Ruddlesden-Popper Phases as Solid Oxide Fuel Cell Cathodes: Electrochemical Performance and *In Situ* Characterisation

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A thesis submitted for the degree of Doctor of Philosophy
I, Russell Woolley, declare that the work presented in this thesis is my own.

Russell Woolley

Date

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Abstract

The aim of this work was to develop oxide fuel cell (SOFC) cathodes made from \((\text{LaNiO}_3)_n\)\(_{\text{LaO}}\) Ruddlesden-Popper (R-P) phases, and to investigate novel \textit{in situ} characterisation techniques for SOFC cathodes.

Cathodes were developed from \(\text{La}_2\text{NiO}_{4+\delta}\) (L2N1) and \(\text{La}_4\text{Ni}_3\text{O}_{10-\delta}\) (L4N3), R-P phases known to have attractive conductivities at SOFC temperatures. These phases were shown to be chemically stable, both with each other and with the common electrolyte material \(\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3-\delta\) (LSGM). LSGM-supported symmetrical cells were fabricated with electrodes of single phase L2N1 and L4N3, and a range of L2N1+L4N3 composites. The performance of these was tested from 500 – 700 °C with the composites giving the lowest area-specific resistance (ASR); a 50:50 wt.% L2N1:L4N3 composition being optimal.

Functionally graded electrodes were developed consisting of a thin compact L2N1 layer deposited onto the LSGM, topped by a thicker porous L2N1+L4N3 composite layer, completed by a thin porous L4N3 current collector. These gave a lower ASR than the ungraded electrodes. Using a 50:50 composite was optimal with ASRs of 15.59, 2.29, and 0.53 \(\Omega\text{cm}^2\) at 500, 600, and 700 °C respectively; amongst the best-in-class for electrodes made from this type of material.

X-ray absorption near-edge spectroscopy was chosen as a method to gain \textit{in situ} information on the redox chemistry of elements within SOFC materials. Initial studies were carried out on powder samples of L2N1 and L4N3; the nickel oxidation state in these was found to reduce on heating to SOFC operating temperatures. Bespoke equipment was developed to enable such studies to be carried out on symmetrical cells under polarisation and with simultaneous AC impedance spectroscopy. The bulk nickel redox chemistry was correlated with the changing concentration of ionic charge carriers in the materials, and was found to be dominated by thermal effects. These techniques were then used to explore \textit{in situ} chromium poisoning of state-of-the-art perovskite cathodes.

The surface chemistry of SOFC materials is key to performance. Low-energy ion scattering was used to find the composition of the outer monolayer for the entire \((\text{LaNiO}_3)_n\)\(_{\text{LaO}}\) R-P series; lanthanum termination was found for each phase.
Acknowledgements

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As Ralph Waldo Emmerson wrote; “It is one of the blessings of old friends that you can afford to be stupid with them”.

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<table>
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>ACIS</td>
<td>alternating current impedance spectroscopy</td>
</tr>
<tr>
<td>ASR</td>
<td>area specific resistance</td>
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<tr>
<td>BEI</td>
<td>back scattered electron imaging</td>
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<tr>
<td>cermet</td>
<td>ceramic-metal composite</td>
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<tr>
<td>CGO</td>
<td>Ce₀.₉Gd₀.₁O₂.₆</td>
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<td>CPE</td>
<td>constant-phase element</td>
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<tr>
<td>ECM</td>
<td>equivalent circuit model</td>
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<td>EDX</td>
<td>energy dispersive X-ray spectroscopy</td>
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<td>EMPT</td>
<td>effective medium percolation theory</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>FRA</td>
<td>frequency response analyser</td>
</tr>
<tr>
<td>GSAS</td>
<td>General Structure Analysis System</td>
</tr>
<tr>
<td>h-BN</td>
<td>hexagonal boron nitride</td>
</tr>
<tr>
<td>HT-SOFC</td>
<td>high temperature solid oxide fuel cell</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>IEDP</td>
<td>isotope exchange depth profile</td>
</tr>
<tr>
<td>IT-SOFC</td>
<td>intermediate temperature solid oxide fuel cell</td>
</tr>
<tr>
<td>L1N1</td>
<td>LaNiO₃</td>
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<td>L2N1</td>
<td>La₂NiO₄₊₅</td>
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<td>L3N2</td>
<td>La₃Ni₂O₇−₅</td>
</tr>
<tr>
<td>L4N3</td>
<td>La₄Ni₃O₁₀−₅</td>
</tr>
<tr>
<td>LEIS</td>
<td>low-energy ion scattering</td>
</tr>
<tr>
<td>LSC</td>
<td>La₁₋ₓSrₓCoO₃−₅</td>
</tr>
<tr>
<td>LSCF</td>
<td>La₁₋ₓSrₓCo₁₋ₓFeₓO₃−₅</td>
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<td>LSGM</td>
<td>La₀₋ₓSr₀.₂Ga₀.₈Mg₀.₂O₃−₅</td>
</tr>
<tr>
<td>LSM</td>
<td>La₁₋ₓSrₓMnO₃</td>
</tr>
<tr>
<td>MEM</td>
<td>maximum entropy method</td>
</tr>
<tr>
<td>MIEC</td>
<td>mixed ionic-electronic conductivity</td>
</tr>
<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>RFM</td>
<td>relative formula mass</td>
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<tr>
<td>Rₚ</td>
<td>polarisation resistance</td>
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<tr>
<td>R-P</td>
<td>Ruddlesden-Popper</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SEI</td>
<td>secondary electron imaging</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary-ion mass spectrometry</td>
</tr>
<tr>
<td>SOFC</td>
<td>solid oxide fuel cell</td>
</tr>
<tr>
<td>SPEM</td>
<td>scanning photoelectron microscopy</td>
</tr>
<tr>
<td>SSZ</td>
<td>scandia-stabilised zirconia</td>
</tr>
<tr>
<td>TEC</td>
<td>thermal expansion coefficient</td>
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<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>TPB</td>
<td>triple-phase boundary</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>YSZ</td>
<td>yttria-stabilised zirconia</td>
</tr>
<tr>
<td>σₑ</td>
<td>electronic conductivity</td>
</tr>
<tr>
<td>σᵢ</td>
<td>ionic conductivity</td>
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<tr>
<td>σₜ</td>
<td>total conductivity</td>
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Chapter 1 - Introduction

