1-x}$Ru$_x$O$_2$. The materials exhibit good surface areas for all the materials. The surface area increases substantially above 0.29 substitution. This suggests that the material with more ruthenium substitution would be more appropriate for use as a catalyst support in PEMFCs.

3.14 References


Chapter 4 – Niobium titanium carbonitrides

4.1 Introduction and Scope of the Chapter

Transition metal carbides and nitrides have high mechanical strength, thermal stability, and conductivity, giving them potential uses in catalysis.\textsuperscript{1–3} Transition metal carbides including titanium, zirconium, tantalum, niobium and molybdenum have been studied as efficient catalysts for redox type reactions, due to their high chemical and thermal stability and electrical conductivity.\textsuperscript{4–6} Ota \textit{et al.} \textsuperscript{7} found that zirconium, tantalum and niobium carbonitride had increased activity towards oxygen reduction reaction (ORR) with increased partial oxidation of the surface.

Niobium carbide, titanium carbide, niobium nitride and titanium nitride all exist in the cubic $Fm\bar{3}m$, rock salt structure as shown in Figure 4.1.\textsuperscript{8–11} Carbides, nitrides and carbonitrides have an unusual combination of metallic, covalent and ionic bonding.\textsuperscript{12–16} The ionic part of the bonding is as a result of charge transfer from the metal to the non-metal atom, whereas the covalent interactions mainly consist of interactions between the metal d-orbitals and the non-metal p-orbitals, but metal to metal interactions also occur. The covalent component of the bonding is stronger in the carbide and weaker in the nitride, this decrease in covalency is accompanied by an increase in ionicity. This can make the nitride materials less stable than the corresponding carbide.\textsuperscript{15,16}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig41.png}
\caption{Structure of cubic NbC with a $Fm\bar{3}m$ space group, where niobium is red and carbon is black.\textsuperscript{11}}
\end{figure}
Tackett et al. found that platinum on niobium carbide shows high hydrogen evolution activity and stability in both acidic and alkaline environments.\textsuperscript{17} They found the catalyst was also resistant to common impurities found in tap water suggesting that Pt/NbC could replace the more expensive Pt catalyst in water electrolysis cell cathodes.\textsuperscript{17} Two-dimensional niobium carbides have been shown by Naguib et al. to have potential use for Li-ion batteries. The Nb$_2$C materials showed good capabilities to handle high charge-discharge rates.\textsuperscript{18} NbC has been shown by Karimi et al. to have excellent electrical conductivity and very good activity, however they found loading with iridium did not produce good oxygen evolution (OER) performance. However, they suggest that this was due to poor surface area.\textsuperscript{19}

Work by Stamatin et al. studied niobium carbonitride as a platinum support for ORR in an acidic environment under potential cycling.\textsuperscript{20} They found that the interaction between the electrocatalyst and the support was better in Pt/NbC$_{1-p}N_p$ than for activated carbon. The NbC$_{1-p}N_p$ support showed greater stability under potential cycling than the carbon support, although the NbC$_{1-p}N_p$ showed lower mass activity and specific electrochemical surface area than the carbon support.\textsuperscript{20}

In work by Nam et al. partially oxidised niobium carbonitrides were investigated as a non-platinum catalyst for the reduction of oxygen in acid.\textsuperscript{21} They found that the onset of ORR was much higher in partially oxidised niobium carbonitride than in just niobium carbonitride. Nam found that this surface oxidation was essential to enhance the catalytic activity for ORR.\textsuperscript{21}

Work by Kimmel et al. evaluated the stability of different transition metal carbides.\textsuperscript{22} They found that Ta, W, Ti and Zr carbide showed stability in acidic media, whereas Ti, Zr, Ta, V and Nb carbide showed stability in alkaline media. They also found that all transition metal carbides are stable for HER/HOR and TaC, TiC and ZrC show stability for ORR or OER.\textsuperscript{22}

Yang et al. reported nanostructured niobium titanium nitrides for use as durable non-carbon supports for ORR.\textsuperscript{23} They found the Nb$_{1-q}$Ti$_q$N ($q = 0.75$ and $0.5$) materials were electrochemically stable until 1.2 V. The electrical conductivities were about one order of magnitude higher than those reported for carbon based fuel cell catalyst supports under similar acidic conditions. The resulting Pt/Nb$_{1-q}$Ti$_q$N catalysts showed electrochemical activities similar to that of the Pt/C towards the ORR.\textsuperscript{23}
Work by Cui et al. developed a Ti$_{0.5}$Nb$_{0.5}$N support with high electrical conductivity and high surface area by a coprecipitation method. They found that the material was kinetically stable in both acid and alkaline media. Electrochemical studies in the potential range for fuel cell cathode operation showed higher stability and activity of Pt/Ti$_{0.5}$Nb$_{0.5}$N than Pt/C.

Li et al. used titanium nitride loaded with iridium as an effective support to catalyse OER. TiN enhanced the dispersion and inhibited the aggregation of the nanoparticle catalyst. Activity was improved in comparison to their non supported counterparts. The materials showed catalytic performance suitable for the water splitting cell, and therefore has potential uses in water electrolyzers.

Avasarala et al. found that titanium nitride nanoparticles can act as catalyst supports for PEMFCs and have shown better activities than conventional platinised carbon electrocatalysts in acidic media. Jin et al. tested titanium nitride and titanium carbonitride hierarchical structures for the ORR and found similar activities to Pt/C. They found the durability in alkaline media to be greater than that of Pt/C.

Carbon supported titanium oxynitride nanoparticles were synthesised by Chisaka et al. and tested for use as a cathode catalyst for PEMFCs. It was shown to be electrochemically stable and gave a mass activity of 0.35 A g$^{-1}$ at 0.74 V in an acidic environment. NH$_3$ treatment was used to give TiN, and it was found that it was not highly active for ORR but the titanium oxynitride was highly active. This suggests that oxygen presence was responsible for the increased activity. Dam et al. found that partially oxidised titanium carbonitride showed significantly enhanced catalytic activity for the ORR when compared to TiC$_{0.5}$N$_{0.5}$ and TiO$_2$. They also found that partially oxidised titanium carbonitride has a high chemical stability in 0.1 M sulfuric acid.

One of the main issues with use of carbonitride and carbides is the difficulty of synthesis due to the high temperatures and reactive gases required. Traditionally the synthesis involves temperature programmed carburisation of a transition metal oxide using a carburising mixture (e.g. 20 (v/v) % CH$_4$/H$_2$) and appropriate temperature programming. Depending on the final carburisation temperature, the thermal decomposition of methane can occur, leading to the formation of pyrolytic carbon that covers the carbide surface and inhibits its catalytic activity. Niobium carbide cannot
be formed below 950 °C via this method\textsuperscript{31,32} and such conditions favour formation of samples with low specific areas.\textsuperscript{34} Chagas \textit{et al.} proposed a new method for synthesis of niobium carbonitride using lower temperatures than traditional methods.\textsuperscript{33} This method reacts guanidine carbonate and ammonium niobate (V) oxalate hydrate at 150 °C in air for 12 hours, followed by heating to 400 °C under helium for 4 hours and subsequently at 450-900 °C under helium for 2 hours.\textsuperscript{33} The work in this chapter aimed to simplify this method and to substitute niobium carbonitrides with other metals, such as titanium, to tune properties such as conductivity, and catalytic activity.

4.2 Synthesis

A synthesis of niobium carbonitride was modified from Chagas \textit{et al.},\textsuperscript{33} to work under nitrogen rather than helium gas, and remove an intermediate heating step, which was found to be unnecessary. The modified synthesis can be divided into 2 steps:

1. A 1:5 molar ratio mixture of ammonium niobate (V) oxalate hydrate (\(\text{NH}_4\text{NbO}(\text{C}_2\text{O}_4)_2\cdot x\text{H}_2\text{O}\) (7.6 g) and guanidine carbonate (6.4 g) was macerated in a pestle and mortar for 5 minutes. TGA was used to calculate the hydration of the ammonium niobate oxalate hydrate. The mixture formed was then heated in an oven at 150 °C in air for 12 hours.

2. The product of step 1 was then heated in a tube furnace under a flow of nitrogen to various temperatures (700-1200 °C) for between 1-24 hours, and then cooled to room temperature.

This synthesis could be modified further to include ammonium titanyl oxalate monohydrate instead of ammonium niobate (V) oxalate hydrate to form titanium carbonitrides. Mixed metal titanium and niobium carbonitrides can be made by varying the ratio of ammonium niobate (V) oxalate hydrate to ammonium titanyl oxalate monohydrate.

4.2.1 Synthesis of Precursor

The precursor was made by macerating guanidine carbonate and ammonium niobate(V) oxalate in varying ratios, where GC is guanidine carbonate and M is the metal from the ammonium metal oxalate (1M:3GC, 1M:4GC, 1M:5GC etc.). This mixture was then heated for 12 hours at 150 °C, the resulting solid was then ground to form a powder. The powder XRD of these materials can be seen in Figure 4.2, where the materials are compared to the starting materials guanidine carbonate and
ammonium niobate(V) oxalate. The materials formed all show a distinct pattern, which is different to that of the starting materials. The precursor materials are labelled hereafter as Nb150 followed by metal to guanidine carbonate ratio e.g. ammonium niobium oxalate precursor made with 1M:3GC ratio would be labelled Nb150 1M:3GC. Other metals would be labelled in similar fashion and mixed metal niobium titanium precursors will be labelled NbTi150.

![Graph showing XRD patterns](image)

**Figure 4.2:** Powder XRD (\(\lambda=1.5418 \text{ Å}\)) of the precursor materials made at 150 °C for 12 hours with different ratios of guanidine carbonate (GC) to metal (M) ratios. These are compared with guanidine carbonate, ammonium niobate oxalate, and niobium oxide.\(^{35,36}\) Aluminium sample holder peaks are greyed out.

Precursors for the titanium materials were made using ammonium titanyl oxalate and guanidine carbonate via the same method as for the niobium materials, the powder XRD can be seen in Figure 4.3. The patterns were compared to the starting materials and titanium dioxide and were found to be a different material to any of these. In order to make the mixed metal niobium titanium precursor different ratios of ammonium titanyl oxalate and ammonium niobate (V) oxalate were mixed and then macerated with guanidine carbonate to form different metal to guanidine carbonate ratios (e.g. 1M:4GC).
Figure 4.3: Powder XRD ($\lambda=1.5418$ Å) of the precursor materials made at 150 °C for 12 hours with different ratios of guanidine carbonate (GC) to metal (M) ratios. These are compared with the starting materials guanidine carbonate, ammonium titanyl oxalate, and titanium oxide.\textsuperscript{37,38}

4.2.2 Synthesis of Carbonitrides

The precursor materials (0.3–20 g) were heated under nitrogen flow of 100 ml/min with a ramp rate of 10 °C/min to between 700-1200 °C and held at the desired temperature for between 4-12 hours. The samples were then cooled at a rate of 20 °C/min, once cooled the gas tight seals were loosened slowly over the course of several hours before the nitrogen gas was switched off and left for a further hour. This was done in order to passivate the surface of the materials as they were reported to be pyrophoric and if removed from the furnace too soon caught fire. If this step was done too quickly the surface would oxidise too much and form a large amount of metal oxide visible by powder XRD and by the white to grey colour of the samples, instead of the desired black powders. Certain conditions were found to increase the chance of this oxidation happening, for example the more titanium present in the sample the more likely it was to oxidise. It is important to note that the system had to be gas tight and oxygen free nitrogen gas was essential.
4.3 Powder XRD

Using a 1M:5GC ratio, samples of niobium carbonitride were made using a range of temperatures (700 – 1200 °C) and synthesis times (4 – 12 hrs). The powder XRD with Pawley fit is shown in Figure 4.4. With increasing temperature of syntheses, the peaks become sharper indicating an increase in crystallinity. The patterns were fitted using a cubic unit cell with space group $Fm\bar{3}m$ as expected for the rock salt structure of NbC, NbN, TiC and TiN.8–11 The lattice parameter increases with increasing reaction temperature until 1100 °C where it plateaus and at 1200 °C it decreases slightly, as shown in Figure 4.5. The crystallite sizes were determined using the Scherrer method and are shown in Figure 4.6. The crystallite size increases with increasing temperature of synthesis of the niobium carbonitrides. Two samples were recorded at 1200 °C, these show variation in crystallite size and show that despite the same reaction conditions, variation within the samples can exist. This could be due to different amounts of precursor to start with or due to hot spots within the tube furnace. In order to prevent a large variation in temperature across the tube, insulation plugs were used at either end. Despite best intentions using TGA to calculate hydration of the starting materials, the materials gained water very quick due to their hygroscopic properties. Therefore, getting the ratios exact was difficult, so slight variation across the samples was possible.
Figure 4.4: Pawley fits of powder XRD of NbC\textsubscript{1-p}N\textsubscript{p} made at different temperatures and reaction times, showing the calculated lattice parameter $a$ for the Fm\textbar m unit cell.
Figure 4.5: Pawley fit lattice parameters of NbC<sub>1-y</sub>N<sub>y</sub> made at different temperatures for 4 hours.

Figure 4.6: Crystallite size of NbC<sub>1-y</sub>N<sub>y</sub> made at different temperatures calculated from Pawley fits of powder XRD using the Scherrer method.
Titanium carbonitrides were made using a 1M:5GC ratio using various temperatures for 4 hours, with powder XRD for these materials shown in Figure 4.7. These materials were more difficult to make without the oxidation of the surface and also appear to have an amorphous structure in the background of the powder XRD. In particular in the pattern for TiC\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C between 20º-35º there is a humped background which is most likely due to amorphous carbon.

Pawley XRD fits for the as made titanium carbonitrides are shown in Figure 4.7, the powder XRD were fitted to a cubic \textit{Fm\overline{3}m} space group. The lattice parameters shown in Figure 4.8 increase from 900 °C synthesis to the 1000 °C and then appear to plateau at 1200 °C. However, at 1100 °C there is a decrease in the lattice parameter. This change in lattice parameters could be due to hot spots within the tube furnace, which were minimised by the use of insulation plugs. The variations could also be due to differences in the mass of the hygroscopic precursor material at the beginning of the reaction, affecting how much carbon or nitrogen combusts during the synthesis.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.7.png}
\caption{Pawley fits of powder XRD of TiC\textsubscript{1-p}N\textsubscript{p} made at different temperatures, showing the calculated lattice parameter a for the \textit{Fm\overline{3}m} unit cell.}
\end{figure}
Mixed metal carbonitrides with a composition of $\text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_1\text{pN}_p$ were made at various temperatures and synthesis lengths, and the powder XRD for these can be seen in Figure 4.9. It was found that with increasing temperature of synthesis the peaks become sharper and therefore show an increase in the samples crystallinity. The samples made at 900 °C for 4 hours and 12 hours show relatively small differences between them and indicate that synthesis time does not appear to affect the samples crystallinity. The refined Pawley lattice parameters are shown in Figure 4.10 for the 4 hours synthesised materials. The lattice parameter increases with increasing temperature of synthesis, suggesting that with higher temperatures more carbon is incorporated into the structure.

**Figure 4.8:** Pawley fit lattice parameters of $\text{TiC}_{1-p}\text{N}_p$ made at different temperatures for 4 hours.
Figure 4.9: Pawley fits of powder XRD of Nb_{0.5}Ti_{0.5}C_{1-p}N_{p} made at different temperatures and reaction times, showing the calculated lattice parameter $a$ for the $Fm\bar{3}m$ unit cell.
Figure 4.10: Pawley fit lattice parameters of $Nb_{0.5}Ti_{0.5}C_{1-p}N_p$ made at different temperatures for 4 hours.

Materials with a 0.95Ti:0.05Nb composition were made in order to try to make one of the conducting $Nb_{0.05}Ti_{0.95}O_2$ materials, as described by Sahasrabudhe et al.,\textsuperscript{39} at the surface of the carbonitride. This is because this oxide is known to be conducting and therefore if the carbonitride oxidises further in the PEMFC, it should form this conducting oxide. The Pawley fits for these materials made at different temperatures can be seen in Figure 4.11, with increasing temperature of synthesis the XRD peaks become sharper indicating increased crystallinity. The Pawley lattice parameters can be seen in Figure 4.12, they show an increase in lattice parameter with increasing temperature, which may indicate more carbon is substituting into the sample with increasing reaction temperature.
Figure 4.11: Pawley fits of powder XRD ($\lambda=1.54056$ Å) of Nb$_{0.05}$Ti$_{0.95}$C$_{1-p}$N$_p$ made at different temperatures and reaction times, showing the calculated lattice parameter $a$ for the Fm$\bar{3}$m unit cell.
Various samples were made at 900 °C for 4 hours with varying niobium to titanium ratios. The Pawley powder XRD refinements are shown in Figure 4.13 and the parameters for these can be seen in Figure 4.14. The unit cell decreases with increasing titanium content, shown by a shift of peaks to the right. The more titanium is substituted the materials have smaller crystal domain size, shown by the increasing peak broadness. This may also indicate an increase in disorder of the sample. The titanium carbonitride does not show this effect and therefore the presence of both metals may be the reason behind this increase in disorder. The lattice parameters in Figure 4.14 show that the more titanium in the sample the more like titanium nitride the unit cell becomes, suggesting that the temperature of synthesis only allows for the titanium materials to form nitrides, whereas the niobium carbonitrides have unit cells more similar to that of the niobium carbide. Increasing the temperature further than 1200 °C could potentially increase the substitution of carbon into the titanium samples.
Figure 4.13: Pawley fits of powder XRD ($\lambda=1.5418$ Å) of $\text{Nb}_{1-q}\text{Ti}_q\text{C}_{1-p}\text{N}_p$ made at 900 °C for 4 hours, where $q$ is the titanium content, showing the calculated lattice parameter $a$ for the cubic $Fm\overline{3}m$ unit cell.
Figure 4.14: Pawley fit lattice parameters of Nb$^{1-q}$Ti$q$C$_{1-p}$N$_p$ made at 900 °C for 4 hours, where $q$ is titanium content. The reference data were taken from the literature.\textsuperscript{8–11}

4.4 Neutron Diffraction and Fits

4.4.1 Neutron Diffraction Patterns

Neutron diffraction was used to determine the carbon and nitrogen ratios with the samples, by using both Rietveld fitting of the neutron diffraction and analysis of the PDF. The bound scattering lengths of carbon (6.6460(12) fm), nitrogen (9.36(2) fm) and niobium (7.054(3) fm)\textsuperscript{40} were thought to be different enough to give different intensities so the carbon to nitrogen ratio could be refined. Neutron diffraction patterns for the Nb$^{1-q}$Ti$q$C$_{1-p}$N$_p$ samples are shown in Figure 4.15. The Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ samples show a decrease in the intensity of the peaks and an increase in broadness indicating a less ordered material. The NbC$_{1-p}$N$_p$ samples show an increase in intensity and sharpness of the peaks with increasing reaction temperature. This suggests the samples become more ordered and more crystalline with increasing reaction temperature. Figure 4.15 inset shows the baseline changes: the lower the temperature of synthesis the higher the baseline suggesting that more hydrogen is present within the sample to which neutrons are highly sensitive. This could be as water of hydration or perhaps
more likely as a part of an amorphous carbon phase, as leftover material from the precursors.

\[ \text{Intensity / a.u.} \]

\[ \text{d - spacing} \]

\[ \text{NbC}_{1-p}\text{N}_p \ 850 \ ^\circ\text{C} \ 4\text{hrs} \]
\[ \text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_p \ 900 \ ^\circ\text{C} \ 4\text{hrs} \]
\[ \text{NbC}_{1-p}\text{N}_p \ 900 \ ^\circ\text{C} \ 4\text{hrs} \]
\[ \text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_p \ 900 \ ^\circ\text{C} \ 12\text{hrs} \]
\[ \text{NbC}_{1-p}\text{N}_p \ 1000 \ ^\circ\text{C} \ 4\text{hrs} \]
\[ \text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_p \ 1200 \ ^\circ\text{C} \ 4\text{hrs} \]
\[ \text{NbC}_{1-p}\text{N}_p \ 1200 \ ^\circ\text{C} \ 4\text{hrs} \]

*Figure 4.15*: Neutron diffraction from bank 3 of POLARIS of NbC\(_{1-p}\)N\(_p\) and Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)N\(_p\) made at different temperatures and reaction times, inset zoomed in on the baseline.

The Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)N\(_p\) samples neutron diffraction shown in Figure 4.16 show an increase in baseline with decreasing sample temperature. It is also possible to see two different phases due to the difference in peak shapes, with a particularly broad peak shown at 1.2 d-spacing. Therefore, the samples were not fitted as the other phase could not be identified.
Figure 4.16: Neutron diffraction from bank 3 of POLARIS of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ made at different temperatures and reaction times.

4.4.2 Rietveld Neutron Fits

Rietveld refinements were performed against the neutron diffraction patterns of NbC$_{1-p}$N$_p$, shown in Figure 4.17 and resulting parameters are shown in Table 4.1. The refinements were performed using the initial crystallographic information file of niobium carbide from Will et al.\textsuperscript{11} with a cubic $Fm\overline{3}m$ unit cell. The parameters shown in Table 4.1 show an increase in unit cell size with increasing temperature of synthesis. The ratio of carbon to nitrogen, shows an increase in the carbon content with increasing reaction temperature matching the expected pattern from the increase in unit cell size, further shown in Figure 4.18. The unit cell size decreases for the 1200 $^\circ$C synthesis, the refinement of the carbon nitrogen ratio suggests this is due to a deficient carbon / nitrogen site.
Figure 4.17: Rietveld fits of neutron diffraction patterns from bank 3 of POLARIS of NbC$_{1-p}$N$_p$ made at different temperatures for 4 hours.
Table 4.1: Rietveld fit parameters of neutron diffraction patterns of NbC_{1-p}N_p made at different temperatures for 4 hours.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter a / Å</th>
<th>Nb</th>
<th>C</th>
<th>N</th>
<th>C and N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Occ Uiso*100 / Å²</td>
<td>Occ</td>
<td>Occ Uiso*100 / Å²</td>
<td></td>
</tr>
<tr>
<td>NbC_{1-p}N_p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>850 °C 4 hrs</td>
<td>4.44587(2)</td>
<td>1</td>
<td>0.3230(10)</td>
<td>0.5710(10)</td>
<td>0.4290(10)</td>
</tr>
<tr>
<td>900 °C 4 hrs</td>
<td>4.451160(12)</td>
<td>1</td>
<td>0.4000(10)</td>
<td>0.5990(10)</td>
<td>0.3970(10)</td>
</tr>
<tr>
<td>1000 °C 4 hrs</td>
<td>4.454940(10)</td>
<td>1</td>
<td>0.4490(10)</td>
<td>0.6550(10)</td>
<td>0.3320(10)</td>
</tr>
<tr>
<td>1200 °C 4 hrs</td>
<td>4.453330(9)</td>
<td>1</td>
<td>0.476(2)</td>
<td>0.6200 (10)</td>
<td>0.3590(10)</td>
</tr>
</tbody>
</table>

Figure 4.18: Rietveld fit parameters and refined carbon and nitrogen content of neutron diffraction patterns of NbC_{1-p}N_p made at different temperatures for 4 hours.
4.5 PDF

Pair distribution function (PDF) was used to look at the local structure of these materials. It was found that the higher the temperature of synthesis the more ordered the material, shown in Figure 4.19 by the increasing intensity of the peaks. The peak at 1.4 Å indicates a C-C bond suggesting the presence of amorphous carbon. This peak increases for the lower temperature syntheses, which indicates more amorphous carbon is present in these samples. The raised baseline in particular of NbC$_{1-p}$N$_p$ 12 hrs 700 °C, indicates the presence of hydrogen within the structure, possibly in the amorphous carbon structure.

![Figure 4.19: PDF of a range of NbC$_{1-p}$N$_p$ materials made at different temperatures and reaction times.](image)

PDF analysis uses the PDF to guide a structure refinement. The fit of the Rietveld derived structure for NbC$_{1-p}$N$_p$ 4 hrs 1200°C is shown in Figure 4.20 and the fitted parameters for this are compared against the literature values in Table 4.2. The fitted structure is very similar to NbC,$^{11}$ with a slightly smaller unit cell indicating the presence of nitrogen within the structure. The C:N ratio was kept at 0.6C:0.4N as found in the Rietveld refinement. It was found that by changing the C:N ratio in the
PDF fit, the goodness of fit did not change very much, possibly due to the similarities of carbon (6.6460(12) fm), niobium (7.054(3) fm) and nitrogen (9.36(2) fm) bound coherent scattering lengths.\(^\text{40}\) The only affects other than slight unit cell change would be change in intensity of peaks. Further fitting may be required to analyse this phase fully by using Reverse Monte Carlos (RMC) fitting.

**Figure 4.20:** PDF fit of NbC\(_{1-p}\)N\(_p\) 4 hrs 1200 °C.

**Table 4.2:** Fitted PDF parameters against reference values. The carbon nitrogen ratio was taken from the neutron Rietveld refinement as 0.6C:0.4N.

<table>
<thead>
<tr>
<th>(C interchangeable with N)</th>
<th>NbC(_{11}) / Å</th>
<th>NbN(_{10}) / Å</th>
<th>NbC(<em>{0.6})N(</em>{0.4}) 4 hrs 1200 °C / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter a</td>
<td>4.4686(1)</td>
<td>4.394(3)</td>
<td>4.46057(13)</td>
</tr>
<tr>
<td>Nb-C</td>
<td>2.234</td>
<td>2.167</td>
<td>2.230</td>
</tr>
<tr>
<td>Nb-Nb and C-C</td>
<td>3.160</td>
<td>3.107</td>
<td>3.154</td>
</tr>
<tr>
<td>Nb-C (next nearest)</td>
<td>3.870</td>
<td>3.805</td>
<td>3.863</td>
</tr>
<tr>
<td>Nb-C-Nb C-Nb-C</td>
<td>4.469</td>
<td>4.394</td>
<td>4.461</td>
</tr>
</tbody>
</table>

PDFs of the Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)N\(_p\) sample with different reaction conditions are shown in Figure 4.21 compared with NbC\(_{1-p}\)N\(_p\) 4 hrs 1200 °C. They all show a large peak at 1.4 Å for C-C amorphous carbon. The peaks show a shift to the left in comparison to NbC\(_{1-p}\)N\(_p\) 4 hrs 1200 °C, indicating a shrink in unit cell. An unknown phase is also present with peaks at 2.4 Å and 2.8 Å.
Figure 4.21: PDF of a range of Nb_{0.5}Ti_{0.5}C_{1-p}N_p materials made at different temperatures and reaction times, compared to NbC_{1-p}N_p 4 hrs 1200 °C.

4.6 TEM and Elemental Mapping

TEM and elemental mapping (EDXA) were used to the look at the dispersion of the elements throughout the samples and well as different particle morphologies across the samples. Figure 4.22 shows TEM imaging of NbC_{1-p}N_p 12 hrs 700 °C. The material has flake-like appearance and large amounts of amorphous carbon appears to surround the NbC_{1-p}N_p material.

Figure 4.22: TEM images of NbC_{1-p}N_p 12 hrs 700 °C.
Figure 4.23 shows NbC$_{1-p}$N$_p$ 4 hrs 850 °C samples TEM imaging and elemental analysis. The sample has a grid like structure at the centre indicating the lattice fringes of the rock-salt structure of the main carbonitride material. The edges show disorder with a swirl like appearance indicating amorphous carbon. The elemental mapping shows niobium, carbon, oxygen and nitrogen across the structure. The oxygen is likely present due to the surface oxidation in order to stabilise the material in air.

![TEM images and elemental mapping of NbC$_{1-p}$N$_p$ 4 hrs 850 °C with Nb in blue, C in yellow, N in green, and O in red.](image)

TEM images of NbC$_{1-p}$N$_p$ 4 hrs 900 °C are shown in Figure 4.24, and show similar sized particles to NbC$_{1-p}$N$_p$ 4 hrs 850 °C. The material appears to have an amorphous carbon layer surrounding the particles. Whereas NbC$_{1-p}$N$_p$ 4 hrs 1000 °C TEM images shown in Figure 4.25, show much larger particle sizes of around 40 nm. The particles show little to no amorphous carbon at the surface, and it is possible to see the lattice fringes, shown by the grid-like structure.

![TEM images of NbC$_{1-p}$N$_p$ 4 hrs 900 °C.](image)
Figure 4.25: TEM images of NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 1000 °C.

Figure 4.26 shows the TEM and elemental mapping of NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 1200 °C material. This sample shows much less amorphous carbon surrounding the material, but there is still a small layer. The elemental analysis shows a spread of niobium, carbon, nitrogen and oxygen across the whole sample, like for sample NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 850 °C.

Figure 4.26: TEM images and elemental mapping of NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 1200 °C with Nb in blue, C in yellow, N in green, and O in red.

Figure 4.27 shows the TEM and elemental mapping of sample NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C. This sample shows a large amount of amorphous carbon surrounding the carbonitride material. The elemental mapping shows that niobium and titanium are present across the entire sample suggesting an atomically mixed sample. However, the titanium does appear to show a correlation with the oxygen suggesting the titanium is present more
at the surface as an oxide, possibly due to the formation of a Ti\(_{1-x}\)Nb\(_x\)O\(_2\) material. Lattice parameters calculated from XRD suggest that the titanium is present throughout the carbonitride as well. This is most likely a surface effect and perhaps suggests that the titanium is more easily oxidised at the surface, which corresponds to the experimental issues generating TiC\(_{1-p}\)N\(_p\) samples without the presence of TiO\(_2\).

*Figure 4.27: TEM images and elemental mapping of Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)N\(_p\) 4 hrs 900 °C with Nb in blue, Ti in pink, C in yellow, N in green, and O in red. Note the TEM grid is carbon.*

Figure 4.28 shows material Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)N\(_p\) 4 hrs 1200 °C TEM imaging and elemental analysis. This sample has less amorphous carbon than the Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)N\(_p\) 4 hrs 900 °C sample, but it still has a visible layer of amorphous carbon, shown by the disorder in the TEM images. The elemental mapping shows a similar pattern to the sample made at a lower temperature. The titanium and niobium are present across the material.
Figure 4.28: TEM images and elemental mapping of $\text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_p$ 4 hrs 1200 °C with Nb in blue, Ti in pink, C in yellow, N in green, and O in red. Note the TEM grid is carbon.

4.7 Thermal Analysis

A variety of different thermal analysis techniques such as thermogravimetric analysis (TGA), $\textit{in-situ}$ thermodiffractometry and TGA mass spectroscopy were used to analyse the heating of samples and their subsequent oxidation.

4.7.1 TGA

Thermogravimetric analysis was used to observe the decomposition of the metal carbonitrides in air to their corresponding metal oxides. This information about the mass change combined with CHN analysis was used to calculate the amount of amorphous carbon present in a sample. The CHN analysis was used assuming that all the nitrogen present is within the carbonitride structure, and the remaining sites are carbon. Therefore, Equation 4.1, Equation 4.2 and Equation 4.3 were used to calculate the mass percentage of amorphous carbon in the starting material.

$$\text{NbC}_{1-p}\text{N}_p + x\text{C} \rightarrow 0.5\text{Nb}_2\text{O}_5 + \text{CO}_y + \text{NO}_z$$

\textit{Equation 4.1}

$$\text{Nb}_{1-q}\text{Ti}_q\text{C}_{1-p}\text{N}_p + x\text{C} \rightarrow 0.5(1-q)\text{Nb}_2\text{O}_5 + q\text{TiO}_2 + \text{CO}_y + \text{NO}_z$$

\textit{Equation 4.2}
$\text{TiC}_{1-p}\text{N}_p + x\text{C} \rightarrow q\text{TiO}_2 + \text{CO}_y + \text{NO}_z$

Equation 4.3

The TGA for the $\text{NbC}_{1-p}\text{N}_p$ samples made at different reaction conditions are shown in Figure 4.29. The lower the temperature of synthesis of the material, the lower temperature the material begins to increase in mass. The mass increase overshoots the expected mass of $\text{Nb}_2\text{O}_5$ before decreasing to the final mass at 700 °C. This may be due to the sample retaining some carbon or nitrogen within the structure as the material oxidises. The lower temperature syntheses show two peaks in mass change. The first is thought to be due to the amorphous carbon oxidising and forming CO and CO$_2$. The second is thought to be due to the oxidation of the niobium. The amorphous carbon calculated in Figure 4.29 shows that with increasing temperature of synthesis there is less amorphous carbon.

Figure 4.29: TGA showing $\text{NbC}_{1-p}\text{N}_p$ made at different temperatures and times heated in air. The amorphous carbon was calculated assuming all niobium oxidises to $\text{Nb}_2\text{O}_5$. 

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The TGA of Nb_{1-q}Ti_qC_{1-p}N_p materials are shown in Figure 4.30. It shows a large increase in mass starting at 200 °C and decreasing to plateau at 550-600 °C, before decreasing to the final mass at about 800 °C for all materials. The initial mass increase may be due to the amorphous carbon oxidising by taking oxygen into the structure before leaving at between 350-450 °C. The Nb_{0.67}Ti_{0.33}C_{1-p}N_p 4 hrs 1200 °C sample appears to be stable to a higher temperature and has higher ending mass, indicating that more of the initial material was metal and formed metal oxides upon heating. The amorphous carbon content was calculated assuming all niobium went to Nb_2O_5 and all titanium went to TiO_2. There is some error associated with this assumption as there is an oxide layer on the material at the start.

![Graph showing TGA data](image)

*Figure 4.30: TGA showing Nb_{1-q}Ti_qC_{1-p}N_p made at different temperatures and times heated in air. The amorphous carbon was calculated assuming all niobium oxidises to Nb_2O_5 and all titanium oxidises to TiO_2.*

The TGA for the TiC_{1-p}N_p materials made under different conditions can be seen in Figure 4.31. The samples have an initial increase in mass before decreasing substantially to the end product of TiO_2. This indicates a high amorphous carbon amount as is calculated assuming starting material is made up of TiN and amorphous carbon and the end product is TiO_2. These materials are thought to have a large amount
of TiO$_2$ at the start which would slightly skew the data. But a large amount of amorphous carbon is thought to be present in particular due to the amorphous background present in the powder XRD.

Figure 4.31: TGA showing TiC$_{1-p}$N$_p$ made at different temperatures and times heated in air. The amorphous carbon was calculated assuming all niobium oxidises to Nb$_2$O$_5$ and all titanium oxidises to TiO$_2$.

The niobium carbonitrides tend to have much less amorphous carbon than either the niobium titanium carbonitrides or the titanium carbonitrides. The higher the temperature of synthesis, the less amorphous carbon is present. But the higher the temperature of synthesis, the more crystalline the product becomes with larger particle sizes as shown by the TEM. Therefore, if a lower temperature synthesis can be made to form less amorphous carbon it would be preferential. The increase in mass, which occurs in the TGA before decreasing to the final mass, needed further analysis by in-situ thermodiffractometry and TGA-MS.

4.7.2 In-situ thermodiffractometry

Thermodiffractometry of NbC$_{1-p}$N$_p$ 4 hrs 700 °C is shown in Figure 4.32, the sample was heated at 10 °C min$^{-1}$ at 50 °C intervals the diffraction pattern was recorded for an hour. The NbC$_{1-p}$N$_p$ peaks disappear at 250 °C and an amorphous phase forms until
550 °C where crystalline Nb\textsubscript{2}O\textsubscript{5} forms. The amorphous phase forms where the TGA shown in Figure 4.29 shows an increase in mass, and the crystallisation of Nb\textsubscript{2}O\textsubscript{5} forms when the TGA decreases sharply in mass.

![Thermodiffraction pattern of NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 700 °C heated in air to 800 °C. Sample holder peaks are greyed out in the initial pattern.](image)

*Figure 4.32: Thermodiffraction of NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 700 °C heated in air to 800 °C. Sample holder peaks are greyed out in the initial pattern.*

The NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C thermodiffractionometry is shown in Figure 4.33. Here the initial phase appears to be stable until 300 °C, it then forms an amorphous phase until Nb\textsubscript{2}O\textsubscript{5} forms at 550 °C. This matches nicely with the TGA shown in Figure 4.29. The peaks appear to shift to the right slightly at 300 °C suggesting the carbon is leaving the structure and rearranging to form niobium nitride.
Figure 4.33: Thermodiffractometry of NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C heated in air to 900 °C.

The thermodiffractometry for NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 1200 °C is shown in Figure 4.34. The sample remains stable until 350 °C where at 400 °C at shifts right to form a more nitride like material, before it becomes amorphous at 450 °C, at 550 °C the sample forms Nb\textsubscript{2}O\textsubscript{5}.
Figure 4.34: Thermodiffractometry of NbC$_{1-p}$N$_p$ 4 hrs 1200 °C heated in air to 875 °C.\textsuperscript{41}

The thermodiffractometry for Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C is shown in Figure 4.35. The material remains stable until about 250-300 °C where it forms an amorphous material. At 600 °C, an unknown mixed metal oxide phase forms before oxidising further to form TiNb$_2$O$_7$. The phase at 600 °C shows a poorly defined pattern. A similar trend is seen in the thermodiffractometry for Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 12 hrs 900 °C shown in Figure 4.36.
Figure 4.35: Thermodiffractometry of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C heated in air to 900 °C.  

Figure 4.36: Thermodiffractometry of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 12 hrs 900 °C heated in air to 900 °C. Sample holder peaks are greyed out in the initial pattern.
The thermodiffractometry for Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 1200 °C is shown in Figure 4.37. Here the initial phase remains stable until about 300 °C where it becomes amorphous until 650 °C. At 650 °C it forms an unknown oxide material until at 800 °C it forms TiNb$_2$O$_7$.

**Figure 4.37**: Thermodiffractometry of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 1200 °C heated in air to 900 °C. Sample holder peaks are greyed out in the initial pattern.

### 4.7.3 TGA -MS

TGA-MS was used to determine the different gases being taken and coming off from the samples as they were heated to 1000 °C at 10 °C min$^{-1}$ in air with a flow of 20-30 ml min$^{-1}$. The mass spectrometer was used to observe changes in the masses at 12, 14, 16, 30, 32, 44 and 46 for C, N, O, NO, O$_2$, CO$_2$ and NO$_2$, respectively. Carbon monoxide could not be observed in air due to the same mass as N$_2$. NbC$_{1-p}$N$_p$ 12 hrs 700 °C TGA-MS is shown in Figure 4.38. From 180-350 °C, there is little change in any masses but the NO, which corresponds to the mass loss shown in the TGA-DSC. From 350-550 °C the amount of C, CO$_2$ and NO$_2$ increases before plateauing and then increases sharply with NO at 575 °C. This occurs when the mass drops to give the final
oxide mass at about 600 °C, after this point there is no noticeable change in the mass spectrometry data. However, the mass does increase over this period until 1000 °C, suggesting that O₂ is being taken in and oxidises the niobium further to Nb₂O₅. Throughout the reaction the O₂ levels decrease over time. This is due to the oxidation of the niobium, carbon and nitrogen within the sample.

![Graph showing changes in mass, heatflow and mass spectrometry of different masses while heating in air.]

\textbf{Figure 4.38: TGA-MS of NbC₁₋₅N₅ 12 hrs 700 °C, showing the changes in mass, heatflow and in mass spectroscopy of different masses while heating in air.}
The TGA-MS of NbC$_1$N$_p$ 4 hrs 850 °C shown in Figure 4.39, shows a much clearer trend. It begins to oxidise at 200 °C where the amount of O$_2$ decreases and the amount of NO, CO$_2$ and NO$_2$ start to increase. The mass increases steadily until 450 °C where it plateaus before decreasing sharply, and the O$_2$ decreases sharply just before C, O, NO, CO$_2$ and NO$_2$ increase sharply before decreasing back to the baseline at 600 °C. This suggests the formation of a material containing Nb, N, C and O before the niobium oxide crystallises at 600 °C. The amorphous carbon and nitrogen most likely burn off in the first step to about 400 °C, but the increase in mass suggests that the niobium is oxidising at the same time, so separation of amorphous carbon from the sample is not possible in air.
Figure 4.39: TGA-MS of NbC$_{1-p}$N$_p$ 4 hrs 850 °C, showing the changes in mass, heatflow and in mass spectroscopy of different masses while heating in air.

The TGA-MS of NbC$_{1-p}$N$_p$ 4 hrs 900 °C, shown in Figure 4.40 shows an interesting trend as well as following similar patterns to the TGA-MS of NbC$_{1-p}$N$_p$ 4 hrs 850 °C. It has a strong increase in C, N, NO, CO$_2$ and NO$_2$ and decrease in O$_2$ and O at 370 °C, corresponding to an exothermic event in the DSC. This suggests that the amorphous phase may contain both carbon and nitrogen and some or all of this phase may have decomposed at this temperature.
Figure 4.40: TGA-MS of NbC$_1$-pN$_p$ 4 hrs 900 °C, showing the changes in mass, heatflow and in mass spectroscopy of different masses while heating in air.

The TGA-MS of NbC$_1$-pN$_p$ 4 hrs 1000 °C shown in Figure 4.41, shows three exothermic events in the DSC. The first, at about 420 °C, displays a decrease in O$_2$ and O and just after an increase in C, N, NO, CO$_2$ and NO$_2$, possibly indicating the loss of amorphous carbon and nitrogen. The second exothermic event occurs at about 450 °C, where the gases change more gradually than the first event but have a similar trend. The final exothermic event happens at 575 °C where the mass decreases sharply.
where N and O decrease and C, O, NO, CO₂ and NO₂ increase. It is not clear if the N is due to fluctuations in the gas flow or an actual feature of the sample reacting.

The TGA-MS of NbC₁₋₇N₇p 4 hrs 1200 °C is shown in Figure 4.42, only two exothermic events are seen in the DSC. One peak at around 475 °C, with increasing C, N, NO, CO₂ and NO₂, and decreasing O₂ and O. The mass increasing indicates some of the
oxygen is being retained within the sample as the niobium oxidises. The second event happens at 500-550 °C, where mass increases sharply before plateauing and C, N, O, NO₂ and CO₂ increase and O and O₂ remain low before increasing back to the baseline. NO plateaus before decreasing back to the baseline, suggesting that there is nitrogen left in the sample before it fully oxidises to Nb₂O₅. The matches with the shift in XRD pattern shown in the thermodiffraactometry shown in Figure 4.34. The mass continues to decrease overtime suggesting it may not be fully oxidised to Nb₂O₅.
Figure 4.42: TGA-MS of NbC$_{1-p}$N$_p$ 4 hrs 1200 °C, showing the changes in mass, heatflow and in mass spectroscopy of different masses while heating in air.

The TGA-MS of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C is shown in Figure 4.43, in this sample the heatflow shows three exothermic events. The first at 300 °C gives an increase in N, O, NO and O$_2$, suggesting that an amorphous nitrogen based phase is oxidising off. The increase in O$_2$ could be due to a fragment of NO$_2$ or slight fluctuations in the gas flow. Just after this, the mass increases and both O and O$_2$ decrease suggesting the sample is taking up oxygen. The second exothermic event happens at 475 °C, the mass
spectrometry shows O₂ decreasing just before C, O and NO₂ increase, and NO increases just after at 525 °C. This corresponds with a plateau in the mass change before it decreases to the final mass. An almost identical trend is seen in the TGA-MS of Nb₀.₅Ti₀.₅C₁₋ₓNxPₓ 12 hrs 900 °C shown in Figure 4.44. This suggests that the nitrogen is last to leave the structure, and reiterates that the mixed metal samples have more nitrogen present in the carbonitride than NbC₁₋ₓNxPₓ made via this method. The third exothermic event occurs at 650 °C, which corresponds to a change in oxide phase seen in the thermodiffractometry.
Figure 4.43: TGA-MS of Nb0.5Ti0.5C1-pNp 4 hrs 900 °C, showing the changes in mass, heatflow and in mass spectroscopy of different masses while heating in air.
Figure 4.44: TGA-MS of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 12 hrs 900 °C, showing the changes in mass, heatflow and in mass spectroscopy of different masses while heating in air.

The TGA-MS of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 1200 °C shown in Figure 4.45 shows three exothermic events in the heatflow at 330 °C, 500 °C and 650 °C. Just before 330 °C, the mass of the sample is decreasing and the loss of some NO is observed. At 330 °C, O$_2$ and O decrease, and C, NO, CO$_2$ and NO$_2$ increase as the material starts to oxidise. The mass increase suggests that the sample is retaining oxygen and some of the carbon
and nitrogen forming an intermediate phase, which is known from thermodiffractometry to be amorphous. The second event at 500 °C shows a decrease in mass as C, O, NO, CO₂ and NO₂ increase, and O₂ and O decrease. The mass loss plateaus before C, NO, CO₂ and NO₂ increase with a peak at 650 °C as the sample reaches its final mass at 800 °C. This matches with the thermodiffractometry of this sample, but also suggests that the unknown phase shown in Figure 4.37 contains some nitrogen and carbon.
Figure 4.45: TGA-MS of Nb$_{0.5}$Ti$_{0.5}$C$_1$pN$_p$ 4 hrs 1200°C, showing the changes in mass, heatflow and in mass spectroscopy of different masses while heating in air.

4.8 CHN Analysis

CHN analysis was used to give carbon:nitrogen ratio of the samples. This was calculated by assuming all nitrogen was within the structure of the metal carbonitride. The amorphous carbon could therefore be calculated and is shown in Table 4.3. The hydrogen present within the samples was between 0.1-1.2 wt% and was assumed to
be from water content. The data shown in Figure 4.46 matches reasonably well with the Rietveld refinements from neutron diffraction.

Table 4.3: Analysis of the CHN data to give ratios of carbon:nitrogen for each metal.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Carbon</th>
<th>Nitrogen</th>
<th>Amorphous Carbon / wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbC_{1-p}N_p 12 hrs 700 °C</td>
<td>0.47</td>
<td>0.53</td>
<td>2.18</td>
</tr>
<tr>
<td>NbC_{1-p}N_p 4 hrs 850 °C</td>
<td>0.61</td>
<td>0.39</td>
<td>0.97</td>
</tr>
<tr>
<td>NbC_{1-p}N_p 4 hrs 900 °C</td>
<td>0.63</td>
<td>0.37</td>
<td>0.76</td>
</tr>
<tr>
<td>NbC_{1-p}N_p 4 hrs 1000 °C</td>
<td>0.67</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>NbC_{1-p}N_p 4 hrs 1200 °C</td>
<td>0.61</td>
<td>0.32</td>
<td>0</td>
</tr>
<tr>
<td>Nb_{0.5}Ti_{0.5}C_{1-p}N_p 4 hrs 900 °C</td>
<td>0.54</td>
<td>0.46</td>
<td>14.8</td>
</tr>
<tr>
<td>Nb_{0.5}Ti_{0.5}C_{1-p}N_p 12 hrs 900 °C</td>
<td>0.54</td>
<td>0.46</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Figure 4.46: Comparison of carbon:nitrogen ratio calculated from neutron refinement with CHN and TGA.

4.9 Surface Area Measurements

The surface area of NbC_{1-p}N_p and Nb_{0.5}Ti_{0.5}C_{1-p}N_p was measured using BET and these are shown in Figure 4.47. The Nb_{0.5}Ti_{0.5}C_{1-p}N_p made at different temperatures had high surface area. However, this is likely to be due to the high amounts of amorphous carbon present in the samples. The NbC_{1-p}N_p surface area decreased with increasing temperature of synthesis. This may be due to a combination of less amorphous carbon present and bigger crystallite size.
Figure 4.47: BET surface area of NbC$_{1-p}$N$_p$ and Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ made for 4 hours against temperature of synthesis.

4.10 XANES

XANES were recorded at the Nb K edge and Ti K edge on B18 Diamond Light Source, from pellets made from polyethylene and the sample. A range of reference samples were used to calculate the oxidation state from the edge shifts.

4.10.1 Ti XANES

Ti K edge XANES are shown in Figure 4.48 of the reference materials, the precursor phases Ti150 and NbTi150, and ammonium titanyl oxalate. This shows the change in edge position of the different samples as well as the pre-edge region. TiC$_{1-p}$N$_p$ materials and Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ materials Ti K edge XANES are shown in Figure 4.49. The edge position was recorded at 0.5 $\chi\mu(E)$ and can be seen in Figure 4.50, where the oxidation states for the references are used to create a line of best fit and the corresponding equation is used to calculate the oxidation state of the unknown oxidation state materials. The precursor materials Ti150 and TiNb150 show around the same oxidation state as the starting material ammonium titanyl (IV) oxalate. This shows that the titanium may change oxidation state slightly during the precursor reaction. It was found that the lower the temperature of synthesis the higher the oxidation state of Ti in the final product. This is thought to be due to the larger surface area in the lower temperature samples, meaning that more of the surface is oxidised.
increasing the average oxidation state of the entire sample. Due to the unusual combination of metallic, covalent and ionic bonding in transition metal carbides and nitrides the oxidation state is not well defined in the literature.\textsuperscript{12–16}

\textbf{Figure 4.48: Ti K edge XANES data of the Ti150 and TiNb150 precursor materials, ammonium titanyl oxalate (ATO) and the reference materials from B18 Diamond Light Source.}
Figure 4.49: Ti K edge XANES data of the titanium and mixed metal niobium titanium carbonitrides measured at B18 Diamond Light Source.

Figure 4.50: Calculated average titanium oxidation states from the XANES data measured at B18 Diamond Light Source.
4.10.2 Niobium XANES

Nb K edge XANES data are shown in Figure 4.51 for the reference materials, ammonium niobate(V) oxalate and the precursor materials Nb150 and NbTi150. This shows the different edge positions of the different materials XANES spectra. The NbC\textsubscript{1-p}N\textsubscript{p} and Nb\textsubscript{0.5}Ti\textsubscript{0.5}C\textsubscript{1-p}N\textsubscript{p} materials XANES data are shown in Figure 4.52, where the change in oxidation state is shown by a shift in the edge position at 0.5 $\chi\mu(E)$. This oxidation state is quantified in Figure 4.53, where the references edge position is used with their known oxidation states to create a line of best fit. This is then used to calculate the average oxidation state of the unknown materials. The lower the temperature of synthesis the higher the oxidation state, which corresponds with the higher the surface area the more surface is oxidised.

As mentioned previously, the unusual combination of metallic, covalent and ionic bonding in transition metal carbides and nitrides the oxidation state is not well defined in the literature\textsuperscript{12–15,43,44}. The covalent component of the bonding is stronger in the carbide and weaker in the nitride, this decrease in covalency is accompanied by an increase in ionicity. This can make the nitride materials less stable than the corresponding carbide\textsuperscript{15,43–45}.

![Figure 4.51: Nb K edge XANES data of the niobium references, ammonium niobate (V) oxalate and the Nb150 and NbTi150 precursor materials measured at B18 Diamond Light source.](image-url)
Figure 4.52: Nb K edge XANES data of the NbC$_{1-p}$N$_p$ and Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ materials measured at B18 Diamond Light source.

Figure 4.53: Calculated average niobium oxidation states from the XANES data measured at B18 Diamond Light Source.
4.10.3 Heating in-situ XANES

Samples of metal carbonitride were mixed with boron nitride and placed in a capillary with two glass wool bungs and a thermocouple. For the measurements in air the ends were left open, the capillary was placed in the line of the X-ray beam in a furnace as shown in Figure 4.54. The temperature and XANES were recorded as the samples were heated at 10 °C/min with scans recording every 50 °C to 700 °C. The measurements were recorded on B18 Diamond Light Source, at the Nb K edge in transmission mode.

![Figure 4.54: Thermal setup on B18 Diamond Light Source.](image)

The Nb K edge data was recorded whilst heating sample NbC_{1-p}N_p 4 hrs 900 °C to 700 °C as shown in Figure 4.55. The aim was to mimic the TGA discussed earlier to try to understand the decomposition process. The sample shows an increase in oxidation state with increasing temperature. Reference materials were used in Figure 4.56 to calculate the average oxidation states across the sample. It was found that the oxidation did not reach completion in this experiment, suggesting that a temperature higher than 700 °C is required for oxidation to Nb_2O_5. The change in oxidation state is plotted alongside the TGA-DSC for NbC_{1-p}N_p 4 hrs 900 °C in Figure 4.57. The oxidation state increases from 300 °C, suggesting that any other changes in mass before this are because of water or amorphous carbon burning off. It then increases until it plateaus at 500-550 °C before increasing again at 600 °C to what is thought to be the final mass. At the highest temperature the average oxidation state is thought to be +4. However, it is possible full oxidation does not occur by this temperature. The sample NbC_{1-p}N_p 4 hrs 900 °C was heated to 1000 °C in air and cooled. This was made into a pellet and Nb K edge XANES were recorded. This showed that the sample does fully oxidise to
It may be that the conditions under which the sample was heated on the beamline were not as oxidising as those of the TGA.

Figure 4.55: Nb K edge XANES data measured while heating niobium carbonitride sample (NbC1-pNp 4 hrs 900 °C) in air to 700 °C and this same sample heated to 1000 °C in air and cooled.
Figure 4.56: Calculated average niobium oxidation states while heating niobium carbonitride sample (NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C) in air to 700 °C and this same sample heated to 1000 °C in air and cooled.

Figure 4.57: Calculated average niobium oxidation states and edge energy while heating niobium carbonitride sample (NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C) in air to 700 °C, with TGA-DSC for comparison.
The Nb K edge XANES were recorded for Nb_0.5Ti_0.5C_1-\_pN_p 4 hrs 900 °C sample while heating to 700 °C in air, as shown in Figure 4.58. The higher the temperature the further the shift in the edge position, with the after heating sample position being most shifted. The oxidation state was calculated using reference materials of a known oxidation state, these can be seen in Figure 4.59 with the calculated oxidation states of the Nb_0.5Ti_0.5C_1-\_pN_p 4 hrs 900 °C sample as it was heated and after. After cooling the sample increases oxidation state suggesting that if this had been done for the NbC_1-\_pN_p 4 hrs 900 °C sample it may have had a higher oxidation state after cooling. In Figure 4.60 the oxidation state is plotted with the TGA-DSC. Here the niobium reaches its maximum oxidation state at 400 °C. At 400 °C the mass is at it is highest, this suggests an intermediate exists with some carbon and nitrogen still present while the niobium has a +5 oxidation state. Attempts were made to measure the Ti K edge for the same sample, but the data quality were not good enough due to the intensity being affected at the lower energy absorption edge by the quartz capillary, boron nitride and niobium in the sample. Difficulties collecting these data were also caused by the expansion of the sample as the sample oxidises, and pockets of gas forming within the capillary.
Figure 4.58: Nb K edge XANES data measured while heating niobium titanium carbonitride sample ($\text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_p$ 4 hrs 900 °C) in air to 700 °C and after heating at room temperature.
Figure 4.59: Calculated average niobium oxidation states while heating niobium titanium carbonitride sample (Nb$_{0.5}$Ti$_{0.5}$C$_1$N$_p$ 4 hrs 900 °C) in air to 700 °C.

Figure 4.60: Calculated average niobium oxidation states and edge energy while heating niobium titanium carbonitride sample (Nb$_{0.5}$Ti$_{0.5}$C$_1$N$_p$ 4 hrs 900 °C) in air to 700 °C with TGA-DSC for comparison.
In order to investigate the intermediate phase, samples from oxidation of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C at 650 °C and 1000 °C were made into pellets and recorded at the Nb K edge and Ti K edge. Figure 4.61 shows the edge positions of the niobium samples and Figure 4.62 shows the calculated average niobium oxidation state. It was found that the intermediate phase at 650 °C appears to have a similar niobium average oxidation state to the final oxidation state at 1000 °C. Figure 4.63 shows the titanium edge positions of the samples and the reference materials and Figure 4.64 shows the calculated average titanium oxidation state, which is the same for the 650 °C sample and the 1000 °C sample. This shows that the material made at 650 °C has the same oxidation state and is probably a rearrangement of structure as opposed to a different composition.

![Figure 4.61: Nb K edge XANES data measured at B18 Diamond Light Source, of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C and the same sample heated to either 650 °C or 1000 °C and cooled to room temperature.](image)
Figure 4.62: Calculated average niobium oxidation states from the Nb K edge XANES data measured at B18 Diamond Light Source, of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C and the same sample heated to either 650 °C or 1000 °C and cooled to room temperature.

Figure 4.63: Ti K edge XANES data measured at B18 Diamond Light Source, of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C and the same sample heated to either 650 °C or 1000 °C and cooled to room temperature.
Figure 4.64: Calculated average titanium oxidation states from the Ti K edge XANES data measured at B18 Diamond Light Source, of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C and the same sample heated to either 650 °C or 1000 °C and cooled to room temperature.

4.11 EXAFS

4.11.1 Nb K edge EXAFS

Nb K edge EXAFS were recorded of pellets of sample bound together with polyethylene on B18 Diamond Light Source. The data were normalised and calibrated to the reference channel using Athena. In order to fit the data, Artemis was used. The NbC crystal structure of Will and Platzbecker$^{11}$ was used for the initial Feff calculation. Due to the cubic nature of the $Fm\bar{3}m$ structure, it was possible to define all path lengths as $\Delta R = \alpha \cdot R_{eff}$, where $\alpha$ is the volumetric expansion coefficient. The mean square variation in path length ($\sigma^2$) was defined in terms of ssC1 and ssNb1, which were refined.

Goodness of fit was determined by the R-factor, the smaller the number the better. The amplitude reduction factor should be less than or equal to 1.1, ideally between 0.7-1. The mean square variation in path length ($\sigma^2$) encapsulates both static and thermal disorder, this should be positive and ideally small. $E_0$ should not be less than -10 eV or greater than 10 eV.
The fit for NbC$_{1-p}$N$_p$ 4 hrs 850 °C can be seen in Figure 4.65 and the refined parameters can be seen in Table 4.4. The fit is relatively good but there is a slight shift in the fit and data for the first peak in the radial distance at 1.8 Å. The slightly longer length of scattering path here suggests the presence of some Nb$_2$O$_5$. The volumetric expansion coefficient is negative suggesting the unit cell of NbC$_{1-p}$N$_p$ is contracted from the NbC from the literature, which means shorter bond lengths. These shorter scattering paths shown in Table 4.4, suggest that nitrogen is present, shrinking the unit cell size.

![Figure 4.65: Nb K edge EXAFS of NbC$_{1-p}$N$_p$ 4 hrs 850 °C sample collected from Diamond Light Source B18. (R-factor=0.18397, $S_0^2=0.64(16)$, $E_0=-6.35$ eV and alpha=-0.006(4))](image)

Table 4.4: Structure parameters fitted against the Nb K edge EXAFS of NbC$_{1-p}$N$_p$ 4 hrs 850 °C sample.