Fuel cells are defined as electrochemical devices for directly converting the chemical energy stored in fuel to electrical energy. The first prototypes of these were developed mid-way through the 19th century, pioneered by Sir William Grove[1]. Since then, many different types of fuel cell have been developed; chemical energy can be converted to electrical in a wide variety of ways utilising many different chemistries. These can be loosely categorised by the temperature of operation, ranging from room temperature up to around 1000 °C. The temperature tends to dictate the type of electrolyte used. At the upper-end of this scale are fuel cells made using solid-oxide electrolytes. These are known as solid oxide fuel cells, or SOFCs, and this thesis focuses purely on fuel cells of this type. In this introductory chapter the basic concepts and science behind SOFCs are discussed.

1.1 Advantages of SOFCs

The need to reduce our reliance on fossil fuels is well-established. A result of work towards this goal has been great advances in the field of renewable energy. What is clear, however, is that it is utopian to believe that such technologies are sufficiently developed and economically viable to provide for all our energy needs. Fossil fuels are central to the global economy and are anticipated to remain so for at least the first half of this century. Within this outlook there is a clear demand for more efficient use of fossil fuels. Energy in fossil fuels is stored chemically. The traditional means of accessing this has been by combusting fuel. This converts chemical energy to heat, which must then be converted to more useful forms of energy, such as electricity. It can be visualised that this will be a less efficient use of fossil fuels than directly converting chemical to electrical energy. SOFCs are able to carry out this direct conversion and so their theoretical efficiency is higher than traditional means. These efficiencies will be discussed in detail later.

Efficient use of fossil fuels should not be confined to one particular type of fuel, rather applied to the broad range of those available. Here SOFCs demonstrate attractive properties of fuel-flexibility. Various mixes of hydrogen, steam, carbon dioxide, carbon monoxide and methane can be used to power the cells. These can be derived from light hydrocarbons which are internally reformed at the high operating temperatures, heavier hydrocarbons if externally reformed, and even gasified coal. This positions SOFCs to take advantage of changing commodity prices and enable the utilisation of all fuel types. Further to this, SOFCs could act as a stepping-stone from our existing fossil fuel-based economy to a future hydrogen-based economy. There is a current paucity of hydrogen infrastructure, in part from the lack of devices ready to utilise it. If SOFCs were widespread
they could easily be fuelled from hydrogen, helping to make it economically viable to invest in hydrogen supply.

SOFCs also have the advantage of scalability. To generate useful amounts of power many individual cells must be connected in series, with the output reflecting the number used. Hence SOFCs offer the possibly of using the same technology over a variety of scales. Target markets for SOFCs range from small-scale portable units for automotive and military applications, through medium-scale combined heat-power units for individual homes, and to large-scale power plants.

1.2 SOFC operation

1.2.1 Thermodynamics

The prototypical SOFC consists of a solid-oxide electrolyte separating anode from cathode. At the cathode oxygen from air is supplied as an oxidant. Here it is reduced to oxide ions according to;

\[
\frac{1}{2} O_2(g) + 2e^- \rightarrow O^{2-} \quad \text{Equation 1.1}
\]

The oxide ions make their way to the anode via the electrolyte, where they oxidise the fuel, releasing electrons that can be used to do useful work. This is depicted in Figure 1.1;

![Figure 1.1: Schematic of an SOFC. Adapted from [2].](image)
As previously discussed, SOFCs are fuel-flexible devices so two examples of reactions are given. With hydrogen as fuel the reaction at the anode is;

\[ \text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \]  
Equation 1.2

the overall cell reaction is;

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \]  
Equation 1.3

or with methane the reaction at the anode is;

\[ \text{CH}_4 + 4\text{O}^{2-} \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + 8\text{e}^- \]  
Equation 1.4

the overall cell reaction is;

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 \]  
Equation 1.5

Under standard conditions tabulated values[3] can be used to find the standard potential, \( E_0 \), for these reactions. When at non-standard conditions the Nernst equation can be used to find the an ideal potential at equilibrium for hydrogen oxidation;

\[ E_{\text{ideal}} = E_0 - \frac{RT}{2F} \ln \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}} \]  
Equation 1.6

and for methane oxidation;

\[ E_{\text{ideal}} = E_0 - \frac{RT}{8F} \ln \frac{P_{\text{H}_2\text{O}} P_{\text{CO}_2}}{P_{\text{CH}_4} P_{\text{O}_2}^{1/2}} \]  
Equation 1.7

where \( R \) is the universal gas constant and \( F \) is the Faraday constant.