<table>
<thead>
<tr>
<th>Name</th>
<th>$N$</th>
<th>$\sigma^2 / \AA^2$</th>
<th>$R_{\text{eff}} / \AA$</th>
<th>$R / \AA$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1.1</td>
<td>6</td>
<td>0.0062(9)</td>
<td>2.23430</td>
<td>2.221(9)</td>
</tr>
<tr>
<td>Nb1.1</td>
<td>12</td>
<td>0.00875</td>
<td>3.15980</td>
<td>3.140(13)</td>
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<tr>
<td>C1.1 Nb1.1</td>
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<td>0.01056</td>
<td>3.81420</td>
<td>3.791(15)</td>
</tr>
<tr>
<td>C1.2</td>
<td>8</td>
<td>0.01071</td>
<td>3.86990</td>
<td>3.846(15)</td>
</tr>
<tr>
<td>Nb1.2</td>
<td>6</td>
<td>0.01237</td>
<td>4.46860</td>
<td>4.441(18)</td>
</tr>
<tr>
<td>C1.1 Nb1.2</td>
<td>12</td>
<td>0.01237</td>
<td>4.46860</td>
<td>4.441(18)</td>
</tr>
<tr>
<td>C1.1</td>
<td>6</td>
<td>0.01237</td>
<td>4.46860</td>
<td>4.441(18)</td>
</tr>
<tr>
<td>C1.1 Nb1.2 C1.1</td>
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<td>0.01237</td>
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<td>4.441(18)</td>
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<td>48</td>
<td>0.01282</td>
<td>4.63200</td>
<td>4.604(19)</td>
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</table>
The NbC$_{1-p}$N$_p$ 4 hrs 900 °C EXAFS shown in Figure 4.66 shows an improved fit in comparison to the NbC$_{1-p}$N$_p$ 4 hrs 850 °C EXAFS, shown by a lowered R-factor. The volume expansion coefficient is about the same as NbC$_{1-p}$N$_p$ 4 hrs 850 °C, suggesting the same amount of carbon and nitrogen are present within the samples.

![Graph showing NbK edge EXAFS of NbC$_{1-p}$N$_p$ 4 hrs 900 °C sample](image)

*Figure 4.66: Nb K edge EXAFS of NbC$_{1-p}$N$_p$ 4 hrs 900 °C sample collected from Diamond Light Source B18. (R-factor=0.16064, S$_0^2$=0.75(19), $E_0=-6.82$ eV and alpha=-0.006(4))

<table>
<thead>
<tr>
<th>Name</th>
<th>N</th>
<th>$\sigma^2$ / Å$^2$</th>
<th>R$_{eff}$ / Å</th>
<th>R / Å</th>
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<td>2.220(9)</td>
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<td>0.00994</td>
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<td>3.790(15)</td>
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<tr>
<td>C1.2</td>
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<td>3.86990</td>
<td>3.846(15)</td>
</tr>
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<td>0.01165</td>
<td>4.46860</td>
<td>4.441(18)</td>
</tr>
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</tr>
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<td>0.01207</td>
<td>4.63200</td>
<td>4.603(19)</td>
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NbC$_{1-p}$N$_p$ 4 hrs 1000 °C EXAFS shown in Figure 4.67, show an improved fit from the lower temperature synthesis samples with a lower R-factor. The volume expansion coefficient is slightly higher at -0.005(4), suggesting slightly more carbon may be present in this sample. The fit parameters are shown in Table 4.6, the path lengths are decreased from the original structure.

![Figure 4.67: Nb K edge EXAFS of NbC$_{1-p}$N$_p$ 4 hrs 1000 °C sample collected from Diamond Light Source B18. (R-factor=0.15413, $S_0^2=0.8(2)$, $E_0=-5.471$ eV and alpha=-0.005(4))](image)

<table>
<thead>
<tr>
<th>Name</th>
<th>N</th>
<th>$\sigma^2 / \text{Å}^2$</th>
<th>Reff / Å</th>
<th>R / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1.1</td>
<td>6</td>
<td>0.0053(9)</td>
<td>2.23430</td>
<td>2.224(9)</td>
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<td>Nb1.1</td>
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<td>3.145(13)</td>
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<td>3.81420</td>
<td>3.796(15)</td>
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<tr>
<td>C1.2</td>
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<td>3.851(15)</td>
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<td>Nb1.2</td>
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<td>0.01056</td>
<td>4.46860</td>
<td>4.447(18)</td>
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<tr>
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<td>0.01056</td>
<td>4.46860</td>
<td>4.447(18)</td>
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<tr>
<td>C1.1</td>
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<td>0.01056</td>
<td>4.46860</td>
<td>4.447(18)</td>
</tr>
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<td>C1.1 Nb1.2 C1.1</td>
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<td>0.01056</td>
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<td>4.447(18)</td>
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<td>0.01095</td>
<td>4.63200</td>
<td>4.610(19)</td>
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NbC_{1-p}N_p 4 hrs 1200 °C EXAFS shown in Figure 4.68, show an improved fit from the lower temperature synthesis samples with a lower R-factor apart from the 1000 °C sample. The volume expansion coefficient is the same at -0.005(4), suggesting the same amount of carbon is present in this sample. The fit parameters are shown in Table 4.7, the path lengths are decreased from the original structure.

Figure 4.68: Nb K edge EXAFS of NbC_{1-p}N_p 4 hrs 1200 °C sample collected from Diamond Light Source B18. (R-factor=0.15865, S_0^2=0.8(2), E_0=-5.704 eV and alpha=-0.005(4))

Table 4.7: Structure parameters fitted against the Nb K edge EXAFS of NbC_{1-p}N_p 4 hrs 1200 °C sample.

<table>
<thead>
<tr>
<th>Name</th>
<th>N</th>
<th>\sigma^2 / Å^2</th>
<th>R_{eff} / Å</th>
<th>R / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1.1</td>
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<td>0.0056(9)</td>
<td>2.23430</td>
<td>2.223(9)</td>
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<td>3.795(15)</td>
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<tr>
<td>C1.2</td>
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<td>3.86990</td>
<td>3.851(15)</td>
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<tr>
<td>Nb1.2</td>
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<td>0.01113</td>
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<td>4.46860</td>
<td>4.446(18)</td>
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<tr>
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<td>0.01113</td>
<td>4.46860</td>
<td>4.446(18)</td>
</tr>
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<td>0.01154</td>
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<td>4.609(19)</td>
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</table>
Table 4.8 summarises the results of the NbC$_{1-p}$N$_p$ materials EXAFS fits. It was found that there is only small variation across the samples and the volumetric expansion coefficient changes very little across the samples. Like the neutron diffraction Rietveld fits, the best fit is NbC$_{1-p}$N$_p$ 4 hrs 1000 °C. The samples show little evidence of a secondary phase being present containing niobium. The lowest temperature sample NbC$_{1-p}$N$_p$ 4 hrs 850 °C shows slight variation in the placement of the first shell, but this due to having more oxide present at the surface than the other samples.

Table 4.8: Nb K edge EXAFS NbC$_{1-p}$N$_p$ materials summary of parameters. (*volumetric expansion coefficient)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_0^2$</th>
<th>$E_0$ / eV</th>
<th>$\alpha^*$</th>
<th>R-factor</th>
<th>N</th>
<th>$\sigma^2$ / Å$^2$</th>
<th>Reff / Å</th>
<th>R / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 850 °C</td>
<td>0.64(16)</td>
<td>-6.35</td>
<td>-0.006(4)</td>
<td>0.18387</td>
<td>6</td>
<td>0.0062(9)</td>
<td>2.2343</td>
<td>2.221(9)</td>
</tr>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 900 °C</td>
<td>0.75(19)</td>
<td>-6.82</td>
<td>-0.006(4)</td>
<td>0.16064</td>
<td>6</td>
<td>0.0058(9)</td>
<td>2.2343</td>
<td>2.220(9)</td>
</tr>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 1000 °C</td>
<td>0.79(20)</td>
<td>-5.47</td>
<td>-0.005(4)</td>
<td>0.15413</td>
<td>6</td>
<td>0.0053(9)</td>
<td>2.2343</td>
<td>2.224(9)</td>
</tr>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 1200 °C</td>
<td>0.76(20)</td>
<td>-5.70</td>
<td>-0.005(4)</td>
<td>0.15865</td>
<td>6</td>
<td>0.0056(9)</td>
<td>2.2343</td>
<td>2.223(9)</td>
</tr>
</tbody>
</table>

4.12 XPS

4.12.1 Niobium carbonitrides

X-ray Photoelectron Spectroscopy (XPS) was used to study the surface of the materials. XPS can be used to determine the elemental ratios at the surface of a sample and to determine the other elements they are bonded to. A survey spectrum is recorded to determine all elements present and elements of interest are analysed further. The elemental percentages for the NbC$_{1-p}$N$_p$ materials are shown in Figure 4.69. This shows that there is the more oxygen present for the lower temperature synthesis samples, which agrees well with the XANES data. The amount of niobium decreases with increasing synthesis temperature, but for NbC$_{1-p}$N$_p$ 4 hrs 1200 °C it increases. This sample also shows an increase in nitrogen content, where the other samples are decreasing. This suggests that the surface of this sample maybe different to that of the lower temperature samples.
Figure 4.69: Elemental ratios calculated from XPS of the NbC₁₋₃N₃ samples.

The niobium 3d spectra is assigned in Figure 4.70. It shows increasing amounts of NbC/NbN present in the sample with increasing reaction temperature and shows a small amount of NbO₂ or oxidised NbN is present. Nb₂O₅ is present at the surface for all the NbC₁₋₃N₃ samples and decreases with increasing temperature of synthesis. The carbon 1s region XPS is shown in Figure 4.71. It indicates all NbC₁₋₃N₃ samples have amorphous carbon at the surface, and the presence of O=C-O bonding, suggesting carbonate at the surface. There is increasing amounts of NbC present with increasing temperature of synthesis.
Figure 4.70: Nb 3d XPS of NbC<sub>1-p</sub>N<sub>p</sub> samples made with various reaction conditions.

Figure 4.71: C 1s XPS of NbC<sub>1-p</sub>N<sub>p</sub> samples made with various reaction conditions.
The N 1s region XPS for NbC\textsubscript{1-p}N\textsubscript{p} is shown in Figure 4.72, which shows the presence of NbN, oxidised NbN and organic N. There are increasing amounts of NbN with lower temperature of synthesis of the NbC\textsubscript{1-p}N\textsubscript{p} materials. There are also increasing amounts of oxidised NbN with increasing synthesis temperature. NbC\textsubscript{1-p}N\textsubscript{p} 12 hrs 700 °C shows the most amount of organic N, which corresponds with the TGA calculations. However, this suggests that the materials contain a mixture of amorphous carbon and nitrogen. Due to the similar molecular masses of carbon and nitrogen, the calculations would change minutely, and the CHN analysis accounts for some of this issue. Therefore, the most accurate way to calculate the C:N ratio within the samples is Rietveld refinements of the neutron diffraction shown previously.

The O 1s region XPS of NbC\textsubscript{1-p}N\textsubscript{p} is shown in Figure 4.73. It shows C=O, C-O, metal oxides and either H\textsubscript{2}O or organic O are present in all the NbC\textsubscript{1-p}N\textsubscript{p} samples. The presence of C=O and C-O suggests that carbonate maybe present at the surface. Metal oxide is expected at the surface of all these materials, due to its unstable nature in air, and this passivated layer allows it to be stable. Some surface water may be present depending on how long the sample has been made, as previously seen the samples appear to gain some water over time. Alternatively, the oxygen for either H\textsubscript{2}O or organic O could be part of the carbonate.
Figure 4.72: N 1s XPS of NbC$_{1-p}$N$_p$ samples made with various reaction conditions.

Figure 4.73: O 1s XPS of NbC$_{1-p}$N$_p$ samples made with various reaction conditions.
A summary of the compositions calculated from the different elemental XPS of NbC$_{1-p}$N$_p$ are shown in Figure 4.74. There is more presence of Nb$_2$O$_5$ with decreasing temperature of synthesis, which matches with the average niobium oxidation state from the XANES data. Therefore, there is more NbC/NbN present with increasing synthesis temperature. There is increasing amorphous carbon, organic nitrogen and metal oxide present with decreasing temperature of synthesis.

4.12.2 Niobium titanium carbonitride

XPS was used to analyse the surface of the Nb$_{0.5}$Ti$_{0.5}$C$_1$N$_p$ materials. Regions of Nb 3d, Ti 2p, C 1s, N 1s and O 1s, were observed and analysed. The Nb 3d region shown in Figure 4.75, shows all three samples have large amounts of Nb$_2$O$_5$ at the surface.
with Nb_{0.5}Ti_{0.5}C_{1-p}N_{p} 4 hrs 1200 °C sample having the least. This sample also has a large amount of NbC/NbN. All of the samples have some either oxidised NbN or NbO_2. The Ti 2p region shown in Figure 4.76, shows TiO_2, TiC and Ti(III) in all samples. The composition is mainly of TiO_2 but some TiC and Ti(III) is also present. The most TiC is present in Nb_{0.5}Ti_{0.5}C_{1-p}N_{p} 4 hrs 1200 °C.

![Graph of Nb 3d XPS of Nb_{0.5}Ti_{0.5}C_{1-p}N_{p} samples made with various reaction conditions.](image)

*Figure 4.75: Nb 3d XPS of Nb_{0.5}Ti_{0.5}C_{1-p}N_{p} samples made with various reaction conditions.*
Figure 4.76: Ti 2p XPS of Nb_{0.5}Ti_{0.5}C_{1-p}N_p samples made with various reaction conditions.

The XPS C 1s region, shown in Figure 4.77, shows amorphous carbon is present in all samples, and shows C-C/C-H on TiO_2 is also present. There is very little NbC present in any of the samples, but O=C=O is present in all the samples indicating a carbonate – like structure at the surface.

The N 1s XPS shown in Figure 4.78, shows organic N, oxidised NbN, NbN and N-O are present in all the samples. The highest temperature synthesis has the least NbN suggesting that NbC is made preferentially over NbN at higher temperature. The presence of organic N in all the samples suggests that a mixture of amorphous carbon and nitrogen is made at the surface of these materials.

The O 1s XPS shown in Figure 4.79 shows all samples have metal oxide, O-C, organic O / H_2O and O=C. This again suggests the formation of carbonate – like material at the surface as well as the expected metal oxides.
Figure 4.77: C 1s XPS of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ samples made with various reaction conditions.

Figure 4.78: N 1s XPS of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ samples made with various reaction conditions.
Figure 4.79: O 1s XPS of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ samples made with various reaction conditions.

Elemental analysis by XPS and the elemental regions compositions are shown in Figure 4.80. The samples show little difference across the regions other than slightly less Nb$_2$O$_5$ in the high temperature synthesis. The elemental composition is dominated by carbon and oxygen, suggesting that oxides and amorphous carbon account for a large amount of the surface structure.
Figure 4.80: Summary of the elemental percentage and the regions of fitted XPS of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_{p}$ 4 hrs 900 °C, Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_{p}$ 12 hrs 900 °C and Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_{p}$ 4 hrs 1200 °C.
4.13 Powder Conductivity

The powder conductivities of NbC$_{1-p}$N$_p$, Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ and TiC$_{1-p}$N$_p$ are shown in Figure 4.81. The NbC$_{1-p}$N$_p$ shows increasing conductivity with increasing temperature of synthesis. NbC$_{1-p}$N$_p$ 12 hrs 700 °C gave a conductivity of 0.01 S cm$^{-1}$, which is quite low and is lower than the optimum conductivity (0.1 S cm$^{-1}$) for application as a catalyst support in PEMFCs. All other niobium carbonitrides have higher than 1 S cm$^{-1}$ conductivity. The TiC$_{1-p}$N$_p$ 4 hrs 900 °C material has a conductivity of 0.65 S cm$^{-1}$, despite the large amount of amorphous carbon present in the sample. The Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C samples gave conductivities of around 0.8 S cm$^{-1}$ making them suitable for application. The Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 1200 °C sample gave a conductivity of about 1.5 S cm$^{-1}$, which is also suitable for application.

![Figure 4.81: Powder conductivity of NbC$_{1-p}$N$_p$, Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ and TiC$_{1-p}$N$_p$ made at different temperatures for 4 hours, apart from the 700 °C sample which was made for 12 hours.](image)

4.14 Conclusions

Niobium carbonitrides have been made via a low temperature synthesis using a guanidine carbonate based method and a nitrogen gas flow. The resulting NbC$_{1-p}$N$_p$ materials have been analysed by powder XRD, neutron diffraction, neutron PDF analysis, TEM with EDXA, TGA-DSC, thermodiffactometry, TGA-MS, CHN, BET surface area, XANES, EXAFS, XPS and powder conductivity. The materials have an
average cubic rock salt structure with a space group of $Fm\bar{3}m$. From PDF analysis the materials are shown to be highly ordered. The materials are shown to have a niobium oxide layer present at the surface and the lower the temperature of synthesis the larger this layer is, which may be due to the increased surface area and decreased crystallite size of these materials. The lower temperatures of synthesis also produce materials with increasing amounts of amorphous carbon. Further work could be performed to remove this impurity. Attempts were made to decarburise the materials, but oxidation of the niobium carbonitride readily occurred. The materials have good powder conductivity and have reasonable surface area for the materials made at or below 900 °C. These properties make them useful as potential catalyst supports and further work is performed on their acid resilience and electrochemical properties in Chapter 6.

Titanium carbonitrides were successfully made via a low temperature guanidine carbonate method, under a flow of nitrogen. These materials were analysed by powder XRD, TGA-DSC and XANES. The materials showed larger quantities of amorphous carbon (45-51 wt%) than the niobium materials, and had average titanium oxidation states of between +3-3.6. This suggests that the materials had large layers of TiO$_2$ present at the surface of the material. The titanium carbonitrides proved more complicated to make and oxidised more readily than the niobium carbonitrides. Further work could performed to modify the synthesis further or to treat the as made material to remove the amorphous carbon.

Mixed metal niobium titanium carbonitrides were made using a low temperature guanidine carbonate method under the flow of nitrogen. The $\text{Nb}_{1-q}\text{Ti}_q\text{C}_{1-p}\text{N}_p$ materials were analysed by powder XRD, neutron diffraction, neutron PDF analysis, TEM with EDXA, TGA-DSC, TGA-MS, CHN, XANES, XPS and conductivity. The materials contained more amorphous carbon (20-30 wt%) than the niobium carbonitrides. The TEM showed the titanium and niobium are evenly distributed across the sample and combined with XRD and neutron diffraction suggests a solid solution has been formed. The neutron diffraction and PDF show a secondary phase present, which is believed to be a form of carbon. The XANES suggest average oxidation states of +3.2-3.5 for titanium and +2.8-3.3 for niobium. The slightly lower oxidation state for niobium could be due to titanium more readily oxidising. XPS suggests that more of the surface is TiO$_2$ than Nb$_2$O$_5$, which supports this. The materials have shown good conductivity and high surface areas suitable for application in PEMFCs. Therefore,
these materials were further tested for acid resilience and electrochemical stability, and the results will be presented in Chapter 6.

4.15 References


Chapter 5 – Exploratory synthesis of other materials

5.1 Introduction and Scope of the Chapter

This chapter describes how the synthesis found in Chapter 4, for titanium carbonitrides and mixed metal niobium titanium carbonitrides, can be used for making other materials. The first section focuses on materials made by removing guanidine carbonate from the niobium titanium carbonitride synthesis, which forms titanium niobium oxides. The reactions of ammonium metal oxalates with varying ratios of guanidine carbonate, were then investigated to potentially produce an entire range of metal and mixed metal carbonitrides.

5.2 Titanium niobium oxides

5.2.1 Introduction

Titanium dioxide has been reported by Sahasrabudhe et al. to increase in conductivity by a million fold through a 3 % incorporation of niobium.\(^1\) Titanium dioxide is inexpensive, chemically stable and a wide band gap semiconductor,\(^1-7\) with a conductivity of \(10^{-7} \text{ S cm}^{-1}\).\(^1\) Titanium dioxide is commonly substituted with niobium in order to improve the electrical conductivity of the material.\(^1,5,8-18\) Sahasrabudhe et al. found a conductivity of \(30 \text{ S cm}^{-1}\) could be reached by substitution of 3 % niobium.\(^1\) However, these materials required heat intensive synthesis. \(\text{Nb}_2\text{O}_5\) and \(\text{TiO}_2\) were ground together and treated at 1000 °C in a tube furnace flowing 5% \(\text{H}_2\) in argon. Grinding and heating processes were repeated until a rutile phase pure material was formed.\(^1\) These high temperature syntheses would produce materials with low surface area.

Other methods of synthesis involve using a template, which is later removed at 500 °C under argon, the material is then heated under hydrogen to between 850 – 1050 °C.\(^{13}\) This produced materials with high surface areas of 75 – 115 \(\text{m}^2\text{g}^{-1}\), but impurities of \(\text{Ti}_4\text{O}_7\) were found in the rutile phase formed at 850 °C.\(^{13}\) A method by Huang et al. involves a template assisted method in ethanol, which is later heated under hydrogen to between 400 – 900 °C. Huang found that lower temperature of synthesis gave anatase and higher than 700 °C gave the rutile structure. The samples made above 700 °C had a surface area of less than 10 \(\text{m}^2\text{g}^{-1}\).\(^{14}\) Morris et al. used a high temperature...
synthesis to form rutile Ti$_{1-x}$Nb$_x$O$_2$ by grinding together NbO$_2$ and TiO$_2$ and firing them at 650 °C for 24 hours and then 950 °C for 48 hours.$^{17}$

Overall these syntheses are complicated and produce low surface area materials if rutile phase and pure. However, these materials have shown promise for the use of catalyst supports in PEM fuel cells.$^{9,13,14}$ Bauer et al. found improved electrochemical ORR stability in comparison to commercially available Pt/C catalyst.$^9$ Cyclic voltammetry showed no significant degradation of the Pt active area over the course of 1000 cycles, in comparison to conventional carbon supports, which lost nearly half of the active area.$^9$ The ORR mass specific activity decreased by 9-15% for the Nb-TiO$_2$ supported Pt catalysts, whereas half the mass specific activity was lost for the carbon supported Pt catalysts.$^9$

Huang et al. found that Pt/Ti$_{1-x}$Nb$_x$O$_2$ (x=0.25) made at 700 °C via a template based method with a surface area of 10 m$^2$g$^{-1}$ showed nearly 10 fold higher ORR activity after potential cycling tests when compared to the Pt/C catalyst.$^{14}$ The Pt/C catalyst showed no activity after 1000 cycles due to sever carbon corrosion. Whereas Pt/Ti$_{1-x}$Nb$_x$O$_2$ showed only a small loss even after 3000 cycles.$^{14}$

This material is of interest due to these potential properties for the use in PEMFCs. This section focuses on the synthesis and characterisation of Ti$_{1-x}$Nb$_x$O$_2$ materials.

### 5.2.2 Synthesis

Various ratios of ammonium niobate (V) oxalate and ammonium titanyl oxalate were macerated in a pestle and mortar before heating in a tube furnace under nitrogen for 4 hours at 900 °C. This produced dark blue powders which were then ground and analysed.

### 5.2.3 Powder XRD

Powder XRD Pawley fits of Ti$_x$Nb$_{1-x}$O$_2$ are shown in Figure 5.1, where the data are fitted to the $P4_2/mnm$ space group. The fitted Pawley lattice parameters are shown in Figure 5.2 and the unit cell volume in Figure 5.3. The lattice parameters $a$ and $c$ both decrease with increasing titanium content, as does the unit cell volume, these match well with the literature values.$^{19-21}$ The presence of a second phase can be observed by a broad Bragg peak at ~41 °, in most of the materials corresponding to the cubic $Fm\bar{3}m$ space group, suggesting the presence of some Nb$_{1-q}$Ti$_q$C$_{1-p}$N$_p$. 


Figure 5.1: Pawley fits of powder XRD of Ti$_x$Nb$_{1-x}$O$_2$ made at 900 °C for 4 hours, showing the calculated lattice parameters for tetragonal P4$_2$/mmm.
Figure 5.2: Pawley fit parameters of $\text{Ti}_x\text{Nb}_{1-x}\text{O}_2$ made at 900 °C for 4 hours compared with values taken from the literature, error bars are too small to see.\textsuperscript{19–21}

Figure 5.3: Pawley fit volumes of $\text{Ti}_x\text{Nb}_{1-x}\text{O}_2$ made at 900 °C for 4 hours compared with values taken from the literature, error bars are too small to see.\textsuperscript{19–21}
5.2.4 XANES
The Nb K edge XANES data shown in Figure 5.4, shows the change in edge position of three of the Ti$_x$Nb$_{1-x}$O$_2$ materials compared to reference materials. The edge position is then plotted against oxidation state for the reference materials with known oxidation state to give the trendline shown in Figure 5.5. This is then used to calculate the average niobium oxidation state of the materials. Both Ti$_{0.95}$Nb$_{0.05}$O$_2$ and Ti$_{0.9}$Nb$_{0.1}$O$_2$ have similar niobium average oxidation states of around +4.5. It was expected that the materials would have a niobium oxidation state of around +5 from work by Bhachu et al.\textsuperscript{15} and the titanium is expected to compensate by forming titanium +3. Higher substitution levels of niobium can lead to the formation of Nb$^{4+}$ as well.\textsuperscript{15} However, the presence of some Nb$_{1-q}$Ti$_q$C$_{1-p}$N$_p$ would lower the expected oxidation state. The average niobium oxidation state for Ti$_{0.18}$Nb$_{0.72}$O$_2$ was found to be around +4, indicating this material is more like NbO$_2$.

![Graph showing Nb K edge XANES data of Ti$_x$Nb$_{1-x}$O$_2$ and reference materials, Nb foil, NbO$_2$ and Nb$_2$O$_5$, from B18 Diamond Light Source.](image)

*Figure 5.4: Nb K edge XANES data of Ti$_x$Nb$_{1-x}$O$_2$ and reference materials, Nb foil, NbO$_2$ and Nb$_2$O$_5$, from B18 Diamond Light Source.*
Figure 5.5: Calculated average niobium oxidation states of Ti<sub>x</sub>Nb<sub>1-x</sub>O<sub>2</sub> from the XANES data measured at B18 Diamond Light Source.

The Ti K edge XANES shown in Figure 5.6, shows the spectra change for different amounts of substitution in Ti<sub>x</sub>Nb<sub>1-x</sub>O<sub>2</sub>, compared to reference materials. The edge position of the reference materials were then used to calculate the average Ti oxidation state as shown in Figure 5.7. Both Ti<sub>0.9</sub>Nb<sub>0.1</sub>O<sub>2</sub> and Ti<sub>0.95</sub>Nb<sub>0.05</sub>O<sub>2</sub> show the same average titanium oxidation state of +3.8. This matches with the average niobium oxidation state of +4.5 to give average oxidation state of the metal of +4. This suggests that some of the titanium is in +3 and +4 oxidation states and niobium is in +5 and +4 oxidation state.

Ti<sub>0.28</sub>Nb<sub>0.72</sub>O<sub>2</sub> gives an average titanium oxidation state of +3.6. This is lower than expected with the niobium average oxidation state being +4 but gives around +3.89 average oxidation state for the metal in the rutile structure, which could suggest some oxygen deficiencies in the structure. Liu et al. found that with substitution of above 20 % of niobium the material had reduced forms of both titanium and niobium, Ti<sup>3+</sup> and Nb<sup>4+</sup>, as well as Ti<sup>4+</sup> and Nb<sup>5+</sup>.
Figure 5.6: Ti K edge XANES data of Ti$_x$Nb$_{1-x}$O$_2$ and reference materials, TiO$_2$ and Ti$_2$O$_3$, from B18 Diamond Light Source.

Figure 5.7: Calculated average titanium oxidation states of Ti$_x$Nb$_{1-x}$O$_2$ from the XANES data measured at B18 Diamond Light Source.
5.2.5 Conductivity and surface area

The powder conductivity was measured of various Ti$_{x}$Nb$_{1-x}$O$_2$ materials and the results are shown in Figure 5.8. The conductivity is low for all the samples in comparison to the 0.1 S cm$^{-1}$ requirement for the catalyst support application in PEM fuel cells. However, TiO$_2$ gives a conductivity of less than $1 \times 10^{-6}$ S cm$^{-1}$ via this method, so substitution of even $(1 - x) = 0.05$ (Ti$_{x}$Nb$_{1-x}$O$_2$) gives an increase of 1000 times conductivity. Sahasrabudhe et al. suggested a million fold increase in conductivity for $(1 - x) = 0.03$, but this is measured using pellets which would be expected to give higher values than those recorded in this work. This is due to grain boundaries causing resistance when a powder is studied.

![Graph](image)

*Figure 5.8: Powder conductivity of Ti$_{x}$Nb$_{1-x}$O$_2$ made at 900 °C for 4 hours.*

The surface area was recorded for Ti$_{0.05}$Nb$_{0.95}$O$_2$ and gave 14.08(9) m$^2$g$^{-1}$. This material has quite low surface area possibly due to the high temperature of synthesis.

5.2.6 TEM

TEM shown in Figure 5.9 shows large particle sizes of more than 200 nm across and an agglomeration of particles. The elemental mapping shows niobium and titanium is well dispersed across the sample.
5.2.7 Conclusion

These results show an interesting and simple method of synthesis of Ti$_{0.95}$Nb$_{0.05}$O$_2$. The materials have been analysed by powder XRD, XANES, BET surface area, TEM and powder conductivity measurements. The materials have increased in conductivity drastically from their pure TiO$_2$ counterparts. The materials still have low conductivity for the use as catalyst supports, however these materials were loaded with iridium and electrochemically tested in Chapter 6.