From this it is evident that the ideal equilibrium potential of the cell reactions decreases with increasing temperature. Also, if the concentrations of the reactants (oxygen and fuel) are lowered the voltage will decrease. This will be the case if using air and mixed-gas fuels. Also the concentration of reactants towards the gas exit of an SOFC will naturally be lower than at the entrance. As a guide, \( E_0 \) for a cell operating at 800 °C, fuelled by pure hydrogen and using pure oxygen as the oxidant, is 0.99 V.

The ideal cell potential can be used to calculate the maximum possible electrical work, \( W \), that the cell can manage;
\[ W = \Delta G = -nFE_{\text{ideal}} \]  

Equation 1.8

where \( \Delta G \) is the change in Gibbs free energy of the reaction, and \( n \) is the number of electrons used in the reaction.

It can be stated that;

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

Equation 1.9

where \( \Delta H \) is the enthalpy change between fuel entering and fuel exiting the cell, which can be thought of as the total available energy. This is reduced by \( T\Delta S \), energy lost by entropy changes, leading to the free energy (i.e. \( \Delta G \)) being lower.

The first law of thermodynamics would state that the energy present in fuel/air entering the cell (i.e. its enthalpy) should be equal to the useful electrical energy produced by the cell, plus any heat energy generated during the electrochemical processes, plus any remaining energy in the fuel/air exiting the cell. This leads us to the concept of efficiency, \( \eta \);

\[ \eta = \frac{\text{useful energy}}{\Delta H} \]  

Equation 1.10

Efficiency can also be discussed in terms of the reduction in the actual cell voltage (\( E_{\text{cell}} \)) over the ideal value. This reduction is contributed to by a variety of phenomena. These are referred to either as polarisations, overvoltages, or overpotentials. The first of these terms is preferred in this text. \( E_{\text{cell}} \) is defined as;

\[ E_{\text{cell}} = E_{\text{ideal}} - \eta_a - \eta_m - \eta_\Omega \]  

Equation 1.11

where

- \( \eta_a \) refers to activation polarisation. This is concerned with the kinetics of the various reactions occurring at the electrodes, namely losses due to their activation energies.
- \( \eta_m \) refers to mass transport polarisation. These are losses concerned with the consumption of reactants at the electrodes. Products must be removed and fresh reactants supplied leading to losses due to limiting mass-transport to and from electrode active sites.
- \( \eta_\Omega \) refers to ohmic polarisation. These are losses due to the resistance to the flow of charge carriers, both electrons and ions. The resistance is ohmic, therefore \( \eta_\Omega = IR \), where \( I \) is the current and \( R \) is the sum of all the cell resistances.
The contribution of these polarisation processes is summarised in Figure 1.2.

![Figure 1.2: Fuel cell voltage/current characteristics, with voltage losses identified. Adapted from [4].](image)

As current is initially drawn slow electrode kinetics ($\eta_a$) cause the initial voltage drop. At the high end of the scale losses are dominated by slow diffusion around reaction sites ($\eta_m$). In normal operation $\eta_\Omega$ is the main factor.

Both $\eta_a$ and $\eta_m$ depend strongly on the characteristics of the particular type of SOFC – its geometry and electrode microstructure – and should be optimised within each particular design. $\eta_\Omega$ depends on these factors too, but also on the fundamental properties of the chosen materials themselves. Contributions to the cell resistance ($R$) from anode, electrolyte, and cathode can be separated. These are typically normalised by the cell area to give the ASR (area specific resistance) in $\Omega \text{cm}^2$. This is a very important parameter as it is relatively transferrable from one type of cell to another, more so than $\eta_a$ and $\eta_m$. Minimising the ASR of different SOFC components is hence the focus of a great deal of research.

Some targets have been suggested in an attempt to focus studies. These are constructive as they give defined goals to work towards, rather than a vague drive toward incrementally lower resistances. A common target is that the ASR of each cell component should not exceed 0.15 $\Omega \text{cm}^2$ [5]. This is derived as follows:

A cell typically operates at a voltage ($E_{\text{cell}}$) of 0.7 V. A reasonable power density to aim for is 0.5 Wcm$^{-2}$, so a current density of 0.5/0.7 is needed, approx. 0.7 Acm$^{-2}$. As stated
previously the voltage of the cell is the voltage under no load minus the various efficiency losses. In this current region this can be approximated to IR, with R being the total ohmic resistance;

\[ E_{\text{cell}} = E_{\text{ideal}} - IR \]  

Equation 1.12

\( E_{\text{ideal}} \) is typically of the order of 1 V, so inputting these parameters mean that R must be approx. 0.43 Ωcm\(^2\). This is for the whole cell, i.e. the sum of the ASR for anode, electrolyte, and cathode, and is rounded to 0.15 Ωcm\(^2\) each to give a convenient target.

### 1.3 Roles and requirements for SOFC components

The three key processes occurring in an SOFC are the oxygen reduction reaction (ORR) followed by incorporation at the cathode, oxide-ion diffusion through the electrolyte to the anode, and fuel oxidation by said ions arriving at the anode. Each component must achieve its role whilst minimising energy losses. As discussed previously, a target is that each component should not contribute more than 0.15 Ωcm\(^2\) to the cell resistance[5]. To generate useful amounts of power many individual fuel cells must be connected in series; this means that the electricity generated by each can be combined. This is achieved by the interconnect material, which can be considered the fourth key component to a working SOFC. The requirements for these components will now be discussed, with particular attention paid to the cathode.