5.3 Tantalum carbonitride

5.3.1 Introduction

Tantalum carbide, nitride and carbonitrides have many different structures reported in the literature, including TaC, TaN, TaC$_{1-x}$N$_x$, Ta$_3$N$_5$, Ta$_2$C, and Ta$_2$N. This may be due to the metastable nature of many of the nitride phases, and work by Stampfl et al. suggests that only 3 nitride phases are stable Ta$_2$N, Ta$_5$N$_6$ and Ta$_3$N$_5$. Terao found that upon heating Ta$_3$N$_5$ under vacuum the phase transformations from Ta$_3$N$_5$→Ta$_4$N$_5$→Ta$_8$N$_6$→hexagonal TaN→Ta$_2$N occurred. Some of the structures of these tantalum nitrides and carbides are summarised in Table 5.1.
Table 5.1: Summary of the different structures of tantalum nitride and carbide phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>$a$ / Å</th>
<th>$b$ / Å</th>
<th>$c$ / Å</th>
<th>$\alpha$ / °</th>
<th>$\beta$ / °</th>
<th>$\gamma$ / °</th>
<th>Unit cell (Ta, N, C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$_3$N$_5$</td>
<td>$Cmcm$</td>
<td>3.893</td>
<td>10.2264</td>
<td>10.264</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>TaN$_3$</td>
<td>$P6m2$</td>
<td>2.936</td>
<td>2.936</td>
<td>2.885</td>
<td>90</td>
<td>90</td>
<td>120</td>
<td>hexagonal</td>
</tr>
<tr>
<td>TaN$_3$</td>
<td>$Fm\bar{3}m$</td>
<td>4.3443</td>
<td>4.3443</td>
<td>4.3443</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>cubic</td>
</tr>
<tr>
<td>TaC$_3$</td>
<td>$Fm\bar{3}m$</td>
<td>4.453</td>
<td>4.453</td>
<td>4.453</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>cubic</td>
</tr>
<tr>
<td>Ta$_2$N$_3$</td>
<td>$P3m1$</td>
<td>3.0476</td>
<td>3.0476</td>
<td>4.9187</td>
<td>90</td>
<td>90</td>
<td>120</td>
<td>hexagonal</td>
</tr>
<tr>
<td>Ta$_5$N$_6$</td>
<td>$I4/m$</td>
<td>6.831</td>
<td>6.831</td>
<td>4.269</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>tetragonal</td>
</tr>
<tr>
<td>Ta$_5$N$_6$</td>
<td>$P\bar{6}3/mcm$</td>
<td>5.176</td>
<td>5.176</td>
<td>10.353</td>
<td>90</td>
<td>90</td>
<td>120</td>
<td>hexagonal</td>
</tr>
</tbody>
</table>
Tantalum nitrides have semi-metallic electrical properties. Ta₃N₅ has an electrical conductivity of 10⁻⁴ S cm⁻¹, with semiconductor-like conductivity. Ta₃N₅ is one of a limited range of semiconductors, which absorbs a broad range of visible light and is thermodynamically stable to split water without external bias potential.

Tantalum carbide, TaC has the rock salt type structure and is known for high hardness, high melting point (3880 °C), good electrical conductivity, chemical stability and resistance to oxidation. Polonsky et al. found that TaC is a promising material for application as an IrO₂ electrocatalyst support for the anodic oxygen evolution reaction in PEM water electrolysers. These properties make it a potentially useful material for use as a catalyst support in PEMFCs.

Synthesis of these tantalum nitrides usually involves using high temperatures (600 – 1100 °C) and gas flows of ammonia and nitrogen, to nitride thin films of tantalum. Ta₃N₅ can be formed by reacting Ta₂O₅ with dry ammonia gas at between 700 – 900 °C. Methods using ammonia gas are considered dangerous and therefore other methods have been suggested.

Buha et al. managed to form nanocrystalline cubic TaN by reacting amorphous Ta₂O₅ with cyanimide at 900 °C under a nitrogen atmosphere. It is suggested by Gao et al. that synthesis of pure tantalum nitride can not be achieved through a urea-based route due to inability to control the reactions. Instead they suggest a Ca-assisted urea method for controlled synthesis of TaON and Ta₃N₅, and that by varying the ratio of urea:Ta the final product can be controlled whilst in the presence of Ca²⁺. However, without Ca²⁺ the material forms mixtures of TaON, Ta₃N₅ and Ta₄N₅.

TaC powders are conventionally made by the carbothermal reduction of tantalum oxide or the direct reaction of tantalum with carbon at temperatures as high as 1300 – 1500 °C. Work by Souza et al. made tantalum carbide from an organometallic precursor, ammonium tantalum oxalate, by carburisation of the complex at 1000 °C in 1 % CH₄/H₂. Similarly Jiang et al. made an organometallic tantalum precursor, which involved pyrolysis at 1000 – 1200 °C under argon to form tantalum carbide.

This work starts from synthesising an ammonium tantalate oxalate complex, and then following on from the successful use of ammonium niobium oxalate in Chapter 4, the material was combined with guanidine carbonate and reacted at 150 °C in air for 12 hours before heating at various temperatures 700-1200 °C under nitrogen. The aim
was to find a low temperature synthesis under unreactive gas flow to produce high surface area materials for potential use as catalyst supports in PEMFCs.

**5.3.2 Synthesis of Tantalum Precursor**

Synthesis of ammonium tantalate oxalate \((\text{NH}_4)_3[\text{TaO(C}_2\text{O}_4)_3]\cdot x\text{H}_2\text{O})\) was modified from the method reported by Lima *et al.*\(^{29}\). Tantalum oxide (8 g) and potassium bisulfate (80 g) were ground together and heated at 600 °C for 2 hours. The resulting material was then dissolved in hot concentrated sulfuric acid (160 ml). The solution was then diluted by carefully adding 500 ml of water, and then neutralising with approximately 650 ml of ammonia to give a pH of between 8-9. The resulting solid was filtered and washed with 1% acetic acid. This material was then complexed by adding 1Ta (all product) : 1.5 oxalic acid (6.8472 g):1.5 ammonium oxalate (7.618 g) to 200 ml of water and heating to 65 °C for 2 hours. The solution was then left for 48 hours before evaporating off the water at 80 °C. The resulting solid was then ground and analysed.

The IR spectrum for as-made ammonium tantalate oxalate is shown in Figure 5.10, and is compared to ammonium titanyl oxalate and ammonium niobate oxalate. The broad absorption band at 3150 cm\(^{-1}\) is due to water of hydration and N-H. The broad band at about 1650 cm\(^{-1}\) is assigned to the oxalate groups C=O coordinated to the tantalum, and 1400 cm\(^{-1}\) C-O, and 1070 cm\(^{-1}\) O=C=O oxalate groups. The peaks at 802 and 715 cm\(^{-1}\) are likely to be due to Ta-O and Ta=O.\(^{29}\) The TGA-DSC shown in Figure 5.11, shows a 1% loss due to water at 200 °C. It then shows a loss of more mass than expected of 72% instead of 59%. This could be due to not washing away excess oxalate present after the complexation.
Figure 5.10: Infrared spectra of ammonium tantalate oxalate hydrate compared to ammonium niobate(V) oxalate and ammonium titanyl oxalate.

Figure 5.11: TGA-DSC of as made ammonium tantalate oxalate hydrate.
5.3.3 Synthesis of Precursor

The as-made ammonium tantalate oxalate hydrate was ground together in various ratios of 1Ta:XGC, where X=2.9-7.1. X was complicated to calculate due to impurities and water in the ammonium tantalate oxalate, and TGA-DSC was used to give more accurate results. This mixture was then heated in air at 150 °C for 12 hours and then was ground and analysed. The powder XRD for the resulting materials is shown in Figure 5.12. The powder XRD shows the presence of some the ammonium tantalum oxalate and guanidine carbonate in the resulting materials.

![Figure 5.12: Powder XRD of as made ammonium tantalate oxalate hydrate, compared with precursor materials made at 150 °C for 12 hours in air with various ratios of tantalum (Ta) to guanidine carbonate (GC).](image)

The TGA-DSC for the precursor materials with different tantalum (Ta) to guanidine carbonate (GC) ratios are shown in Figure 5.13. The materials give around the same final mass, this is probably due to the ammonium tantalum oxalate taking up a large amount of the overall mass. The mass loss also stabilises at around the same temperature, ~550 °C.
5.3.4 Synthesis of Carbonitride

Following the method previously optimised in this thesis for other elements, the precursor materials with various tantalum (Ta) to guanidine carbonate (GC) ratios were then heated in a flow of nitrogen to between 700-1200 °C for 4 hours. The resulting material was cooled and slowly introduced to air to passivate the surface. If air was introduced too quickly oxidation of the sample occurred or the sample caught fire, so caution was needed.

5.3.5 Powder XRD and Fits

It was found that synthesis at 900 °C gave a poorly crystalline material with broad peaks in the powder XRD shown in Figure 5.14. These indicated a rock salt structure, with a space group of $Fm\bar{3}m$, although a secondary phase maybe present indicated by the peak at 27.3 °. When the temperature of the reaction was increased to 1200 °C more crystalline materials were produced as shown in Figure 5.15, where the peaks are sharper and more intense. It is also possible to see a secondary phase present with the main Bragg peak shown at 23 ° in the 1Ta:2.9GC and 1Ta:4.4GC 4 hrs 1200 °C samples.
Figure 5.14: Powder XRD ($\lambda=1.5418$ Å) of tantalum carbonitrides made with different tantalum to guanidine carbonate ratios at 900 °C for 4 hours under nitrogen.

Figure 5.15: Powder XRD ($\lambda=1.5418$ Å) of tantalum carbonitrides made with different tantalum to guanidine carbonate ratios at 1200 °C 4 hours under nitrogen.
The tantalum synthesis appears to be more complicated than for the niobium and titanium carbonitride materials made previously. This is shown in Figure 5.16, where the changes in reaction conditions affect the phases formed. The changes in guanidine carbonate ratios from 1Ta:5.9GC to 1Ta:5.7GC at 1200 °C changed the structure from a cubic rock salt structure $Fm\bar{3}m$, to a hexagonal structure $P\bar{6}m2$. When a synthesis temperature of 1100 °C was used a mixed phase of $P\bar{6}m2$, $I4/m$ and $P63/mcm$ structures was formed. At 1000 °C for 4 hours with a ratio of 1Ta:5.7GC, Ta$_4$N$_5$ forms. Figure 5.17 shows powder XRD of reactions with a 1Ta:2.9GC ratio, at 900 °C for 4 hours the material appears to be $Fm\bar{3}m$ but due to the overlapping peaks there could also be some Ta$_4$N$_5$ $I4/m$ present. When the temperature of synthesis is reduced to only 700 °C, a red powder is formed instead of the usual black powder. This is because Ta$_3$N$_5$ $Cmcm$, has formed as shown in Figure 5.17 by powder XRD. These phases are summarised in Table 5.2. It is important to note that the starting material, ammonium tantalate oxalate hydrate, is hygroscopic and therefore ensuring the exact ratios of Ta:GC was difficult, even when using TGA to calculate the amount of water. These different phases formed at the same temperature may also been as a result of hot spots within the tube furnace, although this was minimised by the use of insulation plugs.
Figure 5.16: Powder XRD ($\lambda=1.5418\,\text{Å}$) of tantalum carbonitrides made with 1Ta:5.7-5.9GC ratio at various temperatures for 4 hrs under nitrogen compared with patterns simulated from structures from the literature. 34–36,38,48
Figure 5.17: Powder XRD (\(\lambda=1.5418\) Å) of tantalum carbonitrides made with 1Ta:2.9GC ratio at various temperatures for 4 hrs under nitrogen compared with patterns simulated from structures from the literature.\textsuperscript{33,36,49}

Table 5.2: Phases identified in tantalum carbonitride in Figure 5.14, Figure 5.15, Figure 5.16 and Figure 5.17.

<table>
<thead>
<tr>
<th>Sample Reaction conditions (all for 4 hrs)</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Ta:7.1 GC 1200 °C</td>
<td>TaN P6m(^{24}) TaC Fm(^{36}) TaN Fm(^{35})</td>
</tr>
<tr>
<td>1Ta:5.9GC 1200 °C</td>
<td>TaC Fm(^{36}) TaN Fm(^{35})</td>
</tr>
<tr>
<td>1Ta:5.7GC 1200 °C</td>
<td>TaN P6m(^{24})</td>
</tr>
<tr>
<td>1Ta:4.4GC 1200 °C</td>
<td>TaN P6m(^{24}) TaC Fm(^{36}) TaN Fm(^{35})</td>
</tr>
<tr>
<td>1Ta:2.9GC 1200 °C</td>
<td>Ta(_2)O(_5) TaN P6m(^{24}) TaC Fm(^{36}) TaN Fm(^{35})</td>
</tr>
<tr>
<td>1Ta:5.9GC 1100 °C</td>
<td>TaN P6m(^{24}) Ta(_4)N(_5) I4/m(^{38}) TaN(_6) P63/mcm(^{38})</td>
</tr>
<tr>
<td>1Ta:5.9GC 1000 °C</td>
<td>Ta(_4)N(_5) I4/m(^{38})</td>
</tr>
<tr>
<td>1Ta:2.9GC 900 °C</td>
<td>TaC Fm(^{36}) TaN Fm(^{35})</td>
</tr>
<tr>
<td>1Ta:4.4GC 900 °C</td>
<td>TaC Fm(^{36}) TaN Fm(^{35})</td>
</tr>
<tr>
<td>1Ta:5.9GC 900 °C</td>
<td>TaC Fm(^{36}) TaN Fm(^{35})</td>
</tr>
<tr>
<td>1Ta:2.9GC 700 °C</td>
<td>Ta(_3)N(_5) Cmcm(^{33})</td>
</tr>
</tbody>
</table>
The Pawley fit for TaC₁₋ₙNₚ 900 °C 4 hrs 1Ta:2.9GC is shown in Figure 5.18, which shows a reasonable fit with the $Fm\bar{3}m$ space group. However, there is clearly a secondary phase present. It is difficult to determine whether this is another tantalum carbonitride phase or an amorphous carbon phase or both. The Pawley fit for TaC₁₋ₙNₚ 1200 °C 4 hrs 1Ta:5.9GC is shown in Figure 5.19, where it fits to the $Fm\bar{3}m$ unit cell well, and gives lattice parameters similar to that of TaC as shown in Table 5.3. The lower temperature synthesis, TaC₁₋ₙNₚ 900 °C 4 hrs 1Ta:2.9GC, gives a material with a unit cell more like the TaN material. This shows similar behaviour to the NbC₁₋ₙNₚ shown in Chapter 4.

*Figure 5.18: Pawley XRD ($\lambda=1.5418$ Å) fit of TaC₁₋ₙNₚ 900 °C 4 hrs 1Ta:2.9GC space group $Fm\bar{3}m$.**
Figure 5.19: Pawley XRD ($\lambda=1.5418$ Å) fit of TaC$_{1-p}$N$_p$ 1200 °C 4 hrs 1Ta:5.9GC space group Fm$\overline{3}$m.

Table 5.3: Pawley fit parameters for TaC$_{1-p}$N$_p$, space group Fm$\overline{3}$m.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter $a$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>TaN$^{35}$</td>
<td>4.3443</td>
</tr>
<tr>
<td>TaC$^{36}$</td>
<td>4.45300(6)</td>
</tr>
<tr>
<td>TaC$_{1-p}$N$_p$</td>
<td>900 °C 4 hrs 4.352(2)</td>
</tr>
<tr>
<td>TaC$_{1-p}$N$_p$</td>
<td>1200 °C 4 hrs 4.4602(6)</td>
</tr>
</tbody>
</table>

The Pawley fit for Ta$_3$N$_{5.1}$C$_k$ 700 °C 4 hrs 1Ta:2.9GC, is shown in Figure 5.20, where it is fitted to the orthorhombic space group $Cmcm$. The lattice parameters were compared to literature values in Table 5.4, no literature at the time of writing this was found to compare with a Ta$_3$C$_5$. However, the unit cell parameters suggest a slightly smaller unit cell than Ta$_3$N$_5$, which could be due to deficiency in nitrogen. This could suggest the carbon remains as an amorphous carbon layer instead of substituting in the structure, as it would be expected to increase the lattice parameter from the nitride structure.
**Figure 5.20:** Pawley XRD ($\lambda=1.5418$ Å) fit of Ta$_3$N$_5$C$_k$ 700 °C 4 hrs $1\text{Ta}:2.9\text{GC}$, orthorhombic space group Cmcm.

**Table 5.4:** Pawley fit parameters for Ta$_3$N$_5$C$_k$ 700 °C 4 hrs $1\text{Ta}:2.9\text{GC}$, orthorhombic space group Cmcm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter $a$ / Å</th>
<th>Lattice parameter $b$ / Å</th>
<th>Lattice parameter $c$ / Å</th>
<th>Volume / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$_3$N$_5^{33}$</td>
<td>3.88620(10)</td>
<td>10.2118(2)</td>
<td>10.2624(3)</td>
<td>407.264(16)</td>
</tr>
<tr>
<td>(Ta$_3$C$_3$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta$_3$N$_5$C$_k$ 700 °C 4 hrs</td>
<td>3.8875(17)</td>
<td>10.160(6)</td>
<td>10.261(7)</td>
<td>405.3(4)</td>
</tr>
</tbody>
</table>

**5.3.6 TEM**

TEM of TaC$_{1-p}$N$_p$ 4 hrs 1200 °C $1\text{Ta}:5.9\text{GC}$ is shown in Figure 5.21. The particles appear as agglomerates of particles and appear to be surrounded by amorphous carbon. The particles are around 10-20 nm in diameter, which shows relatively small particle size despite being made at 1200 °C.
Figure 5.21: TEM image of TaC$_{1-p}$N$_p$ space group Fm$ar{3}$m, made at 1200 °C 4 hrs (1Ta:5.9GC ratio).

5.3.7 Thermogravimetric Analysis

The thermal analysis of the tantalum carbonitrides shown in Figure 5.22, shows the materials to be stable until 500 °C where an increase in mass suggests oxidation occurs and begins to form Ta$_2$O$_5$. The TaC Fm$ar{3}$m sample made at 1200 °C with 1Ta:5.9GC ratio decomposes sooner, gaining mass at 400 °C before stabilising at 650 °C and changing further at 750 °C. This suggests its decomposition mechanism is different from the other materials. Due to the complex nature of these materials it was not considered possible to calculate the amount of amorphous carbon present. This is because the various mixtures of nitrides and uncertainty of the composition. In order to analyse these samples further CHN would be required.
Figure 5.22: TGA-DSC of various tantalum carbonitrides made under different conditions, in air.

5.3.8 Conclusions

Tantalum carbonitrides have been made via a new guanidine carbonate method. The phases formed were more complicated than other guanidinium syntheses of metal carbonitrides, including those shown in Chapter 4. The materials formed a variety of tantalum carbonitride phases including Ta$_3$N$_5$, Ta$_4$N$_5$, hexagonal TaN, hexagonal TaN$_{0.83}$ and cubic TaC, and a variety of mixtures of these phases. Further work in this area could be used to optimise the synthesis of pure phase materials.
5.4 Tantalum Titanium Carbonitrides

In the previous section, ammonium tantalate oxalate was synthesised and this material was found to form tantalum carbonitrides in similar reactions to those used before for ammonium niobate oxalate. Therefore, this material was combined with ammonium titanyl oxalate, in order to form mixed metal tantalum titanium carbonitrides. Tantalum is known to be expensive and less reactive than niobium, and therefore substitution with a cheaper metal such as titanium may provide a way of stabilising titanium carbonitrides.

5.4.1 Synthesis of Precursor

As-made ammonium tantalate oxalate hydrate and ammonium titanyl oxalate monohydrate were ground together with guanidine carbonate to give a ratio of 0.5Ta:0.5Ti:XGC, where X=2-6, here GC is the attempted amount. The resulting mixture was then heated at 150 °C for 12 hours in air. This gave a powder which was then ground and analysed, these materials are denoted as TiTa150. The powder XRD patterns for these materials are shown in Figure 5.23. Unlike in the other syntheses of the niobium and titanium precursors, a distinct phase isn’t formed. A mixture of materials appears to exist, consisting of the starting materials.

![Figure 5.23: Powder XRD (\(\lambda=1.5418 \text{ Å}\)) of TiTa150 precursor materials with different ratios of metal(M) to guanidine carbonate (GC).](image-url)
TGA analysis of the TiTa150 precursor materials shown in Figure 5.24 shows that with increasing amounts of guanidine carbonate in the precursor the more mass is lost during heating in air.

![TGA-DSC of the precursor materials TiTa150 made at 150 °C for 12 hrs of different ratios of metal to guanidine carbonate (GC).](image)

**Figure 5.24**: TGA-DSC of the precursor materials TiTa150 made at 150 °C for 12 hrs of different ratios of metal to guanidine carbonate (GC).

### 5.4.2 Synthesis of Titanium Tantalum Carbonitride

The precursor materials TiTa150 with varying 1M:XGC ratios, where X=2-6, were heated in a flow of nitrogen to 900-1200 °C for 4 hours at a ramp rate of 10 °C/min. The resulting material was cooled and then passivated by slowly introducing air to the system. This step was important due to the pyrophoric nature of the carbonitrides; slow addition of air allows a small surface of oxide to form. Too much air causes more oxide to form and the material can catch fire.

### 5.4.3 Powder XRD fits

Pawley fits of the resulting XRD patterns of Ti0.5Ta0.5C1-pNp are shown in Figure 5.25. The more guanidine carbonate present in the precursor material, the more of an amorphous background is present, likely to be amorphous carbon. The corresponding Pawley lattice parameters are shown in Figure 5.26. The materials appear to become more like the expected carbide, shown by the reference materials in Figure 5.26, until 1M:4GC ratio, above that the lattice parameters decrease again as shown in Figure 5.27.
Figure 5.25: Pawley refinements against powder XRD data ($\lambda = 1.5418$ Å) of \( \text{Ti}_{0.5}\text{Ta}_{0.5}\text{C}_{1-p}\text{N}_p \) at 900 °C for 4 hrs with varying metal (M) to guanidine carbonate (GC) ratios in the precursor materials, fitted to Fm\(\overline{3}\)m cubic space group.
Figure 5.26: Pawley lattice parameter $a$ of $\text{Ti}_{0.5}\text{Ta}_{0.5}\text{C}_{1-p}\text{N}_p$ 4 hrs 900 °C materials compared to literature values.\textsuperscript{35,36,52,53}

Figure 5.27: Pawley lattice parameter $a$ plotted against GC content of $\text{Ti}_{0.5}\text{Ta}_{0.5}\text{C}_{1-p}\text{N}_p$ 4 hrs 900 °C materials.
The 1M:4GC ratio was then used to make a sample at 1200 °C for 4 hours, the powder XRD Pawley fit can be seen for this in Figure 5.28. It shows a much more crystalline material than the sample made at 900 °C. The Pawley lattice parameters are compared in Figure 5.29. The materials show the 1200 °C sample has slightly larger unit cell than the 900 °C sample. Both materials are similar in lattice parameter to the expected carbide value for a material of Ti$_{0.5}$Ta$_{0.5}$C.

![Figure 5.28](image)

*Figure 5.28: Pawley refinements against powder XRD data (λ = 1.5418 Å) of Ti$_{0.5}$Ta$_{0.5}$C$_{1-p}$N$_p$ 1200 °C 4 hrs with precursor ratio of 1M:4GC, fitted to Fm$\overline{3}$m cubic space group.*
5.4.4 Thermogravimetric Analysis

The materials with varying amounts of guanidine carbonate in the precursor materials were heated in air and the mass recorded as shown in Figure 5.30. The amorphous carbon presence has been calculated by assuming all metal goes to TiO$_2$ or Ta$_2$O$_5$. The calculation shows that the lowest amount of guanidine carbonate in the starting material, the least amount of amorphous carbon is present in the end material. However, the amount of guanidine carbonate also affects the amount of carbon and nitrogen present in the carbonitride as seen by the Pawley fit parameters shown in Figure 5.26.

*Figure 5.29: Pawley lattice parameters of Ti$_{0.5}$Ta$_{0.5}$C$_{1-p}$N$_p$ made for 4 hours at different temperatures with a 1M:4GC ratio are fitted to Fm$\bar{3}$m cubic space group.*
Figure 5.30: TGA and calculated weight percent of amorphous carbon of Ti$_{0.5}$Ta$_{0.5}$C$_{1-p}$N$_p$ materials made at 900 °C for 4 hours with varying amounts of guanidine carbonate in the precursor material.

5.4.5 Powder Conductivity

Powder conductivity of some samples was recorded and are shown in Table 5.5. The materials show good conductivity and are above 0.1 S cm$^{-1}$ suggesting potential suitability for use as catalyst supports.

Table 5.5: Powder conductivity of Ti$_{0.5}$Ta$_{0.5}$C$_{1-p}$N$_p$ materials made for 4 hours at 900 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M</th>
<th>GC</th>
<th>Conductivity / S cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{0.5}$Ta$</em>{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C</td>
<td>1</td>
<td>4</td>
<td>0.365</td>
</tr>
<tr>
<td>Ti$<em>{0.5}$Ta$</em>{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C</td>
<td>1</td>
<td>5</td>
<td>0.212</td>
</tr>
</tbody>
</table>

5.4.6 Conclusion

Mixed metal Titanium tantalum carbonitrides were made via a new guanidine carbonate synthesis. The ratio of metal to guanidine carbonate in the precursor material had effects on the properties of the final carbonitride materials. This could be due to
the presence of amorphous carbon, which was analysed by TGA-DSC. These materials exhibit good powder conductivities, but further work is required on surface area measurements. The materials look promising for the use as catalyst supports in PEMFCs.

5.5 Tantalum Niobium Carbonitride

In a previous section, ammonium tantalate oxalate was synthesised and this material was found to form tantalum carbonitrides. Therefore, this material combined with ammonium niobate oxalate, in order to form mixed metal tantalum niobium carbonitrides. This was done in order to determine if a mixed metal tantalum niobium carbonitride gave interesting properties or qualities that the single metal carbonitrides do not possess.

5.5.1 Synthesis of precursor

As-made ammonium tantalate oxalate hydrate and ammonium niobate oxalate hydrate were ground together with guanidine carbonate to give a ratio of 0.5Ta:0.5Nb:XGC, where X=2-6. The resulting mixture was then heated at 150 °C for 12 hours in air. This gave a powder which was then ground and analysed. These materials are denoted as NbTa150 and the powder XRD is shown in Figure 5.31. The XRD shows that with increasing amounts of guanidine carbonate, the resulting material still has some excess guanidine carbonate present. The material appears different from the other two starting materials, as made ammonium tantalate oxalate hydrate and ammonium niobate oxalate hydrate.
Figure 5.31: Powder XRD ($\lambda=1.5418$ Å) of the precursor niobium tantalum materials made at 150 °C for 12 hours with varying metal to guanidine carbonate (GC) ratios.

TGA was performed on these materials in air and the resulting data are shown in Figure 5.32. It shows with increasing guanidine carbonate the material loses more mass as expected.

Figure 5.32: TGA-DSC of precursor tantalum niobium materials made at 150 °C for 12 hours, with metal(M) to guanidine carbonate(GC) ratios.
5.5.2 Synthesis of carbonitride
The precursor materials NbTa150 with varying 1M:XGC ratios, where X=2-6, were heated at a ramp rate of 10 °C/min in a flow of nitrogen to 900-1200 °C for 4 hours. The resulting material was cooled and then passivated by slowly introducing air to the system. This step was important due to the pyrophoric nature of the carbonitrides, slow addition of air allows a small surface of oxide to form.

5.5.3 Powder XRD and fits
Powder XRD Pawley fits for Nb0.5Ta0.5C1-pNp made at 900 °C for 4 hours can be seen in Figure 5.33. The Pawley lattice parameters are shown in Figure 5.34, it shows an increase in lattice parameter $a$ with increasing guanidine carbonate in the precursor material. This suggests that the material becomes more like the reference carbides with increasing guanidine carbonate.

![Figure 5.33: Pawley fits of powder XRD (\( \lambda=1.5418 \) Å) of Nb0.5Ta0.5C1-pNp made at 900 °C for 4 hrs with varying metal (M) to guanidine carbonate (GC) ratios.](image-url)
Figure 5.34: Lattice parameter a calculated from Pawley fits of $Ta_{x}Nb_{1-x}C_{1-p}N_{p}$ made with different metal (M) to guanidine carbonate (GC) ratios at 900 °C for 4 hours, compared with values taken from the literature. 35,36,54,55

5.5.4 Thermogravimetric analysis

Thermogravimetric analysis of $Nb_{0.5}Ta_{0.5}C_{1-p}N_{p}$ made at 900 °C for 4 hours with varying metal to guanidine carbonate ratios are shown in Figure 5.35. The amorphous carbon percentage was calculated assuming all metal forms either Nb$_2$O$_5$ or Ta$_2$O$_5$. The heatflow in Figure 5.35 shows a large difference between the samples. Both 1M:6GC and 1:5GC materials show two exothermic events in the heatflow at 350 °C and 500 °C, the first could be the loss of amorphous carbon, as these samples are calculated to have large amounts of amorphous carbon. The sample made with 1M:4GC ratio shows the least amount of amorphous carbon and has one exothermic event thought to be the oxidation of the metal. The sample with a 1M:3GC ratio has slightly more amorphous carbon present than 1M:4GC.
Figure 5.35: TGA-DSC of Nb$_{0.5}$Ta$_{0.5}$C$_{1-p}$N$_p$ made at 900 °C for 4 hrs with varying metal (M) to guanidine carbonate (GC) ratios.

5.5.5 Powder conductivity

Powder conductivity of the tantalum niobium carbonitrides is shown in Table 5.6, the conductivities are nearing that of the requirement for PEMFC supports of 0.1 S cm$^{-1}$.

Table 5.6: Powder conductivities of Ti$_{0.5}$Ta$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C with different 1M:xGC ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M</th>
<th>GC</th>
<th>Powder conductivity / S cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$<em>{0.5}$Ta$</em>{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C</td>
<td>1</td>
<td>5</td>
<td>0.09</td>
</tr>
<tr>
<td>Nb$<em>{0.5}$Ta$</em>{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C</td>
<td>1</td>
<td>6</td>
<td>0.08</td>
</tr>
</tbody>
</table>

5.5.6 Conclusion

Tantalum niobium carbonitrides have been made for the first time via a guanidinium carbonate route. The materials have shown reasonable thermal stability and powder conductivity, which could make them useful materials in the hunt for PEMFC catalyst supports.
5.6 Iron Carbide

5.6.1 Introduction

Iron carbide, Fe₃C, has an orthorhombic structure, it is a hard brittle material which has chemical stability and magnetic properties.⁵⁶⁻⁵⁸ Iron carbide encapsulated in carbon graphitic layers has proven to be useful material in ORR, and produces highly active and stable materials in both acidic and alkaline electrolytes.⁵⁹,⁶⁰ Some materials with core shell structure with Fe/Fe₃C encapsulated in nitrogen doped carbon exhibits highly catalytic activity for both ORR and OER in alkaline media.⁵⁹⁻⁶¹ Methods of synthesis of Fe₃C involve laser induced pyrolysis of Fe(CO)₅ and C₂H₄.⁵⁶ Snovski et al. prepared Fe₃C by thermal decomposition of a mixture of Fe(CO)₅ and polyvinylpyrrolidone at 300 °C in a sealed cell under inert atmosphere, hydrogen reduction of the resulting iron carbide nanoparticles was used at 450 °C to give an amorphous and graphitic carbon coating.

In this section, synthesis of Fe₃C is explored by the guanidinium route, by combining ammonium iron oxalate and guanidine carbonate via a similar synthesis to Chapter 3.

5.6.2 Synthesis of precursor

Ammonium iron oxalate and guanidine carbonate were macerated in a pestle and mortar in varying ratios of metal (M) to guanidine carbonate (GC), 1M:XGC where X=2-6. The resulting mixture was heated in air to 150 °C for 12 hours. The resulting solid was then ground and analysed, they are referred to as AIO150 hereafter. Powder XRD patterns for these materials are shown in Figure 5.36. The TGA-DSC for various AIO150 with different guanidine carbonate ratios are shown in Figure 5.37. It shows little difference between the materials.
Figure 5.36: Powder XRD ($\lambda=1.5418$ Å) of iron precursor materials made at 150 °C for 12 hours with varying metal to guanidine carbonate (GC) ratios.

Figure 5.37: TGA-DSC of precursor material made at 150 °C for 12 hours with varying metal (M) to guanidine carbonate (GC) ratios.
5.6.3 Synthesis of iron carbide
The AIO150 precursors with varying 1:M:XGC ratios were then heated at 10 °C/min under a flow of nitrogen to 700-900 °C for 4 hours. The resulting material was cooled and then passivated by slowly introducing air to the system. This step was important due to the pyrophoric nature of the carbonitrides, slow addition of air allows a small surface of oxide to form.

5.6.4 Powder XRD
Powder XRD of the resulting iron carbonitride materials is shown in Figure 5.38. Both 1M:2GC and 1M:3GC materials formed iron metal, \(Im\bar{3}m\) space group and an iron carbonitride with the cubic rock salt space group \(Fm\bar{3}m\). The materials with higher ratio of guanidine carbonate to metal formed a Fe3C type structure, with a \(Pnma\) orthorhombic space group, which can be seen in Figure 5.39. It consists of triangular prism polyhedral with carbon at the centre.
Figure 5.38: Powder XRD of iron products from reactions using precursors with different ratios of metal (M) to guanidine carbonate (GC) at 900 °C for 4 hours compared to reference materials.\textsuperscript{52–65}
The 1Fe:5GC ratio material was then made at 700 °C and 900 °C and the XRD of these materials are shown in Figure 5.40. The higher temperature synthesis gives narrower peaks indicating a more crystalline sample.

Figure 5.40: Powder XRD of Fe₃C made at different temperatures using a 1M:5GC ratio compared to a simulated pattern.⁶²
5.6.5 Powder conductivity

Figure 5.41 shows the powder conductivity for the Fe$_3$C materials. It was found that the materials all show good conductivity. However, the sample made with a 1Fe:6GC ratio was found to have a much lower conductivity than the other iron carbide materials. This may be due to a larger amorphous carbon presence.

![Graph showing powder conductivity for Fe$_3$C materials](image)

*Figure 5.41: Powder conductivity of Fe$_3$C 4 hrs 900°C made with different iron (Fe) to guanidine carbonate (GC) ratios.*

5.6.6 Conclusion

Fe$_3$C has been made for the first time via a guanidine carbonate synthesis method. The materials have shown high conductivity suitable for that of catalyst supports in PEMFCs. Further work could involve measuring surface area and acid resilience testing.

5.7 Vanadium Carbonitride

5.7.1 Introduction

VC and VN exist in the rock structure form with a cubic space group of $Fm\bar{3}m$. These form hard ceramic materials, with properties such as high melting temperature, high hardness, efficient electrical and thermal conductivities.\(^6\) Huang *et al.* found that oxygen reduction characteristics of VC increased in stability with the substitution of nitrogen.\(^7\) Yu *et al.* found that the half-wave potential of oxygen reduction of nitrogen doped VC was only 0.04 V lower than that of Pt/C catalyst, it was also found that
nitrogen substitution increased the stability of VC.\textsuperscript{68} This suggests that these V(C,N) materials are promising non-precious metal based catalysts for ORR and have comparable catalytic performance to commercial Pt/C catalyst.\textsuperscript{69}

Vanadium carbide is typically synthesised by reduction of V$_2$O$_5$ under hydrogen at 500 °C to form V$_2$O$_3$, which is then reduced and carburized by methane at 900 °C.\textsuperscript{70} This produces materials with moderate surface areas of \(\sim 60 \text{ m}^2\text{g}^{-1}\).\textsuperscript{70} Vanadium nitride with high surface area, 90 \(\text{m}^2\text{g}^{-1}\), can be formed by temperature programmed reduction and nitridation of V$_2$O$_5$, using ammonia gas flow and high temperatures.\textsuperscript{71} These methods involve reactive gas flows, which are considered to be dangerous. A low temperature synthesis by Ma et al. involves the reaction of magnesium powder with vanadium pentoxide and magnesium carbonate in an autoclave at 650 °C for 10 hours to produce nanocrystalline VC.\textsuperscript{72} This material had good thermal stability and oxidation resistance below 350 °C in air.\textsuperscript{72}

Work by de Souza et al. formed vanadium nitride at low temperature via a “guanindinium-route.”\textsuperscript{73,74} Ammonium metavanadate was combined with guanidinium carbonate with various V:GC ratios (1:1 – 1:5) and heated in air at 150 °C for 12 hours. This material was then heated in helium to 300 °C to remove ammonia gas before heating to between 400 – 800 °C for 4 hours.\textsuperscript{73,74}

This was the starting point for this section, to optimise this synthesis under nitrogen gas flow, and by using a guanidinium route from an ammonium vanadate oxalate material, it was hoped that vanadium carbonitrides could be formed.

### 5.7.2 Synthesis of Vanadium Precursor

Synthesis of ammonium vanadate oxalate ((NH$_4$)$_2$[VO(C$_2$O$_4$)$_2$]) was modified from a method reported by Li et al..\textsuperscript{75} Ammonium orthovanadate (NH$_3$VO$_3$, 10g) was dissolved in 200 ml oxalic acid solution at 80 °C, to give a molar ratio of NH$_4$VO$_3$ to oxalic acid of 1:2. The resulting deep blue solution was evaporated off at 100 °C, to give dark blue green crystals of (NH$_4$)$_2$[VO(C$_2$O$_4$)$_2$]. This material was then dried at 80 °C overnight.

The powder XRD of the resulting ammonium vanadate oxalate material is shown in Figure 5.42. It shows an amorphous material, with no distinguishable Bragg peaks. The material was then compared by IR spectroscopy to the ammonium niobate oxalate
material as shown in Figure 5.43. It shows similar peaks and peak shapes, therefore this material was considered to be ammonium vanadate oxalate.

**Figure 5.42:** Powder XRD of as made ammonium vanadate oxalate.

**Figure 5.43:** Infrared (IR) spectroscopy of as made ammonium vanadate oxalate compared to the IR of ammonium niobate oxalate.
TGA-DSC shown in Figure 5.44, shows a mass loss of 6.5% until 250 °C, which indicates the loss of water. The final mass of 45% suggests that not all of the material is ammonium vanadate oxalate due to the expected final mass being 30.5% of V₂O₅. The endothermic feature in the heatflow at 690 °C indicates the melting point of V₂O₅. The TGA therefore indicates as-made ammonium vanadate oxalate is not a pure material, some starting material or unreacted vanadium intermediate may exist. However, when it is reacted with guanidine carbonate it does form vanadium carbonitrides.

![Graph showing TGA-DSC of as made ammonium vanadate oxalate](image)

*Figure 5.44: TGA-DSC of as made ammonium vanadate oxalate.*

### 5.7.3 Synthesis of Precursor

The as made ammonium vanadate oxalate material or ammonium orthovanadate was macerated together with guanidine carbonate in different ratios of vanadium (V) to guanidine carbonate (GC), V:XGC where X=2-4, at 150 °C for 12 hours. The resulting materials were then ground and analysed. The powder XRD for the ammonium vanadate oxalate materials are shown in Figure 5.45. The powder XRD shows amorphous materials with some distinguishable peaks. The TGA-DSC shown in Figure 5.46, shows an increase in mass lost with increasing amounts of guanidine carbonate present in the starting material.
Figure 5.45: Powder XRD (\(\lambda=1.5418 \text{ Å}\)) of the V150 materials made with different vanadium(V) to guanidine carbonate (GC) ratios compared with as made ammonium vanadate oxalate.

Figure 5.46: TGA-DSC of precursor materials made at 150 °C for 12 hours with different vanadium to guanidine carbonate (GC) ratios compared to as made ammonium vanadate oxalate (AVO). (The greyed out peak at 200 °C was a machine error).
5.7.4 Synthesis of Vanadium Carbonitride

Precursor materials with various 1V:xGC (x = 1-6) ratios were heated under a flow of nitrogen to 900 – 1200 °C for 4 hours. The resulting material was cooled and air introduced slowly to the system to prevent oxidation of the resulting vanadium carbonitride materials.

5.7.5 Powder XRD and Fits

The powder XRD Pawley fits for VC<sub>1-p</sub>N<sub>p</sub> made at 900 °C for 4 hours with various vanadium (V) to guanidine carbonate (GC) ratios, made from ammonium vanadate oxalate are shown in Figure 5.47. The resulting lattice parameters are shown in Table 5.7. It was found that the vanadium to guanidine carbonate ratio does not affect the lattice parameter. However, the material made from 1V:6GC showed two different superimposed peak shapes as is shown in Figure 5.47. This is possibly due to two different crystallite sizes existing across the sample, giving two different FWHM.

![Figure 5.47: Pawley fit of powder XRD of VC<sub>1-p</sub>N<sub>p</sub> made from ammonium vanadate oxalate at 900 °C for 4 hrs with different vanadium (V) to guanidine carbonate (GC) ratios.](image)

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Table 5.7: Pawley lattice parameters of VC_{1-p}N_{p} 4 hrs 900 °C made from ammonium vanadate oxalate compared to literature values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter $a$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>VN</td>
<td>4.137(1)³⁶</td>
</tr>
<tr>
<td>VC</td>
<td>4.16294(6)³⁶</td>
</tr>
<tr>
<td>VC_{1-p}N_{p} 4 hrs 900 °C 1V:3GC</td>
<td>4.1405(10)</td>
</tr>
<tr>
<td>VC_{1-p}N_{p} 4 hrs 900 °C 1V:4GC</td>
<td>4.136(3)</td>
</tr>
<tr>
<td>VC_{1-p}N_{p} 4 hrs 900 °C 1V:5GC</td>
<td>4.136(5)</td>
</tr>
<tr>
<td>VC_{1-p}N_{p} 4 hrs 900 °C 1V:6GC</td>
<td>4.136(4)</td>
</tr>
</tbody>
</table>

The powder XRD Pawley fits for VC_{1-p}N_{p} made at 900 °C for 4 hours with various vanadium (V) to guanidine carbonate (GC) ratios, made from ammonium orthovanadate are shown in Figure 5.48 and the resulting lattice parameters are shown in Table 5.8.

![Graph showing Pawley fits](image)

**Figure 5.48**: Pawley fit of powder XRD ($\lambda=1.54056$ Å) of VC_{1-p}N_{p} made from ammonium orthovanadate at 900 °C for 4 hrs with different vanadium (V) to guanidine carbonate (GC) ratios.
Table 5.8: Pawley lattice parameters of VC$_{1-p}$N$_p$ 4 hrs 900 °C made from ammonium orthovanadate compared to literature values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter $a$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>VN</td>
<td>4.137(1)$^6$</td>
</tr>
<tr>
<td>VC</td>
<td>4.16294(6)$^6$</td>
</tr>
<tr>
<td>VC$_{1-p}$N$_p$ 4 hrs 900 °C 1V:2GC</td>
<td>4.1383(6)</td>
</tr>
<tr>
<td>VC$_{1-p}$N$_p$ 4 hrs 900 °C 1V:3GC</td>
<td>4.1383(19)</td>
</tr>
<tr>
<td>VC$_{1-p}$N$_p$ 4 hrs 900 °C 1V:4GC</td>
<td>4.1399(8)</td>
</tr>
<tr>
<td>VC$_{1-p}$N$_p$ 4 hrs 900 °C 1V:5GC</td>
<td>4.137(2)</td>
</tr>
</tbody>
</table>

The Pawley fits for VC$_{1-p}$N$_p$ made at 1200 °C with varying amounts of guanidine carbonate in the precursor material are shown in Figure 5.49. The resulting lattice parameters are shown in Table 5.9, and show an increase in lattice parameter $a$ with increasing guanidine carbonate. This suggests that more guanidine carbonate promotes this structure to become more like the vanadium carbide. The 1V:6GC sample has a secondary phase present of V$_2$O$_5$, thought to be due to oxidation when passivating the surface.
Figure 5.49: Pawley fit of powder XRD ($\lambda=1.54056$ Å) of VC$_{1-p}$N$_p$ made from ammonium orthovanadate at 1200 °C for 4 hrs with different vanadium (V) to guanidine carbonate (GC) ratios.

Table 5.9: Pawley lattice parameters of VC$_{1-p}$N$_p$ 4 hrs 1200 °C made from ammonium orthovanadate compared to literature values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter $a$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>VN</td>
<td>4.137(1)$^{76}$</td>
</tr>
<tr>
<td>VC</td>
<td>4.16294(6)$^{36}$</td>
</tr>
<tr>
<td>VC$_{1-p}$N$_p$ 4 hrs 1200 °C 1V:3GC</td>
<td>4.1381(4)</td>
</tr>
<tr>
<td>VC$_{1-p}$N$_p$ 4 hrs 1200 °C 1V:4GC</td>
<td>4.14431(7)</td>
</tr>
<tr>
<td>VC$_{1-p}$N$_p$ 4 hrs 1200 °C 1V:5GC</td>
<td>4.1505(4)</td>
</tr>
<tr>
<td>VC$_{1-p}$N$_p$ 4 hrs 1200 °C 1V:6GC</td>
<td>4.1500(10)</td>
</tr>
</tbody>
</table>

The lattice parameters for the 900 °C materials made from ammonium vanadate oxalate, the 900 °C and 1200 °C VC$_{1-p}$N$_p$ samples made from ammonium orthovanadate are shown in Figure 5.50. This shows that the 900 °C syntheses produces materials much more like the vanadium nitride, and that the ammonium orthovanadate produces more well defined peaks, therefore giving less error.
associated with the fitting. The guanidine carbonate content variation doesn’t change the lattice parameter by much in the 900 °C samples made by either method. However, the 1200 °C samples increase in lattice parameter with increasing guanidine carbonate content. This suggests that more carbon is substituting for the nitrogen in the material, and forms vanadium carbonitride.

Figure 5.50: Lattice parameter $a$ compared to the guanidine carbonate content of the precursor material for the 900 °C synthesis from ammonium vanadate oxalate, the 900 °C and 1200 °C syntheses from ammonium orthovanadate, and reference materials.36,76

5.7.6 Thermal Stability
The thermal stability of the VC$_{1-p}$N$_p$ 4 hrs 900 °C made from ammonium vanadate oxalate with different vanadium (V) to guanidine carbonate (GC) ratios are shown in Figure 5.51. The materials made with 1V:3GC and 1V:4GC show very different mass changes to that of the 1V:5GC and 1V:6GC samples. The low GC content samples show increasing mass as the material becomes oxidised to V$_2$O$_5$, whereas the high GC content materials show an overall decrease with a sharp decrease at 500 °C. This is may be due to a larger loss of amorphous carbon in these samples. Amorphous carbon was calculated for 1V:6GC, 1V:5GC, 1V:4GC, 1V:3GC to be 31 wt%, 32 wt%, 12
wt% and 16 wt% respectively. This gives two different sets of materials, despite the unit cells for all the materials being very similar. The amorphous carbon would affect how these materials interact in any environment.

![Graph](image)

**Figure 5.51: TGA-DSC of VC$_{1-p}$N$_p$ 4 hrs 900 °C made with different vanadium (V) to guanidine carbonate (GC) ratios.**

Thermodiffractometry was used to give further detail to the oxidation of the VC$_{1-p}$N$_p$ 4 hrs 900 °C 1V:4GC sample made from ammonium vanadate oxalate and is shown in Figure 5.52. The material was heated in air at 10 °C/min at 50 °C intervals for an hour to record the powder XRD. At 450 °C the material starts to form V$_2$O$_5$ and a secondary phase which degrades quickly to V$_2$O$_5$ as well. The V$_2$O$_5$ then becomes amorphous at about 625 °C, before melting, this can be seen on the TGA-DSC in Figure 5.51 by an endothermic feature at around 675 °C.
Figure 5.52: In-situ thermodiffractometry of VC$_1$pN$_p$ 4 hrs 900 °C 1V:4GC made from ammonium vanadate oxalate in air heating at 10 °C/min from room temperature to 850 °C.

5.7.7 Surface area and conductivity

The surface area and powder conductivities of some VC$_1$pN$_p$ materials made from ammonium orthovanadate are shown in Table 5.10. The materials with 1V:4GC and 1V:5GC show good surface area suitable for catalyst supports. The powder conductivity of the VC$_1$pN$_p$ materials all show good conductivity of above 0.1 S cm$^{-1}$, making these materials of interest for use as catalyst supports in PEMFCs.

Table 5.10: BET surface area and powder conductivities of VC$_1$pN$_p$ materials made from ammonium orthovanadate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area / m$^2$g$^{-1}$</th>
<th>Powder conductivity / S cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC$_1$pN$_p$ 4 hrs 900 °C 1V:2GC</td>
<td></td>
<td>36.7</td>
</tr>
<tr>
<td>VC$_1$pN$_p$ 4 hrs 900 °C 1V:3GC</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>VC$_1$pN$_p$ 4 hrs 900 °C 1V:4GC</td>
<td>84</td>
<td>9.9</td>
</tr>
<tr>
<td>VC$_1$pN$_p$ 4 hrs 900 °C 1V:5GC</td>
<td>126.4</td>
<td>7.1</td>
</tr>
</tbody>
</table>
5.7.8 Conclusion
VN has been made via a guanidinium carbonate method from as made ammonium vanadate oxalate and ammonium orthovanadate. VC$_{1-p}$N$_p$ synthesised from ammonium vanadate oxalate has been analysed by powder XRD, TGA-DSC and in-situ thermodiffractometry. VC$_{1-p}$N$_p$ synthesised from ammonium orthovanadate has been analysed by powder XRD, powder conductivity and BET surface area. These materials have shown useful properties in conductivity and surface area for use as PEMFC catalyst supports but acid resilience testing would be required. In work by Kimmel et al. suggests that these materials would not be stable under acidic ORR. $^{77}$

5.8 Molybdenum Carbonitride

5.8.1 Introduction
Molybdenum carbides are widely used as catalysts due to their activity in many reactions.$^{78}$ Molybdenum carbides and carbonitrides have been reported in the literature to give highly efficient HER in both acidic and alkaline media.$^{79-84}$ Mo$_2$C and Mo$_2$N have catalytic and electronic properties which resemble those of platinum.$^{83}$

The usual synthesis method for producing Mo$_2$C involves high temperature carburisation of metals with graphitic carbon, which produces products with low surface areas.$^{85,86}$ However, Mo$_2$N and Mo$_2$C can be produced via some high surface area methods.$^{78}$ This includes methods such as the “urea glass” method, which involves reacting MoCl$_5$ and ethanol before adding urea in various ratios, and then heating the resulting material for 3 hours at 800 °C under nitrogen, to give Mo$_2$N or Mo$_2$C depending on the Mo:urea ratio.$^{83,87}$ Tišler et al. synthesised Mo$_2$N and Mo$_2$C by using a precursor complex made from hexamethylenetetramine with ammonium heptamolybdate, and multiple heating steps under nitrogen or 20%H$_2$/N$_2$. Other methods include the pyrolysis of organometallic complexes under H$_2$,$^{80}$ reactions of metal oxide vapour and solid carbon under vacuum, and the reaction of metal oxide in the presence of solid carbon.$^{78}$

In this section, two methods were used to produce molybdenum carbonitrides, under low temperature and unreactive gas flows. Initially, attempts were made to form ammonium molybdate oxalate, then combine with guanidine carbonate and follow a similar synthesis to that described in Chapter 4. Secondly, attempts were made to generate molybdenum carbonitrides by starting from ammonium molybdate.
tetrahydrate and guanidine carbonate. Both methods proved successful and the resulting materials were analysed.

5.8.2 Synthesis of molybdenum precursor

Synthesis of ammonium molybdate oxalate was modified from a method reported by Li et al. Ammonium molybdate tetrahydrate (5 g, (NH₄)₆Mo₇O₂₄·4H₂O) was dissolved in 100 ml oxalic acid solution at 80 °C to give a molar ratio of molybdenum to oxalic acid of 1:2. The resulting solution was evaporated off at 100 °C to give blue crystals. The material was then dried overnight at 80 °C. The powder XRD for the as-made material is shown in Figure 5.53, it shows some oxalic acid is unreacted but the rest of the pattern is different to that of the starting materials.

![Figure 5.53: Powder XRD (λ=1.5418 Å) of as made ammonium molybdate oxalate hydrate compared with oxalic acid and simulated ammonium molybdate hydrate from literature.](image_url)
5.8.3 Synthesis of precursors

Two types of precursors were made by starting from either the as made ammonium molybdate oxalate or from ammonium molybdate tetrahydrate. The work on the ammonium molybdate tetrahydrate follows similar work done by de Souza et al. on vanadium nitride made from ammonium orthovanadate and guanidine carbonate. Ammonium molybdate tetrahydrate (1 g) or the as made ammonium molybdate oxalate hydrate (1 g) was macerated with guanidine carbonate to give a metal (m) to guanidine carbonate (GC) ratio of 1M:xGC, where x=2-6, the resulting mixture was heated to 150 °C for 12 hours in air. Resulting in a white powder, which was then ground.

5.8.4 Synthesis of molybdenum carbonitride

The precursor material either made from ammonium molybdate tetrahydrate or ammonium molybdate oxalate hydrate were then heated to between 700-1200 °C under a flow of nitrogen for 4 hours. The resulting material was cooled and passivated in air. This material was then ground and analysed.
5.8.5 Powder XRD and fits

The powder XRD patterns shown in Figure 5.55, show a comparison of the two starting materials made with guanidine carbonate and either ammonium molybdate hydrate or ammonium molybdate oxalate hydrate. The higher temperatures used increase the crystallinity slightly in the samples, but both temperatures form a mixture of phases. The ammonium molybdate hydrate precursor produces a cleaner XRD pattern with more crystalline peaks, and therefore this synthesis was developed further.

![Figure 5.55: Powder XRD (λ=1.5418 Å) of carbonitride materials made, from a precursor material made from either ammonium molybdate hydrate or ammonium molybdate oxalate hydrate, at different temperatures for 4 hours under a flow of nitrogen.](image)

The powder XRD patterns shown in Figure 5.56 show two different materials with varying metal to guanidine carbonate ratios made at 700 °C for 4 hours. It was found that a 1M:2GC ratio produced Mo$_2$C with a space group of $Pbcn$, and a ratio of 1M:4GC produced a mixture of Mo$_2$C and MoN with a space group of $P\overline{3}m1$. This shows that the guanidine carbonate carbon ratio affects the products formed.
Figure 5.56: Powder XRD ($\lambda=1.5418$ Å) of molybdenum carbonitride materials made at 700 °C for 4 hours with varying metal to guanidine carbonate (GC) ratios.$^{91,92}$

A range of materials were made at 900 °C for 4 hours, and the powder XRD patterns for these materials made with various 1M:xGC ratios are shown in Figure 5.57. The XRD patterns are compared to literature simulated patterns and show that a 1M:2GC and 1M:3GC formed an impurity of MoO$_2$, $P2_1/c$, as well as Mo$_2$N, $I4_1/amd$. The higher GC content materials formed Mo$_2$C, $Pbcn$, suggesting more guanidine carbonate helps to form the carbide material.

A range of materials were also made at 1200 °C and the powder XRD patterns for these are shown in Figure 5.58. These materials mainly form the carbide, Mo$_2$C $Pbcn$, however molybdenum metal forms as an impurity in some of the materials, possibly due to the high temperature of the reaction.

These reactions for 700, 900 and 1200 °C are summarised in Table 5.11.
Figure 5.57: Powder XRD ($\lambda=1.5418$ Å) of molybdenum carbonitride materials made at 900 °C for 4 hours with varying metal to guanidine carbonate (GC) ratios. 

Figure 5.58: Powder XRD ($\lambda=1.5418$ Å) of molybdenum carbonitride materials made at 1200 °C for 4 hours with varying metal to guanidine carbonate (GC) ratios.
Table 5.11: Phases identified in molybdenum carbonitride in Figure 5.56, Figure 5.57, and Figure 5.58

<table>
<thead>
<tr>
<th>Synthesis conditions</th>
<th>Phases present</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M:2GC</td>
<td>Mo$_2$C $Pbcn$\textsuperscript{91}</td>
</tr>
<tr>
<td>1M:4GC</td>
<td>Mo$_2$C $Pbcn$\textsuperscript{91}</td>
</tr>
<tr>
<td>1M:2GC</td>
<td>MoO$_2$ $P2_1/c$\textsuperscript{94}</td>
</tr>
<tr>
<td>1M:3GC</td>
<td>MoO$_2$ $P2_1/c$\textsuperscript{94}</td>
</tr>
<tr>
<td>1M:4GC</td>
<td>Mo$_2$C $Pbcn$\textsuperscript{91}</td>
</tr>
<tr>
<td>1M:5GC</td>
<td>Mo$_2$C $Pbcn$\textsuperscript{91}</td>
</tr>
<tr>
<td>1M:2GC</td>
<td>Mo $Im\bar{3}m$\textsuperscript{95}</td>
</tr>
<tr>
<td>1M:3GC</td>
<td>Mo$_2$C $Pbcn$\textsuperscript{91}</td>
</tr>
<tr>
<td>1M:4GC</td>
<td>Mo $Im\bar{3}m$\textsuperscript{95}</td>
</tr>
<tr>
<td>1M:5GC</td>
<td>Mo$_2$C $Pbcn$\textsuperscript{91}</td>
</tr>
</tbody>
</table>

Pawley powder XRD refinements of the Mo$_2$C, $Pbcn$, made under several different conditions are shown in Figure 5.59, and show good fits to the unit cell. The lattice parameters and unit cell volume are summarised in Table 5.12. The unit cell volume becomes smaller with increasing temperature of synthesis.
Figure 5.59: Pawley fits of powder XRD of molybdenum carbides made under different synthesis conditions producing Mo$_2$C, Pbcn.\textsuperscript{91}

Table 5.12: Pawley fit parameters for Mo$_2$C, space group Pbcn.