#### 1.3.1 SOFC cathode requirements

Electrons are prerequisite for oxygen reduction to take place so the first requirement for the cathode is that it should have sufficient electronic conductivity. A typical target is of the order of 100 Scm\(^{-1}\) at operating temperature[6]. A cathode with too low conductivity may present unacceptably high ohmic losses. To avoid high activation losses the cathode must also be sufficiently catalytically active towards oxygen reduction. One of the advantages of the high operating temperature of SOFCs is that many transition metal oxides possess this property under these conditions. This avoids the need for expensive catalysts such as platinum. The next requirement is that the cathode must be porous, as gas must be able to reach the surface of the cathode to be reduced. An interconnected network of regular pores provides for a large surface area and reduces mass transport losses. However, not all regions of the cathode surface are said to be ‘active’. Regions may exist on the cathode where oxygen reduction is occurring, but the resultant O\(^{2-}\) ions cannot make their way to the electrolyte and hence do not contribute to power generation. Such regions are said to be inactive. An active site is one where oxygen can be reduced and has
a facile path by which to reach the electrolyte. Then it can diffuse to the anode where it will ultimately oxidise the fuel, releasing energy. Hence a further requirement for SOFC cathodes is a large number of active sites for oxygen reduction and incorporation. It is apparent that useful oxygen reduction can occur at three potential regions (Figure 1.3 top);

(a) At the air/electrolyte interface
(b) At the air/electrolyte/cathode interface
(c) At the air/cathode interface, provided the cathode has sufficient ionic conductivity

![Figure 1.3: Schematic of porous cathode deposited on dense electrolyte. Top: different interfaces where active ORR can occur; Bottom: schematic of reaction steps for ORR in regions (b) and (c), illustrating bulk and surface paths of $O_2^-$ through cathode to electrolyte.](image)

Region (a) does not contribute significantly towards the ORR in SOFCs as typical materials used in the electrolyte are not catalytically active. Region (b) requires three phases to be in contact, hence it is known as a triple-phase boundary (TPB). This is a necessarily one-dimensional region. For pure-electronic conducting cathodes active sites are confined to
the TPB, the length of which must therefore be maximised. This requires careful consideration of materials engineering. Region (c) just involves the air/cathode interface hence is a two-dimensional region. For this to be active the cathode requires sufficient ionic as well as electronic conductivity, so-called mixed ionic-electronic conductivity (MIEC). Extending the active region over two dimensions is the evident advantage of MIEC cathodes. Once oxygen is reduced at the air/cathode interface it can pass to the electrolyte through the bulk of the cathode, or along its surface (Figure 1.3 bottom), the relative contributions of these depending on the material and microstructure. Oxygen reduction may also not be confined to the generation of O\(^2\); other negatively charged species may contribute\[7\]. For MIEC cathodes the TPB length is still important as the relative contributions towards effective ORR between regions (b) and (c) will depend on the particular material and microstructure. A popular model proposed by Adler predicts that effective ORR will only extend a certain distance from the nearest TPB[8]. This distance is known as \(\delta\), the utilisation length;

\[
\delta \approx \sqrt{\frac{(1 - \epsilon) L_c}{\tau \alpha}} \quad \text{Equation 1.13}
\]

where \(\epsilon\) = porosity, \(\tau\) = tortuosity, \(\alpha\) = surface area, and \(L_c = D'/k\) i.e. a critical length parameter expressing the relative importance of bulk transport over surface exchange in the cathode.

Inputting typical values for high-performing cathodes gives a utilisation length of the order of a few microns.

A further requirement for SOFC cathodes is stability. No detrimental reactions must occur during fabrication or operation. These could involve phase-decomposition due to the high operating temperature and oxidising environment, as well as potential interdiffusion and reactivity with adjacent cell components.

Finally, the thermal expansion coefficient (TEC) of the cathode must be within the tolerances of the other cell components to prevent cracking and delamination during fabrication, operation, and thermal cycling.

### 1.3.2 SOFC anode requirements

Similar to the cathode, the anode requires good electronic conductivity so that the electrons released during fuel oxidation can be utilised as current. It must be able to catalyse the fuel oxidation as well as allowing for internal hydrocarbon reforming. It
should also be tolerant of contamination and deactivation by certain levels of impurity in the fuel. Indeed, fuel-flexibility and tolerance is one of the prime advantages of an SOFC. Porosity is required to enable fuel to enter active sites, as well as for water vapour and unused fuel to exit. For similar reasons to the cathode, mixed conductivity in anodes can be beneficial. Finally, the anode is subject to the same considerations with respect to stability and TEC as the cathode, bearing in mind that it will be under reducing atmosphere.

### 1.3.3 SOFC electrolyte requirements

To reduce ohmic losses the electrolyte should have as high ionic conductivity as possible. Opposite to the two electrodes however, the electrolyte should have essentially zero electronic conductivity. If any were present then electrons generated at the anode from fuel oxidation could pass through to the cathode, creating a short circuit and reducing the cell efficiency. The porosity requirement too is opposite to the electrodes – the electrolyte should contain no connected porosity to prevent any gas leakages, ideally being fully dense. As with the electrodes, the electrolyte must be stable under fabrication and operating conditions, as well as unreactive and TEC-matched towards other cell components.

### 1.3.4 Interconnect requirements

The prime function of the interconnect component is to combine the current generated by each individual cell; hence high electronic conductivity is paramount. Interconnects will be in contact with both anode and cathode so must be chemically stable with each, as well as stable under both oxidising and reducing environments.

### 1.4 Conductivity in ceramics

From the above it is clear that conductivity is a very important property for ceramics in SOFCs. A brief description of the mechanisms behind oxide-ion and electronic conductivity will now be given.

#### 1.4.1 Electronic conductivity

Solids can be classified into three broad types; metallic conductors, semiconductors, and insulators. Metallic materials conduct electricity very well; insulators very poorly; and semiconductors are somewhere in between. The span of electronic conductivity is broad, one of the widest of any natural phenomenon. These properties are dependent on the electronic band structure of the material, in particular whether or not there are partially filled bands. Each band has associated with it a transfer of electrons to the left or right.
When there is no electrical polarisation equal numbers of electrons are in each state, \textit{i.e.} there is no flow of current. Applying a potential difference to the system shifts the energy of the two states, making one higher than the other. If the band is partially filled then there will be a transfer from one state into the other, giving a net flow of current. If the band is fully occupied then no such transfer is possible so there will be no resultant flow of electrons. These states are depicted in Figure 1.4.

![Figure 1.4: Effect of an electric field on energy levels; (a) metal, no field, no net flow; (b) metal, field applied, net flow of electrons to the right; (c) insulator, field applied, no net flow of electrons. Adapted from [9].](image)

Metals therefore require partially filled bands, known as conduction bands. Insulators will have completely filled valence bands and various empty bands at higher energies. The energy difference between highest filled and lowest empty, $\Delta E$, is known as the band gap for the material. If this is small enough then it is possible to thermally excite a small number of electrons into the empty band, creating a partially-filled conduction band with mobile electrons. This will also leave a ‘hole’ ($h^+$) in the valence band which can also move. Materials where this gives appreciable conductivity are known as intrinsic semiconductors. Another means for generating a small number of mobile electrons is via doping or defects. If there are empty energy levels, known as acceptor levels, added just above the valence band electrons can be thermally excited into these, leaving mobile holes in the valence band. These holes are positively charged hence materials with this type of conductivity are known as \textit{p-type} semiconductors. Alternatively, one can add filled levels,
known as donor levels, just below an empty band. Electrons from donor levels can be excited into the band allowing for conductivity. As electrons are negatively charged these materials are known as n-type semiconductors. These states are shown in Figure 1.5. Donor or acceptor states can be formed by doping a material with an element with a different number of valence electrons. For example, germanium doped with gallium would be a p-type semiconductor as gallium has one fewer electron therefore can accept; whereas germanium doped with arsenic is n-type as arsenic has one extra electron that it can donate to germanium.

![Figure 1.5: Energy levels for semiconductors; (a) intrinsic semiconductor; (b) n-type; (c) p-type. Adapted from [9].](image)

Another means for creating donor or acceptor states is via mixed-valence transition metal elements. For example, stoichiometric nickel oxide (NiO) just has Ni$^{2+}$ ions, however it can accommodate excess oxygen forming NiO$_{1+\delta}$ with an associated colour change from green to black. This is charge-compensated by the formation of some Ni$^{3+}$. These ions behave as positively charged holes making NiO$_{1+\delta}$ a p-type semiconductor[10].

Conductivity is proportional to the concentration of charge carriers, and their mobility;

$$\sigma_x = c_x \mu_x z_x e$$  \hspace{1cm} \text{Equation 1.14}

where $\sigma_x$ is the conductivity of species $x$; $c_x$ its concentration; $\mu_x$ its mobility; and $z_x e$ the charge of $x$. 
The concentration of mobile electrons will be much greater for metals than semiconductors; hence metallic conductivity will be higher. As temperature is increased atoms vibrate more creating a larger barrier for electron mobility, hence metallic conductivity decreases with increasing temperature. The process that generates charge carriers in semiconductors is thermally activated. Hence at higher temperatures a great concentration of electrons will be present, offsetting the decreased mobility, increasing conductivity.

### 1.4.2 Oxide-ion conductivity

Charge carriers for oxide-ion conductivity can be vacancies or interstitials. The concentrations of these will be governed by the non-stoichiometry of the material, as well as the intrinsic defect equilibria that are present above zero Kelvin. For Schottky defects, illustrated by a simple binary MO oxide;

\[
\text{nil} \leftrightarrow V_m^{\text{M}} + V_0^{\text{O}^2-} \tag{1.15}
\]

and for Frenkel defects, typically for oxygen;

\[
O_0^{\text{O}^2-} \leftrightarrow V_0^{\text{O}^2-} + O_1^{\text{O}^2-} \tag{1.16}
\]

where \(V_m^{\text{M}}, V_0^{\text{O}^2-},\) and \(O_1^{\text{O}^2-}\) respectively are a metal vacancy, an oxygen vacancy, and an oxygen interstitial shown in conventional Kröger-Vink notation.