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice parameter</th>
<th>Unit cell volume / Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_2$C, Pbcn\textsuperscript{91}</td>
<td>$a$ / Å 6.037(3)</td>
<td>148.663</td>
</tr>
<tr>
<td>700 °C 1M:2GC</td>
<td>4.7481(5)</td>
<td>148.88(5)</td>
</tr>
<tr>
<td>900 °C 1M:5GC</td>
<td>4.7400(4)</td>
<td>148.68(5)</td>
</tr>
<tr>
<td>1200 °C 1M:5GC</td>
<td>4.74071(12)</td>
<td>147.537(7)</td>
</tr>
</tbody>
</table>

5.8.6 Thermal analysis

The TGA-DSC for Mo$_2$C made under different conditions are shown in Figure 5.60. The materials show little to no mass change until 350-400 °C where the material starts to increase in mass and an exothermic peak is visible in the DSC. This is because of the onset of Mo$_2$C oxidation. The mass shows a gradual increase until 750 °C, where it plateaus, suggesting the formation of MoO$_3$. At ~800 °C the material sublimes, shown by an endothermic feature in the DSC, other oxides are then believed to be
formed by 1000 °C. By assuming all the material is MoO$_3$ by 750 °C, it is possible to calculate weight percentage amorphous carbon, which is shown in Figure 5.60. These materials give less than 5 wt% amorphous carbon, with the lowest temperature synthesis giving the highest amount and the highest temperature synthesis the least.

![Figure 5.60: TGA-DSC of Mo$_2$C in air made with various 1Mo:xGC ratios at different temperatures, with calculated weight percentage amorphous carbon.](image)

### 5.8.7 Conclusion
Molybdenum carbide has been made via a low temperature guanidine carbonate method for the first time. The material has been analysed by XRD and TGA-DSC. Further analysis of the materials would need to be done to determine whether these materials are suitable for application.

### 5.9 Tungsten Carbonitride

#### 5.9.1 Introduction
Tungsten carbide is a hard material often used in cutting tools, it has properties such as high melting point, high hardness, high chemical stability and high oxidation resistance.$^{97,98}$ WC has the highest conductivity of $10^5$ S cm$^{-1}$ of any interstitial carbide, and is therefore known as the most metallic carbide.$^{99}$
WC was investigated by Liu et al. as an electrocatalyst support for platinum for the HER and HOR.\textsuperscript{100} It was found that after 300 cycles the Pt/WC electrocatalyst lost only 4% of its activity in comparison to 20% loss in the Pt/C in identical acidic operating conditions.\textsuperscript{100} Work by Yan et al. showed that WC on graphitised carbon showed highly enhanced activity for the ORR after loading with platinum.\textsuperscript{101} In work by Garcia-Esparza et al. it was found that tungsten carbides were efficient cocatalysts for photocatalytic water splitting. WC with high surface area exhibits both high activity and stability in HER over a wide pH range. The material also shows good HOR activity.\textsuperscript{102,103}

Hassan et al. found that Pt on WC/C showed good stability and activity for the HOR in PEMFCs.\textsuperscript{104} It was shown to have resistance to CO poisoning and was shown to be more stable than carbon (Vulcan XC-72) as a support.\textsuperscript{104} It was found by Bott-Neto et al. that Pt on WC/C showed similar activities for ORR to that of Pt/C, however Pt on WC\textsubscript{1-x}/C showed activities of 3.6 times higher than that of Pt/C.

Tungsten carbide microspheres of a mixture of WC and W\textsubscript{2}C phases loaded with platinum were found by Wang et al. to have an ORR catalytic activity of more than double the Pt/C catalyst.\textsuperscript{105}

Traditionally WC is made from direct carburisation of the W metal and carbon at 1400-2000 °C in hydrogen or vacuum.\textsuperscript{99} Islam et al. synthesised porous WC by heat treating a biopolymer-tungsten oxide composite at 1300 °C for 3 hours.\textsuperscript{97} Sun et al. found that tungsten carbonitride could be formed by carbothermal NH\textsubscript{3} reduction on activated carbon at 800 °C from WO\textsubscript{3}.\textsuperscript{106} Synthesis by Medeiros et al. uses ammonium paratungstate as a precursor which is carburised at 850 °C under H\textsubscript{2}/CH\textsubscript{4} gas flow.\textsuperscript{107}

Another route of synthesis by Tomas-Garcia et al. involves heating ammonium metatungstate to 600 °C in air for 5 hours to form WO\textsubscript{3}, this is then heated to 880 °C in CH\textsubscript{4}/H\textsubscript{2} for 2 hours to form WC. Alternatively the WO\textsubscript{3} could be heated in NH\textsubscript{3} to 680 °C for 2 hours to form W\textsubscript{2}N, which could be heated further in CH\textsubscript{4}/H\textsubscript{2} to 780 °C for 2 hours to WC.\textsuperscript{108} Giordano et al. uses a synthesis method without the use of reactive gas flows, MoCl\textsubscript{5} and ethanol were mixed with various ratios of urea, and dried to form films, which were then treated 800 °C for 3 hours.\textsuperscript{97}

Tungsten carbides have shown overall good catalytic activities and stability across the literature. The current synthesis methods involve high temperature and reactive gas...
flows, which can be dangerous. Therefore, these materials were considered for synthesis via similar methods to Chapter 3, under nitrogen gas.

### 5.9.2 Synthesis of tungsten precursor

Synthesis of ammonium tungstate oxalate was modified from a method reported by Li et al.\textsuperscript{[75]} Ammonium metatungstate hydrate (5 g, (NH\textsubscript{4})\textsubscript{6}H\textsubscript{2}W\textsubscript{12}O\textsubscript{40}\cdot xH\textsubscript{2}O) was dissolved in 100 ml oxalic acid solution at 80 °C to give a molar ratio of tungsten to oxalic acid of 1:2. The resulting solution was evaporated off at 100 °C to give yellow crystals. The material was then dried overnight at 80 °C. The powder XRD of the resulting material is shown in Figure 5.61, and is compared to oxalic acid and ammonium metatungstate hydrate. It was found that some oxalic acid remains unreacted in the final material. The IR spectrum of ammonium tungstate oxalate hydrate was compared with that of ammonium niobate oxalate hydrate as shown in Figure 5.62. It shows similar peak positions, suggesting that a similar phase has been formed.

![Figure 5.61: Powder XRD (\(\lambda=1.5418 \ \text{Å}\)) of as made ammonium tungstate oxalate hydrate compared to oxalic acid and simulated pattern ammonium metatungstate hydrate from literature.\textsuperscript{[109]}](image)
5.9.3 Synthesis of precursor

Ammonium metatungstate hydrate or the as made ammonium tungstate oxalate was ground together with guanidine carbonate in metal (M) to guanidine carbonate (GC) ratios of 1M:xGC, where x=2-6, and heated at 150 °C for 12 hours. The powder XRD of the resulting materials made from ammonium metatungstate are shown in Figure 5.63. This shows materials with a different powder XRD pattern to that of the starting materials, suggesting the formation of another phase.

The powder XRD of the materials made from ammonium tungstate oxalate are shown in Figure 5.64. This shows that the material has a different powder XRD pattern from the starting materials and suggests the formation of another phase or material. These patterns also contain an impurity of oxalic acid from the initial complexation reaction.

After the reaction with guanidine carbonate, the powder XRD shows two different phases are formed depending on the starting material. This could suggest variation in the carbonitrides depending on the initial starting material.
Figure 5.63: Powder XRD ($\lambda=1.5418$ Å) of precursor materials made from ammonium metatungstate hydrate and guanidine carbonate at 150 °C in air with different tungsten (W) to guanidine carbonate (GC) ratios.

Figure 5.64: Powder XRD ($\lambda=1.5418$ Å) of precursor materials made from as made ammonium tungstate oxalate and guanidine carbonate at 150 °C in air with different tungsten (W) to guanidine carbonate (GC) ratios.
5.9.4 Synthesis of tungsten carbonitride
The precursor material either made from ammonium metatungstate hydrate or ammonium tungstate oxalate hydrate, were then heated to between 700-1200 °C under a flow of nitrogen for 4 hours. The resulting material was cooled and passivated in air. This material was then ground and analysed.

5.9.5 Powder XRD and fits
Due to the difference in the two tungsten precursors after reacting with guanidine carbonate the two methods were compared. The powder XRD for these materials is shown in Figure 5.65. It was found that there was little difference between the powder XRD patterns of the materials, therefore it was decided that starting from the ammonium metatungstate hydrate was a simpler reaction.

![Figure 5.65: Powder XRD of tungsten carbonitrides made from either ammonium metatungstate hydrate or ammonium tungstate oxalate starting material, at different temperatures.](image.png)

Powder XRD shown in Figure 5.66 show tungsten materials made at 700 °C for 4 hours with different 1W:xGC ratios. It was found that most of the materials contained a mixture of phases as shown in Table 5.13. All the materials contained an amorphous material, which was unidentifiable by powder XRD.
Figure 5.66: Powder XRD ($\lambda = 1.5418$ Å) of tungsten carbonitride materials made at 700 °C for 4 hrs, compared to patterns simulated from the literature.\textsuperscript{110-113}

Table 5.13: Summary of tungsten materials made at 700 °C for 4 hours with different $1W:xGC$ ratios identified by powder XRD.

<table>
<thead>
<tr>
<th>W</th>
<th>GC</th>
<th>Materials formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>Unidentified amorphous phase</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>Unidentified amorphous phase</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>Unidentified amorphous phase</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Unidentified amorphous phase</td>
</tr>
</tbody>
</table>

Figure 5.67 shows the powder XRD for tungsten materials made at 900 °C for 4 hours. The materials assigned by powder XRD are shown in Table 5.14. The materials with low ($x < 3$) $1W:xGC$ ratios showed a mixture of phases or the formation of metal. When the GC content was increased to $1W:4GC$ or $1W:5GC$, a hexagonal WN or WC phase was formed, with a space group of $P\bar{6}m2$. 

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Figure 5.67: Powder XRD (λ=1.5418 Å) of tungsten carbonitride materials made at 900 °C for 4 hrs, compared to patterns simulated from the literature.\textsuperscript{112–115}

Table 5.14: Summary of tungsten materials made at 900 °C for 4 hours with different 1W:xGC ratios identified by powder XRD.

<table>
<thead>
<tr>
<th>W</th>
<th>GC</th>
<th>Materials formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>WN/WC ( \text{P}6\text{m}2 )</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>WN/WC ( \text{P}6\text{m}2 )</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>( \text{W}_2\text{C} \ \text{P}\overline{3}\text{1m} )</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>( \text{W}_2\text{C} \ \text{P}\overline{3}\text{1m} )</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>W metal ( \text{Im}\overline{3}\text{m} )</td>
</tr>
</tbody>
</table>

Figure 5.68 shows the powder XRD for tungsten materials made at 1200 °C for 4 hours. The materials assigned by powder XRD are shown in Table 5.15. The high temperature of synthesis causes the formation of tungsten metal. However, the 1W:6GC ratio forms the hexagonal WC or WN with the \( \text{P}6\text{m}2 \) space group.
Figure 5.68: Powder XRD (λ=1.5418 Å) of tungsten carbonitride materials made at 1200 °C for 4 hrs, compared to patterns simulated from the literature.\textsuperscript{111,112,115}

Table 5.15 Summary of tungsten materials made at 1200 °C for 4 hours with different 1W:xGC ratios identified by powder XRD.

<table>
<thead>
<tr>
<th>W</th>
<th>GC</th>
<th>Materials formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>WN/WC (P\bar{6}m2)</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>WN/WC (P\bar{6}m2)</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>WN/WC (P\bar{6}m2)</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>WN/WC (P\bar{6}m2)</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>W metal (Im\bar{3}m)</td>
</tr>
</tbody>
</table>

The tungsten carbonitride materials with single phase XRD data were refined to the hexagonal \(P\bar{6}m2\) space group and these are shown in Figure 5.69. The peak shape of these materials proved difficult to fit and suggested the materials weren’t entirely phase pure. The relatively amorphous pattern of the material made from 1W:6GC at 700 °C is shown for comparison. Unfortunately, due to the amorphous nature of this material it was not possible to identify it. The other materials may contain some of this phase contributing to the poorness of fit.
Figure 5.69: Pawley powder XRD refinements of WC$_{1-p}$N$_p$ refined to hexagonal $P\overline{6}m2$ space group.

5.9.6 Thermal analysis

The WC$_{1-p}$N$_p$ materials made thermal stability was analysed by TGA-DSC and are shown in Figure 5.70. The materials show stability until 400 °C, where the mass begins to increase suggesting oxidation of the material. The mass reached at 900 °C is assumed to be the fully oxidised WO$_3$ material. This was used to calculate the weight percentage of amorphous carbon in the materials shown in Figure 5.70. The material made with 1W:6GC at 900 °C shows a similar percentage of amorphous carbon as the material made at 1200 °C. However, the WC$_{1-p}$N$_p$ made with 1W:5GC at 1200 °C shows much less amorphous carbon than either the other materials.
Figure 5.70: TGA-DSC of WC$_{1-p}$N$_p$ materials made under different conditions, shown with the calculated weight percent of amorphous carbon.

5.9.7 TEM

TEM images of the WC$_{1-p}$N$_p$ materials are shown in Figure 5.71. The 900 °C material shows less agglomeration and smaller particle size than the WC$_{1-p}$N$_p$ made at 1200 °C. The materials both appear to form agglomerates of small particles and it is unclear how much amorphous carbon is present from these images.
5.9.8 Powder conductivity

The powder conductivity for some WC$_{1-p}$N$_p$ materials are shown in Table 5.16. The conductivity is high and is good enough (>0.1 S cm$^{-1}$) for potential application as catalyst supports in PEMFCs. The material made at 1200 °C from the ammonium metatungstate shows higher conductivity than the material made at 900 °C from the ammonium tungsten oxalate.

Table 5.16: Powder conductivity of WC$_{1-p}$N$_p$ materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Starting material</th>
<th>Conductivity / S cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC$_{1-p}$N$_p$ 4 hrs 900 °C</td>
<td>ammonium tungstate oxalate</td>
<td>4.2</td>
</tr>
<tr>
<td>(1W:4GC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC$_{1-p}$N$_p$ 4 hrs 1200 °C</td>
<td>ammonium metatungstate</td>
<td>11.8</td>
</tr>
<tr>
<td>(1W:6GC)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.9.9 Conclusion

Tungsten carbonitrides have been made for the first time via a guanidine carbonate synthesis route. The pure WC$_{1-p}$N$_p$ materials could be made at 900 °C and 1200 °C, whilst at 700 °C an amorphous material form, more work could be done to analyse this material further. The materials have been analysed by powder XRD, TGA-DSC, TEM.
and powder conductivity. The powder conductivity measurements gave conductivities suitable for application, however surface area measurements would need to be recorded before further testing could be done.

5.10 Conclusion
A range of different materials have been made using similar synthesis routes to those reported in Chapter 4. It was found that Ti$_x$Nb$_{1-x}$O$_2$ could be made via a new synthesis route, producing potential materials for use in PEMFCs, which will be electrochemically tested in Chapter 6.

A wide range of carbonitrides were formed using a new guanidine carbonate synthesis including tantalum, tantalum titanium, tantalum niobium, iron, vanadium, molybdenum and tungsten. These materials have all been characterised by powder XRD and some other techniques including TGA-DSC and TEM. These materials have been shown to have conductivity and some to have good surface areas for use in applications. However, further work would be needed on these materials before further testing. This method of synthesis of other carbonitrides has been shown to give high surface area materials, and therefore it is hoped these materials would have these properties as well.

5.11 References
7. X. Lü, W. Yang, Z. Quan, T. Lin, L. Bai, L. Wang, F. Huang and Y. Zhao, *J.


Z. W. Cui, X. K. Li, Y. Cong, Z. J. Dong, G. M. Yuan and J. Zhang, *New


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Chapter 6 – Acid resilience testing and electrochemistry

6.1 Introduction and scope of the chapter

The stability of materials for use as catalyst supports is vital to their eventual application in fuel cells. As mentioned in Chapter 1, the support’s stability can affect mechanisms like nanoparticle agglomeration, nanoparticle dissolution and nanoparticle detachment.\textsuperscript{1,2} During fuel cell operation, the variation in potential can degrade the MEA, particularly in vehicular use due to the range of potentials seen during start and stop protocols.\textsuperscript{3} The typical conditions in a fuel cell during different operating conditions are shown in Table 6.1.

\textit{Table 6.1: Typical gases present and approximate electrode potentials during various operating conditions of a PEMFC, reproduced from Perry.}\textsuperscript{3}

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Fuel electrode (Anode)</th>
<th>Air electrode (Cathode)</th>
<th>Cell potential / V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>Potential / V</td>
<td>Gas</td>
</tr>
<tr>
<td>Normal</td>
<td>H\textsubscript{2}</td>
<td>0.05</td>
<td>Air</td>
</tr>
<tr>
<td>Idle</td>
<td>H\textsubscript{2}</td>
<td>0.0</td>
<td>Air</td>
</tr>
<tr>
<td>Open circuit</td>
<td>H\textsubscript{2}</td>
<td>0.0</td>
<td>Air</td>
</tr>
<tr>
<td>Off</td>
<td>Air</td>
<td>1.1</td>
<td>Air</td>
</tr>
<tr>
<td>Start</td>
<td>H\textsubscript{2}/air</td>
<td>0.0/1.1</td>
<td>Air</td>
</tr>
<tr>
<td>Stop</td>
<td>Air/H\textsubscript{2}</td>
<td>1.1/0.0</td>
<td>Air</td>
</tr>
<tr>
<td>Partial H\textsubscript{2} coverage</td>
<td>H\textsubscript{2}/inert</td>
<td>0.05/1.1</td>
<td>Air</td>
</tr>
<tr>
<td>Fuel starvation</td>
<td>H\textsubscript{2}/inert</td>
<td>&gt;1.5</td>
<td>Air</td>
</tr>
<tr>
<td>Air starvation</td>
<td>H\textsubscript{2}</td>
<td>0.05</td>
<td>Air/H\textsubscript{2}</td>
</tr>
</tbody>
</table>

Durability of PEMFCs has to be tested using accelerated stress test (AST) protocols due to the desired durability in practice being between 5000 – 80000 hours. AST protocols usually consist of either high potential holds or highly cycling conditions.\textsuperscript{3,4} Good ASTs should reduce the time and cost required to test new products.\textsuperscript{3}
In order to test new materials, various electrochemical cells can be used including conventional 3-electrode cells, half cells, and single cells. The catalyst to be tested forms the working electrode, the potential of which or the current passing through which is controlled or monitored. The working electrode and the counter electrode form a circuit and the current flowing through this circuit will cause a reaction on the counter electrode as well. This is not of interest, other than it does not interfere with the working electrode. In order to minimise the electrolyte resistance, another circuit is formed with the reference electrode and working electrode. The reference electrode should maintain a stable potential. Typically a 3-electrode cell is used to screen new catalysts. The catalyst is usually made into an ink with Nafion™, and made to form a layer on an electrochemically inactive electrode disc, such as glassy carbon, to form the working electrode. The electrolyte is usually either 0.1 – 1 M sulfuric acid or perchloric acid, due to fuel cell reactions involving protons. The temperature conditions of such systems are usually controlled by a water or oil bath.

A wide range of electrochemical protocols exist in the literature for testing the stability of catalysts or catalyst layers. Borup et al. used linear potential sweep from 0.1 V to an upper limit of 0.8-1.5 V at 0.1 mV s⁻¹ in increments of 300 cycles at 80 °C. More et al. used linear sweep from 0.1 V to either 1.0 or 1.2 V, at either 60 or 80 °C. Frisk et al. held the cathode at 1.2 V relative to the anode at 80 °C. The Department of Energy, USA, (DOE) suggests for a catalyst support AST a steady hold of potential at 1.2 V for 200 hrs at 95 °C or until catalytic activity loss reaches 60 %, electrochemical surface area decreases by 40 % or performance is reduced by 30 mV at 1.5 A cm⁻². For PEM electrocatalysts the DOE suggest cycling between 0.7 V and 0.9 V for 30000 cycles or until catalytic activity loss reaches 60 %, electrochemical surface area decreases by 40 % or performance is reduced by 30 mV at 0.8 A cm⁻².

This chapter focuses on the acid stability and electrochemical properties of the materials made in the previous chapters. This includes acid resilience tests, electrochemical testing of the as-made materials and electrochemical testing of the materials loaded with iridium. The performance as a catalyst support was assessed by its stability in acid, its stability in acid whilst under potential, and its mass activity of the iridium loaded supports. Mass activity is a measure of how active a material is per gram of platinum group metal (PGM), in this case iridium. These properties were
compared to a commercial IrO$_2$ material and carbon loaded with iridium via the same method as the other materials.

6.2 Experimental

6.2.1 Acid resilience testing

In order to determine if the samples described in earlier chapters were suitable for catalyst supports in acidic electrochemical applications such as the PEM fuel cell, acid resilience tests were performed. This involved heating accurately weighed 50 mg of sample in 50 ml of 1 M sulfuric acid or triflic acid at 80 °C for 24 hours whilst stirring. An approximate value for the dissolution was initially determined by the mass of sample at the end; however, these results had high errors due to the loss of sample in the weighing process. Therefore, ICP-OES was used to calculate the concentration of metal ions in solution at the end of the acid test. The resulting loss of metal ions from the solids were then determined before the solid materials were analysed further.

6.2.2 Electrochemical testing

To fabricate the electrodes, 0.1 g of sample was combined with 0.02 g of aqueous Nafion™ solution (11.92 wt% solids) and 3 drops of water were added. This was then mixed in a planetary mixer for 15 seconds at 3000 rpm. The resultant ink was shear-mixed in a planetary mixer using 5 mm diameter yttrium stabilised zirconia ceramic beads and a further drop of water was added if required before mixing for a further 2 minutes at 3000 rpm. The ink was stirred manually with a spatula to break up any sediment at intervals during the mixing. The resulting ink was further diluted by adding 2 g of water. The ink was then sprayed on to a 7 × 7 cm$^2$ square of Toray paper (hydrophobic gas diffusion layer (GDL) 60, a carbon fibre composite paper) by diluting 0.25 ml of the ink, with 0.75 ml isopropanol and 1.5 ml water in the spray gun before spraying a uniform layer of material onto the Toray paper on a hot plate at 80 °C. The resulting layer was weighed to get an approximation of the thickness of layer aiming for between 0.05 – 0.15 mg cm$^{-2}$, before using X-ray fluorescence (XRF) spectroscopy to analyse the evenness of spread. From the resulting square of ink on Toray paper, 20 mm diameter buttons were cut out and further analysed by XRF.

The support materials were loaded with iridium by a polyol method previously reported by Karimi et al.$^{10}$ 0.5 g of support was slurried in 100 ml of ethylene glycol with 0.5 g NaOH. Iridium was added in the form of 0.5 g of chloroiridic acid to give
30 wt% iridium in the resulting catalyst. The slurry was heated to 160 °C and stirred for 2 hours. After cooling, 1 M H$_2$SO$_4$ was used to dilute the solution to reach a pH of 2. This was then filtered and washed 3 times with 100 ml of deionised water, and the solid material was then dried at 80 °C. The materials were then treated the same as above in order to make 20 mm diameter buttons with 0.2 mg cm$^{-2}$ of iridium by XRF.

The oxygen evolution reaction (OER) starts at about 1.23 V vs the reversible hydrogen electrode (RHE) under acidic conditions. Wet cell testing was done in 0.1 M H$_2$SO$_4$ at 60 °C to establish the activity of the catalyst supports. The button loaded with sample was wetted in 200 ml of 0.1 M H$_2$SO$_4$ overnight whilst under vacuum, to allow ingress of solution into the Toray paper. 5 ml of the soaking solution was taken for ICP-MS before the button was attached to a gold wire to form the working electrode as shown in Figure 6.1. The cell was filled with 100 ml of 0.1 M H$_2$SO$_4$ and was degassed with nitrogen. Once the button was in place and the cell set up, another 5 ml sample was taken for ICP-MS, before replacing the solution with fresh 0.1 M H$_2$SO$_4$. The counter electrode was a Pt wire and the reference electrode the RHE, consisting of hydrogen bubbled over a Pt/C catalyst. First the cell was cycled between 0 – 1.35 V vs RHE at different scan rates (300 – 5 mV s$^{-1}$), then an activity sweep was performed between 1 – 1.55 V vs RHE at 1 mV s$^{-1}$ at the beginning of life (BOL). A sample of 5 ml was then taken for ICP-MS and replaced with fresh 0.1 M H$_2$SO$_4$. Then a degradation cycle between 0.6 – 1.35 V vs RHE at 100 mV s$^{-1}$ for 1000 cycles was performed (~4 hours 10 minutes). This was chosen as the potential is brought up to the onset of OER, while not forming bubbles which could affect the results. Another 5 ml sample was taken for ICP-MS analysis. An end of life (EOL) activity test was then performed after the degradation cycles equivalent to at the start of life (CVs at different scan rates then an activity sweep).

The mass activity of the materials was calculated either by mass activity A/g of iridium present or by mass of as made material present in the case of the samples not loaded with iridium.
6.3 Manganese ruthenium oxides acid resilience testing

It was found that after acid resilience tests, the manganese ruthenium oxides decreased in crystallinity illustrated by a broadening of the XRD peaks shown in Figure 6.2. The XRD also shows manganese sulfate has crystallised at the surface of some of the materials, suggesting manganese has left the structure. Figure 6.2 also shows the results of EDXA before and after the acid testing: this shows an increase in the relative amount of ruthenium within the remaining solid, indicating that the manganese has been leached from the structures. Table 6.2 shows the percentage of remaining metal calculated from the ICP of the solution. It shows that the manganese is leached significantly from the sample while the ruthenium within the sample is relatively stable.
Figure 6.2: Powder XRD of $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ before and after acid test in 1 M H$_2$SO$_4$ at 80 °C for 24 hours, with $x$ calculated from EDXA of the sample. MnSO$_4$ crystallised in some of the samples after the acid test, a reference pattern is shown in blue.\textsuperscript{12}

Table 6.2: Percentage of manganese, ruthenium and total metal remaining after acid test, in 1 M H$_2$SO$_4$ for 24 hours, calculated from ICP of the resulting acid test solution, where $x$ is $\beta$-Mn$_{1-x}$Ru$_x$O$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$</th>
<th>%Mn remaining</th>
<th>%Ru remaining</th>
<th>% metal remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-Mn$_{1-x}$Ru$_x$O$_2$</td>
<td>0.13</td>
<td>83.2</td>
<td>99.5</td>
<td>86.6</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>79.9</td>
<td>99.5</td>
<td>85.7</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>78.8</td>
<td>99.7</td>
<td>87.8</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>80.9</td>
<td>99.7</td>
<td>89.8</td>
</tr>
<tr>
<td></td>
<td>0.48</td>
<td>81.1</td>
<td>99.6</td>
<td>92.8</td>
</tr>
</tbody>
</table>

Attempts to form buttons with Nafion\textsuperscript{TM} were made. However, it was found that the samples were completely dissolved during the ink making process. Further acid tests were done using triflic acid an acid similar to that of Nafion\textsuperscript{TM}, in an attempt to see why the samples dissolved in Nafion\textsuperscript{TM}. The sample was tested using 50 mg of sample to 50 ml of 1 M triflic acid at 80 °C for 24 hours. The percentage of metal remaining in the sample was calculated from ICP-OES of the resulting acid solution as shown in
Table 6.3. This shows that the triflic acid test resulting in 19.2% more leaching of the manganese than in the 1 M sulfuric acid test. Pawley XRD fits were performed on the resulting materials and can be seen in Figure 6.3. The fitted unit cell parameters for these fits can be seen in Table 6.4, which shows an increase in the lattice parameters after the 1 M sulfuric acid test with a further increase seen with the triflic acid test. This indicates that the manganese is leached from the sample and therefore the unit cell expands due to the larger concentration of ruthenium present in the solid. This is backed up by the EDXA values shown in Figure 6.3, which show the ruthenium content is increased from the initial material. From these acid tests it is possible to see that the samples are inappropriate for use in the PEM fuel cell where Nafion™ is the proton exchange membrane. However, the samples do show reasonable stability within the 1 M sulfuric acid, with 90% of the metal remaining.

Table 6.3: Acid test results of β-Mn$_{0.67}$Ru$_{0.33}$O$_2$ using 1 M H$_2$SO$_4$ and 1 M triflic acid, showing the calculated percentage of remaining manganese, ruthenium and total metal from ICP of the solution. EDXA was used to calculate x after the acid test, where x is β-Mn$_{1-x}$Ru$_x$O$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>%Mn remaining</th>
<th>%Ru remaining</th>
<th>% metal remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>After acid test in 1 M sulfuric acid</td>
<td>0.34</td>
<td>80.9</td>
<td>99.7</td>
<td>89.8</td>
</tr>
<tr>
<td>After acid test in 1 M triflic acid</td>
<td>0.63</td>
<td>61.7</td>
<td>99.4</td>
<td>79.5</td>
</tr>
</tbody>
</table>
Figure 6.3: Pawley fits of powder XRD of $\beta$-Mn$_{0.67}$Ru$_{0.33}$O$_2$ before acid tests, after acid test in 1 M H$_2$SO$_4$ and after acid test in 1 M triflic acid. EDXA was used to calculate the values of $x$ after the tests, where $\beta$-Mn$_{1-x}$Ru$_x$O$_2$.