Three mechanisms allow for ion migration.

a) Vacancy mechanism: A vacancy can be filled by an ion adjacent to it, the net result being the movement of the vacancy.

b) Interstitial mechanism: An interstitial ion can move to an adjacent vacant interstitial site. More common for small interstitial ions.

c) Interstitialcy mechanism: This a combination of (a) and (b) thus, an ion moves onto an interstitial site leaving behind a vacant site, which is then filled by another interstitial ion adjacent to this vacancy, the net result being the movement of an interstitial ion from one site to another.

These are shown in Figure 1.6. The ions around the migrating species form the resistance to conductivity due to their size. This energy barrier is overcome thermally, meaning that charge carrier mobility is greater at higher temperatures, i.e. ionic conductivity in a phase increases with temperature.
1.4.3 Mixed conductivity

Materials can conduct simultaneously by a variety of different charge carriers. If this is the case then the total conductivity is simply the sum of the conductivity of each individual carrier. If electronic conductivity is appreciable, i.e. the material is a metal or semiconductor, this tends to dominate the conductivity. Contributions are quantified by the transport number;

\[
t_x = \frac{\sigma_x}{\sigma_{\text{total}}} \tag{1.17}
\]

where \( t_x \) is the transport number for carrier \( x \), and \( \sigma_{\text{total}} \) the total conductivity.

For SOFC electrolytes the oxide-ion transport number should be as close to unity as possible.

1.5 Summary

The advantages of SOFCs have been discussed, and the basic theory behind their operation introduced. A main area of efficiency loss was identified as ohmic polarisation. This can be minimised by developing materials with low ASR, a suggested target being \(<0.15 \ \Omega cm^2\) for each of anode, electrolyte, and cathode. Specific requirements for these components were discussed, with particular attention paid to the cathode. The conductivity of ceramics is of high importance so the fundamentals behind this were presented. The next chapter will review materials used in SOFCs, both traditionally and the current state-of-the-art.
References

Chapter 2 - Materials for solid oxide fuel cells

The following section will consist of a review of the types of material commonly used in SOFCs. More attention will be paid to cathode materials as cathode development is the focus of this thesis.

2.1 Electrolyte

The role of this component is to allow for oxide ions to transfer from the cathode to the anode. The barrier to the flow of ions will be the intrinsic resistance of the material chosen, and the distance that the ions need travel. Therefore the ionic conductivity of a material at a certain temperature limits the maximum allowed thickness for the electrolyte. For example, a conductivity of $10^{-2}$ Scm$^{-1}$ requires an electrolyte no thicker than 15 μm to meet the 0.15 Ωcm$^2$ ASR target[1]. Ionic conductivity in ceramic materials is proportional to temperature; hence a lower limit for the operating temperature of an SOFC is that at which the electrolyte material has sufficient conductivity with respect to its thickness. To operate below this a different material with higher ionic conductivity is required. Some important categories of electrolyte are now reviewed.

2.1.1 Stabilised zirconia

ZrO$_2$, or zirconia, can exist in a variety of different phases depending on the temperature. At room temperature a monoclinic 7-fold coordinate structure known as baddeleyite is thermodynamically favoured, above 1100 °C there is a tetragonal form, and above 2300 °C a cubic 8-fold coordinate fluorite structure is favoured[2] (Figure 2.1). These transitions occur with significant cell volume changes and hence can lead to cracking of the material.

![Figure 2.1: Schematic representation of the fluorite structure adopted by the cubic ZrO$_2$ polymorph. Red: oxygen; blue: zirconia.](image)
ZrO$_2$ is tolerant to a wide range of substitutions, with suitably-sized M$^{3+}$ ions readily entering the structure on Zr$^{4+}$ sites. This has the effect of stabilising the cubic structure at lower temperatures hence these are often known as ‘stabilised zirconias’. Charge-compensation for the substitution is achieved by formation of oxygen vacancies thus;

\[
\text{Equation 2.1}
\]

Typical dopants are yttrium, giving yttria-stabilised zirconia (YSZ); and scandium, giving scandia-stabilised zirconia (SSZ). The vacancies formed are mobile within the cubic structure allowing for ionic conductivity. Increasing the dopant concentration increases the number of vacancies leading to higher ionic conductivity. However, above a certain level, more complex effects occur including defect association. These act to reduce the conductivity. Optimal dopant levels for YSZ are from 8 – 11 mol.%. For 8%-doped YSZ a conductivity of 10$^{-2}$ Scm$^{-1}$ is reached above 700 °C[4]. The typical TEC for YSZ electrolytes is $10.8 \times 10^{-6}$ K$^{-1}$[4]. The high temperature required for adequate conductivity in YSZ limits its uses in modern SOFCs.

2.1.2 Doped ceria

Ceria, CeO$_2$, adopts the same cubic structure as high-temperature zirconia (Figure 2.1) over its full temperature range[5]. It can be doped with M$^{3+}$ ions leading to oxygen vacancies, analogous to zirconia. The ionic conductivity allowed by these vacancies approaches the level required for an SOFC at much lower temperatures than YSZ or SSZ; 0.01 Scm$^{-1}$ is achieved at 500 °C [3]. The predominant dopant used is gadolinium between 10 and 20 mol.%. These electrolytes are abbreviated as CGO (i.e. cerium-gadolinium oxide) followed by the % of Gd, i.e. CGO10 for Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$. The typical TEC for CGO10 is $13.5 \times 10^{-6}$ K$^{-1}$[4]. It could be tempting to use this electrolyte at high temperatures hoping for exceptionally high ionic conductivity; however problems arise with CGO under these conditions. At high temperatures under reducing conditions at the anode some Ce$^{3+}$ is formed. This allows for electronic conductivity leading to cell losses via a short circuit, and lattice parameter changes which can lead to cracking[1]. This means that doped ceria electrolytes are often designed to work at temperatures below 600 °C.