Table 6.4: Pawley fit parameters of $\beta$-Mn$_{0.67}$Ru$_{0.33}$O$_2$ before acid tests, after 1 M sulfuric acid test and after 1 M triflic acid test, compared against the pure end members synthesised by the same method

<table>
<thead>
<tr>
<th>Pawley fit unit cell parameters (tetragonal, $P4_2/mnm$)</th>
<th>$a=b$ / Å</th>
<th>$c$ / Å</th>
<th>Volume / Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-MnO$_2$</td>
<td>4.4055(3)</td>
<td>2.8728(3)</td>
<td>55.757(13)</td>
</tr>
<tr>
<td>$\beta$-Mn$<em>{0.67}$Ru$</em>{0.33}$O$_2$</td>
<td>4.449(2)</td>
<td>2.926(1)</td>
<td>57.92(7)</td>
</tr>
<tr>
<td>After acid test in 1 M sulfuric acid</td>
<td>4.466(3)</td>
<td>2.948(2)</td>
<td>58.80(12)</td>
</tr>
<tr>
<td>After acid test in 1 M triflic acid</td>
<td>4.505(5)</td>
<td>2.984(3)</td>
<td>60.6(2)</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>4.55(2)</td>
<td>3.08(1)</td>
<td>63.8(8)</td>
</tr>
</tbody>
</table>
6.4 Niobium titanium carbonitrides acid resilience testing

Acid resilience tests were performed in 1 M H$_2$SO$_4$ at 80 °C for 24 hours in order to mimic the harsh conditions seen within a PEM fuel cell. The resulting solid was analysed by a range of techniques including PXRD, XPS and XANES.

6.4.1 Powder XRD

Powder XRD Pawley fits shown in Figure 6.4 and the corresponding lattice parameters shown in Figure 6.5, show an increase in the unit cell parameters for the materials NbC$_{1-p}$N$_p$ 12 hrs 700 °C and NbC$_{1-p}$N$_p$ 4 hrs 900 °C after acid testing. This suggests that the materials are becoming more like niobium carbide ($a = 4.4686(1)$ Å$^{13}$) instead of niobium nitride ($a = 4.394(3)$ Å$^{14}$), and therefore the materials are losing some nitrogen from the unit cell. The NbC$_{1-p}$N$_p$ 4 hrs 1200 °C sample shows little change in lattice parameter.
Figure 6.4: Pawley refinements against powder XRD data of NbC$_{1-p}$N$_p$ materials made with different synthesis conditions, before and after acid testing 50 mg in 1 M H$_2$SO$_4$ at 80 °C for 24 hours.
Crystallite size was calculated using Scherrer analysis and the resulting values are shown in Figure 6.6. Crystallite size decreased for both NbC$_{1-p}$N$_p$ 12 hrs 700 °C and NbC$_{1-p}$N$_p$ 4 hrs 900 °C. Crystallite size for the NbC$_{1-p}$N$_p$ 4 hrs 1200 °C samples remains unchanged.

**Figure 6.5:** Lattice parameter $a$ calculated from the Pawley refinements of NbC$_{1-p}$N$_p$ made at different temperatures of synthesis, the 700 °C sample was reacted for 12 hours and the other materials for 4 hours, before and after acid testing.

**Figure 6.6:** Crystallite size of NbC$_{1-p}$N$_p$ made at different temperatures, the 700 °C sample was reacted for 12 hours and the other materials for 4 hours, before and after acid testing in 1 M H$_2$SO$_4$ at 80 °C for 24 hours calculated from Pawley fits of powder XRD using the Scherrer method.
Powder XRD for NbC\(_{1-p}\)\(_N\)\(_p\) 4 hrs 900 °C, Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)\(_N\)\(_p\) 4 hrs 900 °C and TiC\(_{1-p}\)\(_N\)\(_p\) 4 hrs 900 °C before and after acid testing, are compared in Figure 6.7. The NbC\(_{1-p}\)\(_N\)\(_p\) 4 hrs 900 °C sample shows good stability and a small increase in peak broadeness, suggesting some decrease in crystallite size. Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)\(_N\)\(_p\) 4 hrs 900 °C shows some stability but forms an amorphous secondary phase, with a feature present at about 25 ° 2θ in the powder XRD. The TiC\(_{1-p}\)\(_N\)\(_p\) 4 hrs 900 °C sample shows little stability and forms ammonium titanium oxide sulfate during the acid test.

![Figure 6.7: Powder XRD of carbonitride samples before and after acid testing 50 mg in 50 ml of 1 M H\(_2\)SO\(_4\) at 80 °C for 24 hours compared to ammonium titanium oxide sulfate from the literature.](image)

### 6.4.2 ICP-OES

ICP-OES was performed on the resulting solutions from the acid tests as reported in Table 6.5. It was found that NbC\(_{1-p}\)\(_N\)\(_p\) samples released very little Nb to solution and >98.5% remained in the solid. The Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)\(_N\)\(_p\) samples ICP shown in Table 6.6 showed very little Nb ions dissolved into solution but some Ti ions were found in solution. Therefore, the resulting solid had ~98.5% of Nb remaining but only ~86% of Ti remaining. This corresponds to total metal remaining of ~94%, showing reasonable stability in strongly acidic conditions. The TiC\(_{1-p}\)\(_N\)\(_p\) 4 hrs 900 °C ICP showed that 37.2% of titanium is remaining in the solid, but powder XRD showed that the remaining solid was actually ammonium titanium oxide sulfate, and therefore showed little stability under these strongly acidic conditions.
Table 6.5: Percentage of remaining niobium in the sample after acid testing of NbC$_{1-p}$N$_p$ made under various conditions calculated from the ICP of the acid test solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Nb remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbC$_{1-p}$N$_p$ 12 hrs 700 °C</td>
<td>99.2</td>
</tr>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 850 °C</td>
<td>98.5</td>
</tr>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 900 °C</td>
<td>98.6</td>
</tr>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 1000 °C</td>
<td>98.5</td>
</tr>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 1100 °C</td>
<td>98.6</td>
</tr>
<tr>
<td>NbC$_{1-p}$N$_p$ 4 hrs 1200 °C</td>
<td>98.5</td>
</tr>
</tbody>
</table>

Table 6.6: Percentage of remaining metals in the sample after acid testing of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ made under various conditions calculated from the ICP of the acid test solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Nb remaining</th>
<th>%Ti remaining</th>
<th>% Metal remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$<em>{0.5}$Ti$</em>{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C</td>
<td>99</td>
<td>86</td>
<td>94.6</td>
</tr>
<tr>
<td>Nb$<em>{0.5}$Ti$</em>{0.5}$C$_{1-p}$N$_p$ 12 hrs 900 °C</td>
<td>98.6</td>
<td>86</td>
<td>94.3</td>
</tr>
<tr>
<td>Nb$<em>{0.5}$Ti$</em>{0.5}$C$_{1-p}$N$_p$ 4 hrs 1200 °C</td>
<td>98.5</td>
<td>86.8</td>
<td>94.5</td>
</tr>
</tbody>
</table>

6.4.3 XPS

XPS was used to analyse the surface of the materials before and after acid testing. The Nb 3d region is analysed in Figure 6.8, which shows that no NbN/NbC is present at the surface of NbC$_{1-p}$N$_p$ 12 hrs 700 °C and that after acid testing more Nb$_2$O$_5$ is present. A similar trend is seen in NbC$_{1-p}$N$_p$ 4 hrs 900 °C after acid testing where less NbN/NbC is present. But the NbC$_{1-p}$N$_p$ 4 hrs 1200 °C sample shows an increase in the amount of NbN/NbC at the surface and less Nb$_2$O$_5$. This suggests that these materials act differently under acidic conditions possibly due to their different C:N ratios, surface areas and other characteristics.
Figure 6.8: Nb 3d XPS of NbC$_{1-p}$N$_p$ 12 hrs 700 °C, NbC$_{1-p}$N$_p$ 4 hrs 900 °C and NbC$_{1-p}$N$_p$ 4 hrs 1200 °C before and after acid testing for 24 hours at 80 °C in 1 M H$_2$SO$_4$.

XPS of the C 1s region is shown in Figure 6.9. It shows that all the samples lose the feature at 288.8 eV, corresponding to O=C-O, after acid testing. This suggests that some of the surface is either rearranging or dissolving, to form a cleaner surface. The NbC$_{1-p}$N$_p$ 4 hrs 1200 °C sample shows an increase in carbide at the surface after acid testing, corresponding with the Nb 3d region results.
Figure 6.9: C 1s XPS of NbC\(_{1-p}\)N\(_p\) 12 hrs 700 °C, NbC\(_{1-p}\)N\(_p\) 4 hrs 900 °C and NbC\(_{1-p}\)N\(_p\) 4 hrs 1200 °C before and after acid testing for 24 hours at 80 °C in 1 M \(\text{H}_2\text{SO}_4\).

XPS of N 1s region are shown in Figure 6.10, NbC\(_{1-p}\)N\(_p\) 4 hrs 1200 °C shows a decrease in the organic nitrogen present after the acid testing, and only has oxidised NbN present at the surface. This may be the cause of the decrease of nitrogen within the sample indicated by the lattice parameters calculated previously. The NbC\(_{1-p}\)N\(_p\) 4 hrs 900 °C sample shows an increase in N-O and organic N present at the surface, whereas NbC\(_{1-p}\)N\(_p\) 12 hrs 700 °C shows no nitrogen present at the surface after acid testing.
Figure 6.10: N 1s XPS of NbC$_{1-p}$N$_p$ 12 hrs 700 °C, NbC$_{1-p}$N$_p$ 4 hrs 900 °C and NbC$_{1-p}$N$_p$ 4 hrs 1200 °C before and after acid testing for 24 hours at 80 °C in 1 M H$_2$SO$_4$.

XPS of O 1s region is shown in Figure 6.11. It shows NbC$_{1-p}$N$_p$ 4 hrs 1200 °C after acid testing has less metal oxide present at the surface and an O=C layer is present both before and after acid testing. NbC$_{1-p}$N$_p$ 4 hrs 900 °C sample shows more O=C present after acid testing and less H$_2$O/organic O. The NbC$_{1-p}$N$_p$ 12 hrs 700 °C sample shows more O-C present at the surface after acid testing, suggesting some of the amorphous carbon may become oxidised.
Figure 6.11: O 1s XPS of NbC1-pNp 12 hrs 700 °C, NbC1-pNp 4 hrs 900 °C and NbC1-pNp 4 hrs 1200 °C before and after acid testing for 24 hours at 80 °C in 1 M H2SO4.

The XPS analysis is summarised in Figure 6.12 with the elemental analysis from XPS shown in Figure 6.13. The Nb 3d region shows nearly all the Nb is Nb2O5 at the surface of NbC1-pNp 12 hrs 700 °C, and the N 1s region shows no nitrogen is present at the surface, for the acid test sample. For NbC1-pNp 4 hrs 1200 °C the Nb 3d region and the C 1s region shows more NbC present after acid testing and the N 1s region shows more oxidised NbN. The NbC1-pNp 4 hrs 900 °C sample after acid testing shows more Nb2O5 present in the Nb 3d region, and the presence of N-O in the nitrogen 1s region. The elemental analysis shows sodium and fluorine are present on the surface of some of the samples. This is probably due to some contamination. Fluorine is a common contaminant in XPS and could come from fluorinated packaging or deionised water. The elemental analysis shows less carbon present at the surface after acid tests suggesting the acid does clean up the surface of some of the amorphous carbon present. There is also very little nitrogen at the surface possibly due to it being contained within the structure as NbC1-pNp.
Figure 6.12: Summary of the regions of fitted XPS of NbC$_{1-p}$N$_{p}$ 12 hrs 700 °C, NbC$_{1-p}$N$_{p}$ 4 hrs 900 °C and NbC$_{1-p}$N$_{p}$ 4 hrs 1200 °C before and after acid testing for 24 hours at 80 °C in 1 M H$_2$SO$_4$. Note no nitrogen was found in NbC$_{1-p}$N$_{p}$ 12 hrs 700 °C after acid test. (Nb 3d depth 7.3 nm, C 1s depth 6.9 nm, N 1s depth 6.4 nm and O 1s depth 5.8 nm)
Figure 6.13: Elemental composition calculated from XPS of NbC_{1-p}N_{p} 12 hrs 700 °C, NbC_{1-p}N_{p} 4 hrs 900 °C and NbC_{1-p}N_{p} 4 hrs 1200 °C before and after acid testing for 24 hours at 80 °C in 1 M H_{2}SO_{4}.

The XPS shows that the materials change at the surface after acid testing. The lower temperature materials change differently to the high temperature materials. The materials all lose some surface carbon, with the lower temperature materials forming, more Nb_{2}O_{5} at the surface whereas NbC_{1-p}N_{p} 4 hrs 1200 °C increases its NbN/NbC content at the surface. This suggests that these materials would interact differently as catalyst supports in the PEMFC.

6.4.4 XANES

Nb K edge XANES of NbC_{1-p}N_{p} 12 hrs 700 °C before and after acid testing is shown in Figure 6.14, compared to materials with known niobium oxidation states. It shows that after acid testing the material becomes more oxidised. This is shown in Figure 6.15, where before acid testing the material has an average niobium oxidation state of about +3.5 but after acid testing it is oxidised further to +4. This indicates that the material is forming more oxide at the surface, and is consistent with the XPS.
Figure 6.14: Nb K edge XANES of NbC_{1-p}N_p 12 hrs 700 °C before and after acid testing at 80 °C for 24 hours, compared to reference materials, recorded on B18 at Diamond Light Source.

Figure 6.15: Average niobium oxidation state calculated from Nb K edge XANES of NbC_{1-p}N_p 12 hrs 700 °C before and after acid testing at 80 °C for 24 hours, compared to reference materials, recorded on B18 at Diamond Light Source.
The Nb K edge XANES for the Nb$_{0.5}$Ti$_{0.5}$C$_1$-$p$N$_p$ materials before and after acid testing is shown in Figure 6.16. The average niobium oxidation states were calculated from the reference materials and the calculated average niobium oxidation states are shown in Figure 6.17. The materials all show an increase in niobium average oxidation state after acid testing suggesting that the materials are more oxidised. The Nb$_{0.5}$Ti$_{0.5}$C$_1$-$p$N$_p$ 4 hrs 1200 °C sample shows the least change in average niobium oxidation state from +2.8 to +3, whereas the other materials increase in oxidation state by +0.8 after acid testing.

![Graph showing Nb K edge XANES](image)

**Figure 6.16: Nb K edge XANES of Nb$_{0.5}$Ti$_{0.5}$C$_1$-$p$N$_p$ samples made under different reaction conditions before and after acid testing at 80 °C for 24 hours, compared to reference materials, recorded on B18 at Diamond Light Source.**
Figure 6.17: Average niobium oxidation state calculated from Nb K edge XANES of Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ samples made under different reaction conditions before and after acid testing (AT) at 80 °C for 24 hours, compared to reference materials, recorded on B18 at Diamond Light Source.

The Ti K edge XANES for Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ materials before and after acid testing are shown in Figure 6.18. They show small shifts in the edge position, which are summarised in terms of average titanium oxidation state in Figure 6.19. The materials show a slight decrease in titanium oxidation state after acid testing. This shows a different pattern than the niobium oxidation state and could suggest that the material formed could be a Nb$_{0.5}$Ti$_{0.5}$O$_2$, where the niobium oxidation state is higher than that of the titanium.
Figure 6.18: Ti K edge XANES of Nb<sub>0.5</sub>Ti<sub>0.5</sub>C<sub>1-p</sub>N<sub>p</sub> samples made under different reaction conditions before and after acid testing at 80 °C for 24 hours, compared to reference materials, recorded on B18 at Diamond Light Source.

Figure 6.19: Average titanium oxidation states calculated from Ti K edge XANES of Nb<sub>0.5</sub>Ti<sub>0.5</sub>C<sub>1-p</sub>N<sub>p</sub> samples made under different reaction conditions before and after acid testing at 80 °C for 24 hours, compared to reference materials, recorded on B18 at Diamond Light Source.
6.5 Niobium titanium carbonitrides electrochemical testing

6.5.1 Electrochemical testing of as made materials

The mass activity curves for NbC$_{1-p}$N$_p$ materials and Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 1200 °C are shown in Figure 6.20, before and after the 1000 degradation cycles. A value of 1.47 V was used to read off the activity values reported in Figure 6.21. The activity of the NbC$_{1-p}$N$_p$ materials shows a decrease after the degradation cycles. This suggests that some surface area could be lost or oxidation states could change triggering this loss in activity, as shown in the cyclic voltammograms in Figure 6.22. The Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ material showed double layer charging features across the potentials scanned, with no visible OER activity. As the double layer charging dominates, the mass activity at 1.47 V cannot be taken as an OER mass activity.

![Figure 6.20: Mass activity of the NbC$_{1-p}$N$_p$ and Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ materials recorded with a linear scan at 1 mV/s in 0.1 M H$_2$SO$_4$.](image)

The mass activity curves for NbC$_{1-p}$N$_p$ materials and Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 1200 °C are shown in Figure 6.20, before and after the 1000 degradation cycles. A value of 1.47 V was used to read off the activity values reported in Figure 6.21. The activity of the NbC$_{1-p}$N$_p$ materials shows a decrease after the degradation cycles. This suggests that some surface area could be lost or oxidation states could change triggering this loss in activity, as shown in the cyclic voltammograms in Figure 6.22. The Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ material showed double layer charging features across the potentials scanned, with no visible OER activity. As the double layer charging dominates, the mass activity at 1.47 V cannot be taken as an OER mass activity.
Figure 6.21: Mass activity values taken at 1.47 V of the $\text{NbC}_{1-p}\text{N}_p$ and $\text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_p$ materials.

Cyclic voltammetry shown in Figure 6.22, shows the cycles at 50 mV/s at beginning of life (BOL) and end of life (EOL). The double layer shown between 0.8-1 V shows a decrease at the EOL of each material. This suggests some loss of surface area and possible oxidation of the surface. The $\text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_p$ 4 hrs 1200 °C shows the largest double layer suggesting large surface area, but this material is known to have the largest amount of amorphous carbon out of these materials tested, and this could be a factor in the result. The smallest double layer is the $\text{NbC}_{1-p}\text{N}_p$ 4 hrs 1200 °C sample: this is due to the material having a smaller surface area due to the higher temperature of synthesis causing larger particle sizes, but it also has the least amount of amorphous carbon.
Figure 6.22: Cyclic voltammograms (50 mV s\(^{-1}\)) of the NbC\(_{1-p}N_p\) and Nb\(_{0.5}Ti_{0.5}C_{1-p}N_p\) materials at beginning of life (BOL) and end of life (EOL) after 1000 cycles.

6.5.2 Electrochemical testing of materials loaded with iridium

For comparison purposes, the NbC\(_{1-p}N_p\) 4 hrs 900 °C sample and the Nb\(_{0.5}Ti_{0.5}C_{1-p}N_p\) 4 hrs 900 °C sample were selected for loading with iridium via the polyol method and further electrochemical testing. These were compared with carbon, which was loaded with iridium via the same polyol method, and an IrO\(_2\) commercial material from Alfa Aesar.

The iridium is well dispersed on the NbC\(_{1-p}N_p\) 4 hrs 900 °C sample as shown in Figure 6.23 and Figure 6.24. The iridium is found across the sample, particularly at the surface of the sample.
Figure 6.23: EDXA mapping from TEM of NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C loaded with iridium, showing N in turquoise, O in white, Nb in red and Ir in green.

Figure 6.24: EDXA mapping from TEM of NbC\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C loaded with iridium showing Nb in red and Ir in green.

In Nb\textsubscript{0.5}Ti\textsubscript{0.5}C\textsubscript{1-p}N\textsubscript{p} 4 hrs 900 °C loaded with iridium, the sample shows reasonable dispersion across the sample, as shown in Figure 6.25 and Figure 6.26. However, there is also some agglomeration of the iridium particles, shown by clustering of iridium in the EDXA.
Figure 6.25: EDXA mapping from TEM of Nb$_{0.5}$Ti$_{0.5}$C$_1$-pN$_p$ 4 hrs 900 °C loaded with iridium, showing C in white, N in turquoise, O in white, Ti in blue, Nb in red and Ir in green.

Figure 6.26: EDXA mapping from TEM of Nb$_{0.5}$Ti$_{0.5}$C$_1$-pN$_p$ 4 hrs 900 °C loaded with iridium, showing Ti in blue, Nb in red and Ir in green.

The carbon loaded with iridium TEM images are shown in Figure 6.27. The iridium is reasonably well dispersed across the sample, although some clustering is present. Average iridium particle size in well dispersed areas was 1.5 nm, however large agglomerates of iridium also existed. Particle size analysis could not be carried out for the NbC$_{1}$-pN$_p$ and Nb$_{0.5}$Ti$_{0.5}$C$_{1}$-pN$_p$ samples because no areas with well separated nanoparticles could be found, indicative of the lower surface area of these supports.
Figure 6.27: TEM images of carbon loaded with iridium.

Two buttons of each carbonitride material were tested for repeatability. The mass activity OER measurements are shown in Figure 6.28 and the activity values at 1.47 V are shown in Figure 6.29 and Figure 6.30. The carbon loaded with 30 wt% iridium and the IrO₂ commercial material show little change in activity. The NbC₁₋₃N₃ 4 hrs 900 °C loaded with 30 wt% iridium shows lower activity levels than both the commercial IrO₂ and the carbon loaded with 30 wt% iridium. The material, however, shows reasonable stability and has an activity of around 10 A g⁻¹ of iridium. The activity values of Nb₀.₅Ti₀.₅C₁₋₃N₃ 4 hrs 900 °C loaded with 30 wt% iridium shown in Figure 6.30, show an increase in activity over both the commercial IrO₂ catalyst and the carbon loaded with 30 wt% iridium. Ir metal will oxidise to IrO₂ during the OER test, but will form a more active material than when IrO₂ is preformed.¹⁶ Nb₀.₅Ti₀.₅C₁₋₃N₃ 4 hrs 900 °C loaded with 30 wt% iridium shows a decrease in activity after the cycling degradation process but is still more active than the carbon loaded with 30 wt% iridium and the commercial IrO₂. When Nb₀.₅Ti₀.₅C₁₋₃N₃ 4 hrs 1200 °C material was tested without the iridium loading it was found to be inactive. Before additions of iridium the Nb₀.₅Ti₀.₅C₁₋₃N₃ 4 hrs 900 °C material contained higher (27 wt%) amorphous carbon content than the 1200 °C sample (21.6 wt%).
Figure 6.28: Mass activity measurements with the activity values taken at 1.47 V of the NbC$_{1-p}$N$_p$ and Nb$_{0.5}$Ti$_{0.5}$C$_1$N$_p$ materials loaded with 30 wt% iridium compared with carbon loaded with 30 wt% iridium and IrO$_2$ commercial catalyst.

Figure 6.29: Mass activity values taken at 1.47 V of NbC$_{1-p}$N$_p$ 4 hrs 900 °C loaded with 30 wt% iridium compared with carbon loaded with 30 wt% iridium and the IrO$_2$ commercial catalyst.
Figure 6.30: Mass activity values taken at 1.47 V of \(\text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_{p}\) 4 hrs 900 °C loaded with 30 wt% iridium compared with carbon loaded with 30 wt% iridium and the \(\text{IrO}_2\) commercial catalyst. The cyclic voltammogram for \(\text{NbC}_{1-p}\text{N}_{p}\) 4 hrs 900 °C loaded with 30 wt% iridium is shown in Figure 6.31, and compared with the carbon loaded with 30 wt% iridium. The carbon shows a slight increase in the double layer size suggesting an increase in surface area, where as the \(\text{NbC}_{1-p}\text{N}_{p}\) 4 hrs 900 °C loaded with iridium shows a slight decrease in the double layer from the BOL to the EOL. This suggests either a loss in surface area or a change in oxidation state of the material.
Figure 6.31: Cyclic voltammograms (50 mV s\(^{-1}\)) of the NbC\(_{1-p}\)N\(_p\) 4 hrs 900 °C loaded with 30 wt% iridium compared with carbon loaded with 30 wt% iridium at beginning of life (BOL) and end of life (EOL) after 1000 cycles.

The cyclic voltammogram for Nb\(_{0.5}\)Ti\(_{0.5}\)C\(_{1-p}\)N\(_p\) 4 hrs 900 °C loaded with 30 wt% iridium is shown in Figure 6.32, for the BOL and EOL. It is compared to the carbon loaded with 30 wt% iridium. The material has a smaller double layer than carbon loaded with iridium and shows a slight decrease in the double layer size at EOL. However, it shows a larger double layer at EOL than the NbC\(_{1-p}\)N\(_p\) 4 hrs 900 °C iridium loaded material.
Figure 6.32: Cyclic voltammograms (50 mV s$^{-1}$) of the Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_{p}$ 4 hrs 900 °C loaded with 30 wt% iridium compared with carbon loaded with 30 wt% iridium at beginning of life (BOL) and end of life (EOL) after 1000 cycles.

ICP-MS was recorded of solution samples taken during the electrochemical testing. Sample 1 was taken from the solution wetting the button overnight, sample 2 from the initial solution in the cell, sample 3 from after the first activity tests and sample 4 from after the 1000 cycles in the cell at the end of life. Figure 6.33 shows the dissolution from NbC$_{1-p}$N$_{p}$ 4 hrs 900 °C loaded with 30 wt% iridium. Less then 0.2% of the niobium dissolves in either of the button tests and less than 0.4% of the iridium dissolves. This shows the high stability of the NbC$_{1-p}$N$_{p}$ 4 hrs 900 °C sample loaded with iridium.

The calculated dissolution for Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_{p}$ 4 hrs 900 °C loaded with iridium is shown in Figure 6.34. It shows low dissolution of the iridium and niobium into solution, however the titanium dissolves readily under these conditions. Nearly 40% of the titanium dissolves into solution. Therefore, the high activity of the material may be due to agglomeration of the iridium particles onto the surface of the remaining niobium material.
Figure 6.33: Percentage of metal dissolved from NbC$_{1-p}$N$_p$ 4 hrs 900 °C loaded with iridium button 1 (B1) and button 2 (B2) electrochemical testing calculated from ICP-MS.

Figure 6.34: Percentage of metal dissolved from Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C loaded with iridium button 1 (B1) and button 2 (B2) electrochemical testing calculated from ICP-MS.
The percentage of iridium dissolved during the electrochemical tests are compared for NbC$_{1-p}$/N$_p$ 4 hrs 900 °C, Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$/N$_p$ 4 hrs 900 °C and carbon all loaded with iridium, in Figure 6.35. This shows that the niobium titanium carbonitride is the least stable with nearly 2.5% of the iridium dissolving into solution, possibly due to the loss of titanium making the Ir unstable. For the carbon loaded with iridium only 0.5% dissolves into solution. The most stable material is the NbC$_{1-p}$/N$_p$ with less than 0.4% of the iridium dissolving.

![Graph showing percentage of iridium dissolved](image)

**Figure 6.35:** Percentage of iridium dissolved from NbC$_{1-p}$/N$_p$ 4 hrs 900 °C, Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$/N$_p$ 4 hrs 900 °C and carbon all loaded with iridium, button 1 (B1) and button 2 (B2) electrochemical testing calculated from ICP-MS.

### 6.6 Titanium niobium oxides acid resilience testing

Acid resilience testing of the Ti$_{0.39}$Nb$_{0.11}$O$_2$ shows the material to be stable after acid testing at 80 °C for 24 hours in 1 M H$_2$SO$_4$. The powder XRD shown in Figure 6.36, shows Pawley refinements of the material before and after acid testing and shows little to no change in the resulting lattice parameters. The metal remaining in the sample is calculated from ICP and is shown in Table 6.7. This shows that a small amount of niobium dissolves in solution, but the titanium is relatively stable. The overall stability suggests that 97.4% of metal is remaining in the material. This suggests that the material is stable under acidic conditions.
Figure 6.36: Pawley powder XRD ($\lambda = 1.54056$ Å) refinements of Ti$_{0.89}$Nb$_{0.11}$O$_2$ before and after acid testing in 1 M H$_2$SO$_4$ at 80 °C for 24 hours.

Table 6.7: Percentage of remaining metals in the sample after acid testing of Ti$_{0.89}$Nb$_{0.11}$O$_2$ calculated from the ICP of the acid test solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% metal remaining</th>
<th>% metal remaining</th>
<th>% metal remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{0.89}$Nb$</em>{0.11}$O$_2$</td>
<td>92.8</td>
<td>98.5</td>
<td>97.4</td>
</tr>
</tbody>
</table>

6.7 Titanium niobium oxides electrochemical testing

Ti$_{0.89}$Nb$_{0.11}$O$_2$ was loaded by the polyol method with 30 wt% iridium and this was then electrochemically tested. This was compared with carbon, which was loaded with 30 wt% iridium via the same polyol method, and IrO$_2$ commercial catalyst.

The dispersion of the iridium onto the Ti$_{0.89}$Nb$_{0.11}$O$_2$ material is shown in the EDXA and TEM shown in Figure 6.37 and Figure 6.38. Figure 6.37 shows good dispersion across the sample, however Figure 6.38 shows some agglomeration of the iridium in places.
Figure 6.37: EDXA mapping from TEM of Ti$_{0.89}$Nb$_{0.11}$O$_2$ loaded with iridium, showing O in white, Ti in blue, Nb in red and Ir in green.