2.1.3 Doped lanthanum gallate

Lanthanum gallate, LaGaO$_3$, adopts the perovskite structure shown in Figure 2.2. The generic description of this structure is ABO$_3$. In the case of LaGaO$_3$ lanthanum is on what is known as the A-site and gallium on what is known as the B-site.
Figure 2.2: Schematic representation of the perovskite structure adopted by LaGaO$_3$. Red: oxygen; green: lanthanum (A-site cation); blue: gallium (B-site cation).

Oxygen vacancies can be created in LaGaO$_3$ by doping the A and/or B site with subvalent ions. To maintain a lack of electronic conductivity the dopant ions are chosen to be of noble gas configuration; strontium on the A site and magnesium on B, giving La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-δ}$ (LSGM). The electrolyte properties are optimised for $0.10 \leq x \leq 0.2$ and $0.15 \leq y \leq 0.20$[3]. Ionic conductivity bettered $10^{-2}$ Scm$^{-1}$ at 550 °C[4], with values of 0.17 and 0.08 Scm$^{-1}$ at 800 and 700 °C for La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$[6]. The typical TEC is $11.1 \times 10^{-6}$ K$^{-1}$[4]. LSGM is more tolerant as an electrolyte to reducing conditions than CGO. A drawback is the formation of stable impurity phases during processing, including LaSrGa$_3$O$_7$, LaSrGaO$_4$, and La$_4$Ga$_2$O$_9$ [6, 7]. Further to this, LSGM is expensive as gallium is in demand due to the widespread use of gallium nitride and gallium arsenide in the electronics industry [2]. The conductivity of LSGM, CGO and YSZ electrolytes is compared in Figure 2.3.

2.1.4 The role of the electrolyte in the operating temperature of SOFCs

The properties of stabilised zirconias are long-established hence these were the electrolyte materials chosen for the early generations of fuel cell. They require high temperatures to give sufficient conductivity, of the order of 700 – 1000 °C. Fuel cells operating under these conditions are said to be ‘high-temperature’ SOFCs (HT-SOFCs), or may be known as ‘traditional’ SOFCs. Operating at such temperatures places stringent requirements on the materials making up the rest of the SOFC.
This has particular ramifications for the interconnect component. In HT-SOFCs this must be fabricated from ceramic materials, often LaCrO$_3$. These are brittle and difficult to process industrially. It would be more desirable to use steel as the interconnect, it being cheaper and easily machinable, but it cannot tolerate these temperatures[7]. Further disadvantages to HT-SOFCs include high degradation rates and long start-up/shut-down times[11]. Hence there has been a concerted effort to lower the operating temperature of SOFCs. The discovery of new electrolyte materials such as CGO and LSGM has allowed for this, permitting the use of steel-based interconnects. Definitions for these recent advances vary, with the prefixes ‘reduced-temperature’, ‘intermediate-temperature’ or ‘low-temperature’ often used. The author prefers the term intermediate-temperature SOFC, or IT-SOFC, and considers an appropriate temperature range for this to be 500 – 700 °C.

### 2.2 Anode

Standard anode materials are composites of a ceramic phase with good ionic conductivity, combined with an elemental metal. These are known as cermets, a portmanteau of ceramic and metal. The metal catalyses fuel oxidation and reforming, and provides the electronic conducting pathway. Nickel is the typical choice due to cost[10]. This is dispersed over a porous ceramic structure, the ionic-conducting nature of which allows for a large TPB length. Often the ceramic is chosen to be the same material as the electrolyte as this ensures compatibility between the two components. Hence for a YSZ electrolyte a Ni-YSZ cermet anode would be common. Anode development is outside the scope of this thesis, so for further details on the current state of research the interested reader is referred to the
recent review by Cheng and co-workers [12]. It is noted that in the search for improvements at the anode MIEC materials are being considered. These are attractive as they allow for fuel oxidation to be extended beyond the TPB, in a similar manner to the chemistry described at the cathode.

2.3 Cathode

2.3.1 Doped lanthanum manganite

Traditional cathode materials have been strontium-doped lanthanum manganites [13]. The parent compound, LaMnO$_3$, adopts the perovskite structure (Figure 2.2) and has $p$-type electronic conductivity of the order of 0.1 Scm$^{-1}$ at HT-SOFC temperatures. Doping with strontium replaces lanthanum in the structure. Charge compensation is achieved via the redox chemistry of manganese rather than oxygen vacancy formation [10];

$$\text{La}^{3+}\text{Mn}^{3+}\text{O}_3 \xrightarrow{\text{xSr}} \text{La}_{1-x}^{3+}\text{Sr}_{x}^{2+}\text{Mn}_{1-x}^{4+}\text{O}_3$$