Figure 6.38: EDXA mapping from TEM of Ti$_{0.89}$Nb$_{0.11}$O$_2$ loaded with iridium, showing O in white, Ti in blue, Nb in red and Ir in green.
Two buttons of the Ti$_{0.89}$Nb$_{0.11}$O$_2$ iridium loaded material were tested for repeatability. The mass activity measurements are shown in Figure 6.39, and the mass activities at 1.47 V are compared in Figure 6.40. It was found that the mass activity of the Ti$_{0.89}$Nb$_{0.11}$O$_2$ was lower than that of the carbon loaded with 30 wt% and the IrO$_2$ commercial catalyst. However, the Nb$_{0.89}$Ti$_{0.11}$O$_2$ material showed only a small reduction in activity after 1000 cycles.

\[ \text{Figure 6.39: Mass activity values taken at 1.47V of Ti}_{0.89}\text{Nb}_{0.11}\text{O}_2 \text{loaded with 30 wt% iridium compared with carbon loaded with 30 wt% iridium and IrO}_2 \text{commercial catalyst.} \]
Figure 6.40: Mass activity values taken at 1.47 V of Ti$_{0.89}$Nb$_{0.11}$O$_2$ loaded with 30 wt% iridium compared with carbon loaded with 30 wt% iridium and the IrO$_2$ commercial catalyst.

The cyclic voltammetry for Ti$_{0.89}$Nb$_{0.11}$O$_2$ loaded with 30 wt% iridium is compared with the carbon loaded with 30 wt% iridium in Figure 6.41. The double layer for the Ti$_{0.89}$Nb$_{0.11}$O$_2$ material is much smaller than the carbon double layer suggesting a lower surface area. The double layer for the Ti$_{0.89}$Nb$_{0.11}$O$_2$, however, does not change from BOL to EOL, suggesting that this material is stable under these harsh acidic conditions whilst under potential.
Figure 6.41: Cyclic voltammograms (50 mV s$^{-1}$) of Ti$_{0.89}$Nb$_{0.11}$O$_2$ loaded with 30 wt% iridium compared with carbon loaded with 30 wt% iridium at beginning of life (BOL) and end of life (EOL) after 1000 cycles.

The ICP-MS of the solution sampled during the electrochemical testing was used to calculate the percentage of metals dissolved into solution. The results are shown in Figure 6.42. The titanium dissolves the most with ~0.35% of titanium dissolved into the solution. Less than 0.1% of niobium is dissolved into solution and ~0.1% iridium is dissolved into solution. This shows how stable the Ti$_{0.89}$Nb$_{0.11}$O$_2$ material is under these harsh conditions.

The percentage iridium dissolved is compared in Figure 6.43 to the carbon loaded with iridium sample. About 0.57% of iridium is dissolved in solution from the carbon loaded with iridium, whereas only 0.12% of iridium is dissolved from Ti$_{0.89}$Nb$_{0.11}$O$_2$ loaded with iridium. This shows stability of nearly 5 times that of the carbon loaded with iridium.
Figure 6.42: Percentage of metal dissolved from $\text{Ti}_{0.89}\text{Nb}_{0.11}\text{O}_2$ loaded with iridium button 1 (B1) and button 2 (B2) electrochemical testing calculated from ICP-MS.

Figure 6.43: Percentage of iridium dissolved from $\text{Ti}_{0.89}\text{Nb}_{0.11}\text{O}_2$ loaded with iridium button 1 (B1) and button 2 (B2), compared to carbon loaded with iridium electrochemical testing calculated from ICP-MS.
6.8 Conclusion

The manganese ruthenium oxides initially appear to be stable under acid resilience testing using 1 M H$_2$SO$_4$ at 80 °C. However, when the acid was changed to triflic acid the manganese was preferentially leached from the materials. Attempts were made to make buttons and electrochemically test them, but manganese leaching also occurred in the inks suggesting the acidic environment of the Nafion™ corrodes the material. This suggests that these materials are not appropriate for the application as catalyst supports in PEMFCs, under acidic conditions.

The acid resilience testing of the niobium carbonitrides showed good stability in 1 M sulfuric acid, with no niobium being found in solution. The materials were analysed by a range of methods after acid testing including powder XRD, XPS and XANES. These showed that the oxidation state of the materials increases slightly suggesting more of the surface of the materials is oxidised. However, when these materials were electrochemically tested there was not a substantial loss of activity suggesting that the oxide layer formed either is not large enough to affect the conductivity or that the oxide formed could be conductive. Another reason for the small loss in activity could be due to dissolution of the amorphous carbon contaminant. The nature of the amorphous carbon has not been fully analysed and the XPS suggests some of the organic layer could contain some nitrogen and oxygen. It is unknown what effect this material could have on the activity or behaviour of the samples. When the NbC$_1$-pN$_p$ 4 hrs 900 °C sample was loaded with iridium the iridium was dispersed evenly across the sample. When electrochemically tested, it was found that the mass activity values are within the useful range for application. The mass activity values are lower than that of the commercial IrO$_2$ material and the carbon loaded with iridium, but they are high enough to form useful catalyst materials. The stability of these materials shows great promise for their application in PEMFCs as catalyst supports.

The Nb$_{0.5}$Ti$_{0.5}$C$_1$-pN$_p$ materials showed lower stability under the acid resilience testing than the NbC$_1$-pN$_p$ materials, with a small amount of the titanium and niobium leaving the material. The TiC$_1$-pN$_p$ showed no stability under acid resilience testing and instead formed ammonium titanium oxide sulfate. The Nb$_{0.5}$Ti$_{0.5}$C$_1$-pN$_p$ materials were analysed further after acid testing by XANES, where the niobium average oxidation state was found to have increased but the titanium oxidation state decreased. This could suggest the formation of a Ti$_{1-x}$Nb$_x$O$_2$ material at the surface of the acid tested.
material. Powder XRD suggests a loss in crystallinity of the material. However, when Nb_{0.5}Ti_{0.5}C_{1-p}N_p 4 hrs 1200 °C was tested electrochemically the material became inactive by the EOL. In contrast, when Nb_{0.5}Ti_{0.5}C_{1-p}N_p 4 hrs 900 °C was loaded with iridium and electrochemically tested it was found that the activity values were higher than both the IrO_2 commercial catalyst and the iridium loaded carbon. This implied improved activity however when ICP-MS of the solutions were measured it was found that the titanium was leaching from the material. This suggests that the final material has a larger amount of iridium, which may have agglomerated onto the surface of the resulting niobium material. Although a surprising activity was seen, this is more likely due to corrosion.

The Ti_{0.89}Nb_{0.11}O_2 showed stability during acid resilience tests, and the powder XRD showed no change in the lattice parameters suggesting the material is stable. When the material was loaded with 30 wt% iridium, it was found that the iridium was evenly distributed across the sample but agglomeration did occur in places. When the material was electrochemically tested, it was found that it was stable, with its mass activity, although lower than the carbon loaded with 30 wt% iridium and the IrO_2 commercial catalyst, showing stability from BOL to EOL, and the ICP-MS showed less than 0.1% of iridium had dissolved into solution. This suggests this material is the most stable, out of those tested, to electrochemical dissolution.

6.9 References


Chapter 7 – Conclusions and further work

7.1 Manganese ruthenium oxides

Manganese ruthenium oxides with various ruthenium contents in the rutile structure have been synthesised for the first time by hydrothermal synthesis. These materials were made under acidic conditions hydrothermally with the intention of crystallising materials that would be acid resilient. They have been analysed by a range of techniques including powder XRD, SEM, TEM, EDXA, ICP, TGA-DSC, TGA-MS, thermodiffractometry, XANES, EXAFS, XPS, powder conductivity and BET surface area.

Powder XRD showed increasing lattice parameters with increasing ruthenium content and decreasing crystallite size. SEM and TEM shows that these form agglomerated materials with increasing ruthenium content. Thermodiffractometry shows that $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$, where $x \leq 0.19$ are stable until 600 °C, whereas for $x = 0.52$ the material is stable until 300 °C, after which both phases separate into binary oxides. TGA-MS showed that with increasing ruthenium content there was increasing water of crystallisation, suggesting that water exists within the structure of the more substituted materials.

The average oxidation states calculated from XANES analysis show manganese oxidation state decreases (+3.9 to 3.6) with increasing ruthenium content, whereas ruthenium oxidation state increases (+4 to 4.4). This gives average metal oxidation states of about +4 as would be expected for stoichiometric rutile structures. EXAFS suggests the presence of Mn$^{3+}$ at the surface of all of the $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ materials including the $\beta$-$\text{MnO}_2$ material. However, it is likely that this must only be a surface effect due to the XANES showing a slight decrease in average manganese oxidation state. The XPS of the lower ruthenium content materials ($x \leq 0.19$) show more ruthenium present than the EDXA, this suggests that the ruthenium may not be uniform throughout the structure and may be enriched at the surface. This could suggest that a $\text{Mn}_{2y}\text{Ru}_y\text{O}_3$ ($y < 2$) “nanoskin” has been formed at the surface with a $\beta$-$\text{Mn}_{1-x}\text{Ru}_x\text{O}_2$ core, as has previously been suggested for ruthenium oxide by Donakowski et al.

EXAFS shows an increase in both the Mn – O and Ru – O distances with increasing ruthenium content. This agrees with the Pawley powder XRD fits, suggesting
increasing unit cell size with increasing ruthenium content. Further work on this could include analysing either neutron or X-ray PDF data, as previously used by Donakowski for hydrated RuO$_2$.\cite{Donakowski} This could show more about the disorder in the system and how well the manganese and ruthenium are mixed within the structure.

The $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials show increasing powder conductivity with increasing ruthenium content, ranging between 0.03 and 0.49 S cm$^{-1}$. A substitution of $x = 0.29$ or above gives a conductivity of the required 0.1 S cm$^{-1}$ for application as a catalyst support. The surface area of the $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials are between 56 – 163 cm$^2$g$^{-1}$. These all have suitable surface areas for use as catalyst supports. Surface area increases with increasing ruthenium substitution corresponding well with the decrease in crystallite size.

Further work on these materials would include PDF analysis of the $\beta$-Mn$_{1-x}$Ru$_x$O$_2$ materials in order to determine if the “nanoskin” structure exists, and to determine if the results match well with the existing EXAFS data. The materials were made under acidic conditions at high temperatures, therefore it was thought that the materials would be stable under acidic conditions. However, this work proved this was not true in this instance, therefore further work could include determining why these materials dissolve. Determining why the manganese is leached from the samples may help to find other materials with more stability. This could include in-situ experiments or running a range of new syntheses with various reaction times to determine if longer reactions caused the manganese to be leached from the resulting material.

### 7.2 Niobium titanium carbonitrides

Niobium, niobium titanium and titanium carbonitrides were made via a new low temperature synthesis using a guanidine carbonate based method with a nitrogen gas flow. The resulting materials were analysed by a range of techniques including powder XRD, neutron diffraction, neutron PDF analysis, TEM, EDXA, TGA-DSC, thermodiffraetctometry, TGA-MS, CHN, BET surface area, XANES, EXAFS, XPS and powder conductivity.

$\text{NbC}_{1-p}\text{N}_p$ with a cubic rock salt structure showed increasing unit cell size with increasing temperature of synthesis, and at 1200 °C this decreases slightly due to a carbon/nitrogen deficiency. From neutron diffraction it was possible to determine the carbon and nitrogen ratios, and the relative carbon content increased with increasing
temperature of synthesis. Crystallite size increased with increasing temperature of synthesis to give an average crystallite size of between 30 and 70 nm. Neutron PDF was used to analyse the NbC$_1$-p$_N$$_p$ samples. A decrease in order occurred with decreasing temperature of synthesis, and an increase in a peak at 1.4 Å indicating a C – C bond distance, suggesting an increase in the presence of amorphous carbon in the lower temperature materials. This amorphous carbon presence is confirmed by calculations from TGA-DSC and CHN analysis. PDF fitting of NbC$_1$-p$_N$$_p$ 4 hrs 1200 °C shows a highly ordered system. Further work could be performed using Reverse Monte Carlo (RMC) fitting, to analyse this order further.

TEM of NbC$_1$-p$_N$$_p$ materials showed increase in particle size with increasing temperature of synthesis, and at lower temperatures of synthesis amorphous carbon surrounds the particles. TGA calculations suggest amorphous carbon content of between 0.5 and 15 wt%, with the lowest temperature synthesis containing the most. CHN analysis suggests that this is much lower at between 0 and 2.18 wt%. The difference is likely to be due to the Nb$_2$O$_5$ layer at the surface, which XPS and XANES suggest is larger with a lower temperature of synthesis. Nb K edge XANES suggests an average oxidation state of between +1.8 and 3.4, increasing with lower temperature of synthesis, suggesting more oxide in the material. XPS, a surface sensitive technique, gives a similar trend, suggesting that it is a surface effect, with the core of the material being carbonitride. The Nb K edge EXAFS shows a similar trend with the lower temperatures of synthesis showing a small peak for Nb$_2$O$_5$, whereas samples prepared at 1000 °C and 1200 °C show no visible Nb – O peak suggesting more of the structure is NbC$_1$-p$_N$$_p$.

Thermodiffraclactometry shows that the NbC$_1$-p$_N$$_p$ materials are stable until about 300 °C where an amorphous intermediate forms. This was analysed further by in situ XANES, at 300 °C the material started to oxidise reaching +4 by 700 °C, the material further oxidised to +5 when cooled. Nb$_2$O$_5$ crystallises at about 550 °C as shown by thermodiffraction and TGA-MS, where a large peak in CO$_2$ and NO is observed.

The NbC$_1$-p$_N$$_p$ materials show good powder conductivity of between 0.01 and 33 S cm$^{-1}$, NbC$_1$-p$_N$$_p$ 12 hrs 700 °C has a conductivity of below 0.1 S cm$^{-1}$. However, all the other NbC$_1$-p$_N$$_p$ materials have conductivities above this, making them suitable for use as catalyst supports. The surface area for NbC$_1$-p$_N$$_p$ ranges between 4.4 – 73 cm$^2$g$^{-1}$. 311
The materials made at 700 – 900 °C have surface areas which are potentially useful as catalyst supports, whereas the 1000 °C and 1200 °C sample are too low.

Nb\textsubscript{0.5}Ti\textsubscript{0.5}C\textsubscript{1-p}N\textsubscript{p} with a cubic rock salt structure showed increasing unit cell size with increasing temperature of synthesis, which also plateaued at the 1200 °C synthesis. Nb\textsubscript{0.05}Ti\textsubscript{0.95}C\textsubscript{1-p}N\textsubscript{p} also showed increased lattice parameter with increasing temperature of synthesis suggesting a more carbide like material. A range of Nb\textsubscript{1-q}Ti\textsubscript{q}C\textsubscript{1-p}N\textsubscript{p} materials were made at 900 °C for 4 hours and it was found that with more niobium content the material lattice parameters were more like the niobium carbide material, but with increasing titanium content the material became more like titanium nitride. Neutron diffraction of Nb\textsubscript{0.5}Ti\textsubscript{0.5}C\textsubscript{1-p}N\textsubscript{p} showed a secondary phase present as well as an increased background level suggesting the presence of hydrogen, possibly as part of an amorphous carbon phase. Neutron PDF shows a large peak at 1.4 Å for C – C bonds in amorphous carbon, and an unknown phase present with peaks at 2.4 Å and 2.8 Å.

TGA-DSC of Nb\textsubscript{0.5}Ti\textsubscript{0.5}C\textsubscript{1-p}N\textsubscript{p} suggests amorphous carbon content of between 21 and 27 wt%, but further analysis with CHN suggests this is lower at 14 and 15 wt%. TEM shows amorphous carbon around all of the different temperature of synthesis Nb\textsubscript{0.5}Ti\textsubscript{0.5}C\textsubscript{1-p}N\textsubscript{p} materials. EDXA mapping shows the niobium and titanium evenly spread across the samples, suggesting it is atomically mixed. In situ thermodiffractometry shows the materials are stable until between 200 – 250 °C, where an amorphous intermediate forms. This was analysed further by in-situ Nb K edge XANES, the oxidation state began to increase at 200 °C reaching +4.8 by 500 °C. The thermodiffractometry shows a crystalline phase forming at 600 °C, which then changes into TiNb\textsubscript{2}O\textsubscript{7} by 800 °C. TGA-MS shows NO loss at between 200 and 350 °C and a further loss of CO\textsubscript{2}, NO\textsubscript{2} and NO at between 400 and 550 °C. The unknown phase that forms at 600 °C may contain some carbon and nitrogen as a small loss of CO\textsubscript{2} and NO\textsubscript{2} shows in the TGA-MS.

XANES of Nb\textsubscript{0.5}Ti\textsubscript{0.5}C\textsubscript{1-p}N\textsubscript{p} materials shows average titanium oxidation state of between +3.25 and 3.45 and an average niobium oxidation state of between +2.8 and 3.1. This may be due to more TiO\textsubscript{2} present at the surface. XPS shows the presence of Nb\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2} at the surface of the materials. The surface is mainly made up of oxygen and carbon. Almost all the carbon present is as amorphous carbon species.
Some organic nitrogen is also present. The $\text{Nb}_{0.5}\text{Ti}_{0.5}\text{C}_{1-p}\text{N}_{p}$ materials have high surface areas of between 218 and 230 m$^2$g$^{-1}$, this may be due to the high amorphous carbon content. They also have much lower powder conductivities than the $\text{NbC}_{1-p}\text{N}_{p}$ materials, of between 0.85 and 1.44 S cm$^{-1}$, which is suitable for use as catalyst supports.

The pure $\text{TiC}_{1-p}\text{N}_{p}$ materials made at different temperatures often oxidised during the passivation step and contained high amounts of amorphous carbon, forming an amorphous background on the powder XRD. This made them more difficult to analyse. TGA-DSC suggested amorphous carbon content of between 45 and 51 wt%, but this calculation could have been shifted due to the presence of TiO$_2$ so could be lower than this. Ti K edge XANES analysis gave average titanium oxidation state as between +3 and 3.5. The oxidation state increases with decreasing temperature of synthesis, suggesting the presence of more oxide. Powder conductivity of $\text{TiC}_{1-p}\text{N}_{p}$ 4 hrs 900 °C was found to be 0.66 S cm$^{-1}$, which is suitable for use as catalyst supports. However, due to the amount of amorphous carbon these materials were not explored further.

Further work could be performed to decrease the amount of amorphous carbon present in the niobium carbonitrides, niobium titanium carbonitrides and the titanium carbonitrides. This could involve changing the synthesis conditions such as the guanidine carbonate to metal ratio, temperature and length of synthesis. By decreasing the amount amorphous carbon present at the surface, the activity of the materials could be attributed more to the metal carbonitride. The surface of the material could greatly affect the activity of a sample, and any remaining amorphous carbon could undergo COR reactions in a PEMFC unless a good OER catalyst is also present. So by decreasing the amorphous carbon content the material should be more stable to the harsh conditions used in a PEMFC.

Other further work could include trying to push the reactions towards more carbide like materials, which as mentioned previously in Chapter 4, are more stable than the nitrides. To do this synthesis conditions could be further explored including increasing the reaction temperature or changing the guanidine carbonate to a different precursor material. This could help to tune the carbon and nitrogen content of the carbonitride materials.
7.3 Exploratory synthesis of other carbonitrides

Titanium niobium oxides were made via a simple method from ammonium titanyl oxalate and ammonium niobate oxalate under nitrogen gas. The materials were analysed by powder XRD, XANES, BET surface area, TEM and powder conductivity. Powder XRD showed the Ti$_x$Nb$_{1-x}$O$_2$ materials had the rutile structure with a tetragonal unit cell, $P4_2/mnm$ space group. The materials showed an increase in unit cell size with increasing niobium content. The XANES spectroscopy showed the average niobium oxidation state was increased above +4, to between +4 and 4.5 and the average titanium oxidation state decreased to +3.6 and 3.8. For the low niobium content materials this averages to give an average metal oxidation state of +4. For Ti$_{0.28}$Nb$_{0.72}$O$_2$ the average metal oxidation state of +3.89, which could suggest some oxide deficiencies within the structure. The powder conductivity of these materials was in general low (less than 0.01 S cm$^{-1}$), but this may be due to grain boundary effects in the pelletisation of the samples. The surface area of these materials was also considered to be low (14 m$^2$g$^{-1}$) for use as catalyst supports. Further work could include optimising this synthesis to create materials with a higher surface area, possibly be using lower temperatures of synthesis.

Tantalum carbonitrides were made for the first time via a low temperature guanidine carbonate method under a flow of nitrogen. The tantalum starting tantalum material was an ammonium tantalate oxalate synthesised for this purpose. Tantalum produced a range of different carbonitride structures including Ta$_3$N$_5$ ($Cmcm$), Ta$_4$N$_5$ ($I4/m$), hexagonal TaN ($P\bar{6}m2$), hexagonal TaN$_{0.83}$ ($P\bar{6}m2$) and cubic TaC ($Fm\bar{3}m$). Lower temperature synthesis favoured the formation of Ta$_3$N$_5$, higher temperatures of synthesis favoured the formation of TaC$_1$-pN$_p$ in either hexagonal or cubic forms. These materials were analysed by powder XRD, TGA-DSC and TEM. Further work could be performed to optimise the synthesis of pure phase materials and further analysis of these materials could be performed such as XANES, EXAFS, CHN analysis, powder conductivity and BET surface area.

Tantalum titanium carbonitrides were made for the first time via a low temperature guanidine carbonate method under a flow of nitrogen. The resulting materials were analysed by powder XRD, TGA-DSC and powder conductivity. The Ti$_{0.5}$Ta$_{0.5}$C$_{1-p}$N$_p$ materials were found to have the cubic rock salt structure, $Fm\bar{3}m$. A ratio of 1M:4GC, where metal (M) and guanidine carbonate (GC), was selected as forming the most
carbide like material at 900 °C. The same ratio gave a highly crystalline material at 1200 °C. However, TGA showed that the lower ratios of guanidine carbonate gave the lowest amount of amorphous carbon. Two materials with 1M:4GC and 1M:5GC ratios made at 900 °C for 4 hours, had powder conductivities of between 0.212 and 0.365 S cm\(^{-1}\). This is suitable for application as catalyst supports. Further work could involve recording BET surface area, XANES, EXAFS and CHN analysis.

Tantalum niobium carbonitrides were made via a low temperature guanidine carbonate method using a flow of nitrogen. The resulting materials were analysed by powder XRD, TGA-DSC and powder conductivity. The \(\text{Nb}_{0.5}\text{Ta}_{0.5}\text{C}_{1-p}\text{N}_p\) materials were shown to have a cubic rock salt structure. Higher guanidine carbonate to metal ratios gave more carbide like materials. However, lower guanidine carbonate to metal ratios gave higher amounts of amorphous carbon. The materials have between 10.3 and 24.3 wt% amorphous carbon, calculated from TGA. The materials with a 1M:5GC and 1M:6GC ratio made at 900 °C for 4 hours were shown to have a conductivity of 0.08 – 0.09 S cm\(^{-1}\). The conductivities nearing that of 0.1 S cm\(^{-1}\) required for application as a catalyst support. Further work required would include BET surface area, XANES, EXAFS, and CHN analysis.

Iron carbide has been made via a guanidine carbonate method under a flow of nitrogen. The \(\text{Fe}_3\text{C}\) material formed had an orthorhombic unit cell with the \(Pnma\) space group. Other iron carbonitride materials formed with the cubic \(Fm\bar{3}m\) space group, but often had an impurity of iron metal. The \(\text{Fe}_3\text{C}\) was shown to have high conductivity of 1.8 and 7.5 S cm\(^{-1}\). Further work would involve BET surface area and acid resilience testing.

Vanadium nitride has been made via two methods both using guanidine carbonate under nitrogen flow. VN synthesised from ammonium vanadate oxalate has been analysed by powder XRD, TGA-DSC and in situ thermodiffractometry. VN synthesised from ammonium orthovanadate has been analysed by powder XRD, powder conductivity and BET surface area. The materials have shown conductivities of between 7.2 and 36.7 S cm\(^{-1}\) and surface areas of between 84 and 126.4 m\(^2\)g\(^{-1}\). These give them properties suitable for application as catalyst supports. However it was suggested by Kimmel \textit{et al.} that the materials would not be stable under acid ORR.\(^3\)
Further work would include optimising the synthesis and analysing the amorphous carbon content for both synthesis methods, as well as acid resilience testing.

Molybdenum carbonitride was synthesised by two different guanidine carbonate methods starting from either as made ammonium molybdate oxalate or ammonium molybdate tetrahydrate. Ammonium molybdate tetrahydrate produced cleaner powder XRD and therefore was analysed further by optimisation of synthesis and TGA-DSC. It was found that a range of molybdenum carbonitrides could be formed including Mo$_2$C (orthorhombic, $Pbcn$), MoN (hexagonal, $P\overline{3}m1$) and Mo$_2$N (tetragonal, $I4_1/amd$). High temperatures lead to the formation of molybdenum metal. The materials gave less than 5 wt% amorphous carbon and showed stability from TGA-DSC until 300 °C. Further work would need to be performed on the structure of these materials such as XANES and EXAFS. Other work including thermodiffractometry, powder conductivity, acid resilience testing and BET surface area, should be performed to determine if this set of materials can be used as catalyst supports.

Tungsten carbonitrides were made via a guanidine carbonate method using either ammonium tungstate oxalate or ammonium metatungstate hydrate. It was found that by powder XRD there was little difference between the materials made by these two different methods at either 900 °C or 1200 °C. Therefore, tungsten carbonitrides made from ammonium metatungstate were studied further as it was a simpler reaction. The materials made at 700 °C with different metal(M) to guanidine carbonate(GC) ratios formed an amorphous phase and either W$_2$C (trigonal, $P\overline{3}1m$) or W metal. The materials made at 900 °C formed WC$_{1-p}$N$_p$ (hexagonal, $P\overline{6}m2$) when 1M:6GC or 1M:5GC, when less guanidine carbonate was present a mixture of phases or W metal formed. The 1200 °C synthesis produced WC$_{1-p}$N$_p$ (hexagonal, $P\overline{6}m2$) pure with 1M:6GC ratio, but W metal formed as well with lower GC content. The hexagonal $P\overline{6}m2$ materials showed less than 5 wt% amorphous carbon from TGA-DSC and were stable until 400 °C. TEM shows large agglomerates of smaller particles. Powder conductivity of the materials gives between 4.2 – 11.8 S cm$^{-1}$. This suggests some properties suitable for use as catalyst supports. Further work would include BET surface area and acid resilience testing.

Further work for Chapter 5 would include tuning the syntheses to produce materials with lower amorphous carbon content and with a high surface area. In order to get a
better understanding of these materials and to produce materials with properties tuned to purpose, a greater understanding of the reaction may be necessary. To do this in-situ XRD experiments could be used to monitor the formation of different carbonitrides and oxides at different reaction temperatures and to monitor how the samples change over time. This would enable better tuning of the reaction synthesis allowing the formation of desired materials with greater accuracy.

7.4 Acid resilience and electrochemical testing

Manganese ruthenium oxides were found to dissolve under the harsh conditions that replicate those within a fuel cell. Therefore, these materials although they show some stability in 1 M sulfuric acid, are considered too unstable for this application as a catalyst support in a PEM fuel cell.

The niobium titanium carbonitrides show stability in 1 M sulfuric acid during acid resilience testing. The material after acid testing was analysed by powder XRD, XANES and XPS, and were found to have increased in niobium oxidation state suggesting a more oxidised surface, but titanium oxidation state decreased suggesting the formation of a Ti$_{1-x}$Nb$_x$O$_2$ material at the surface. However, when tested under electrochemical potential in 0.1 M sulfuric acid at 60 °C, it was found that a small amount of niobium and titanium was leached from the material. When Nb$_{0.5}$Ti$_{0.5}$C$_{1-p}$N$_p$ 4 hrs 900 °C was loaded with iridium and electrochemically tested it was found that the activity values were higher than those of the iridium loaded carbon. However, the ICP-MS results suggest that titanium is leached from the material and therefore 2.5 % of the iridium is subsequently dissolved.

The niobium carbonitrides show more stability than the niobium titanium carbonitrides. The materials showed good stability in 1 M sulfuric acid at 80 °C for 24 hours. The resulting acid tested materials were analysed by a range of techniques including powder XRD, XPS and XANES. The oxidation state of the niobium increased slightly suggesting more surface oxidation, which is confirmed by XPS. When these materials were electrochemically tested, they were found to have good stability and undetectable amounts of niobium were found in solution. The NbC$_{1-p}$N$_p$ 4 hrs 900 °C sample was loaded with iridium and electrochemically tested. The mass activity values were lower than that of the carbon loaded with iridium, however, less iridium (0.4 %) dissolved into solution and the activity found is useful for application.
These materials show great promise for their application in PEMFCs as catalyst supports. Further work on analysing these materials in an MEA could performed to further assess their use as catalyst supports. Further scale-up of synthesis would also be required for future work.

The titanium niobium oxide \((\text{Ti}_{0.89}\text{Nb}_{0.11}\text{O}_2)\) showed stability during acid testing and powder XRD showed no change to the material afterwards. The material was loaded with iridium and electrochemically tested. The material was found to have lower activity than the carbon loaded with iridium, but showed stability during the testing, and ICP-MS showed less than 0.1 % of the iridium had dissolved during the testing. This suggests this material is the most stable out of those tested in this project and could be tested further for application in fuel cells and other electrochemical devices. This would require a scale-up of synthesis for future work.

Further work would be needed to find the acid resilience of the materials studied in Chapter 5. By finding the acid resilience of different carbonitride materials, mixed metal carbonitrides could be tuned to have properties, which make them suitable for use as catalyst supports in PEMFCs. The niobium carbonitrides and niobium titanium oxides could be tested further by making the materials part of a MEA and then testing them by either a half cell or full cell testing technique. By running accelerated testing protocols on these materials their full potential as catalyst supports for PEMFCs could be unlocked.

7.5 References