Equation 2.2

Increasing the Sr-content increases the $p$-type conductivity up to dopant levels of 50 mol.%, with $\sigma = 290$ Scm$^{-1}$ at 1000 °C for La$_{0.5}$Sr$_{0.5}$MnO$_3$ [10]. However at high dopant levels various deleterious effects occur including a higher TEC [13] and reactivity with YSZ to forming SrZrO$_3$ [14]. Therefore strontium levels are typically kept lower than 30 mol.% [15]. Other possible reactions with YSZ include the formation of the insulating pyrochlore phase La$_2$Zr$_2$O$_7$ at high temperatures [16]. This can be mitigated by limiting fabrication temperatures [13, 17], and using A-site deficient LSM [18-20]. Oxygen non-stoichiometry in LSM is a complex phenomenon with both deficiency and excess possible under varying conditions [21]. Under SOFC conditions however LSM is nearly oxygen-stoichiometric meaning that is has negligible ionic conductivity [15, 22]. This necessitates that successful oxygen reduction at LSM cathodes is confined to the TPBs, so attention has focussed on materials engineering to improve the length of these regions. A common approach for this is the formation of a composite with a phase of high ionic conductivity. This is typically chosen to be the same material as the electrolyte as this also helps mitigate any TEC mismatch between cathode and electrolyte. Therefore LSM+YSZ composites are used in HT-SOFCs. Ostergard et al. [23] demonstrate reduced ASRs, from 2.7 to 0.5 Ωcm$^2$, for pure LSM vs. composite LSM+YSZ cathodes respectively at 1000 °C. Improvements to composite cathodes which can give further performance enhancements are functionally-graded cathodes. These utilise layers with different compositions, each geared towards a certain role in the electrode. This allows for better accommodation of TEC-strains between different materials via a gradual change in composition over the layers. When applied to
LSM+YSZ cathodes ASRs have been reduced to as low as 0.2 Ωcm$^2$ at 750 °C [24] or 0.21 Ωcm$^2$ at 700 °C [25]. Despite these advances, LSM remains intrinsically limited by its lack of ionic conductivity meaning that its performance in the intermediate-temperature range is insufficient [15]. LSM is therefore being supplanted by alternative materials in the continuing drive to lower the operating temperature of SOFCs.

### 2.3.2 Doped lanthanum cobaltite

Lanthanum cobaltite, LaCoO$_3$, is a perovskite with significant $p$-type electronic conductivity; higher than LSM under similar conditions [17]. However, it is less stable than LSM at HT-SOFC temperatures [13]. Doping strontium onto the A site forms La$_{1-x}$Sr$_x$CoO$_{3-δ}$ (LSC), improving stability and maintaining good electronic conductivity, above 1300 Scm$^{-1}$ in the intermediate-temperature range [26]. An added advantage is appreciable ionic conductivity; it is a mixed conductor. A drawback to LSC is its unacceptably-high TEC of the order of 20×10$^{-6}$ K$^{-1}$ [27]. This is due to transitions between low- and high-spin states of the octahedrally-coordinated Co$^{3+}$ 3$d^6$ ion [28]. This can be attenuated by replacing some of the cobalt with iron, forming La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-δ}$ (LSCF). La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ (LSCF6428) is a common composition. The properties of this material are remarkably attractive; electronic conductivity is high: 350 and 250 Scm$^{-1}$ at 600 and 800 °C [29]; ionic conductivity is significant: >10$^{-2}$ Scm$^{-1}$ at 800 °C [30]; TEC is adequate: ≈15×10$^{-6}$ K$^{-1}$ [29]. Deleterious reactivity does occur with YSZ but not with CGO [31] meaning that LSCF is typically studied using the latter as the electrolyte, or with a doped ceria barrier layer if the use of YSZ is desired [32-34]. This solution is complicated by the possibility of reactivity between YSZ and CGO forming (Ce,Zr,Gd,Y)O$_{2-δ}$ phases of lower ionic conductivity [35]. This example highlights the challenges posed by development of high-temperature ceramic devices.

Pure-LSCF cathodes give low ASRs at relatively low temperatures, e.g. 0.3 Ωcm$^2$ at 700 °C [36]. These can be improved on by the formation of composites with CGO, analogous to the LSM+YSZ composites discussed earlier. This indicates that the length of TPB regions is still of importance for these MIEC cathodes. Kilner and Dusastre show an ASR of 0.16 Ωcm$^2$ at 700 °C [37] for their LSCF+CGO cathode; this has subsequently been improved at this temperature by Wang and Mogensen to the remarkable value of 0.026 Ωcm$^2$ [38].

Bearing in mind the target of 0.15 Ωcm$^2$ suggested by Brandon and co-workers [7], it is clear that these high-performance LSCF cathodes must have other problems associated with them. Otherwise it would be difficult to explain the current paucity of commercial SOFCs. The main factor behind this is cathode degradation during operation. Two
processes that contribute towards this are strontium segregation and chromium poisoning. For the former, it is known that strontium in LSCF segregates toward the surface under operating conditions[39]. This results in a SrO layer terminating the structure, i.e. at the cathode/air interface. This layer is known to have a passivating effect, impairing the oxygen reduction and incorporation kinetics[40-42]. Similar behaviour has also been observed for LSM cathodes[43]. It has been shown that ageing LSCF and LSC in humid air exacerbates this strontium segregation[44, 45]. This suggests that control of the atmosphere at the cathode may be required to ensure stability, an unwanted modification to an SOFC.

Chromium poisoning relates to the metallic interconnects used in IT-SOFCs. The steels of choice contain chromium which can vaporise during operation and come into contact with the cathode. Here they form chromium-containing deposits which degrade the cathode[46, 47]. There is some debate over the processes by which this occurs however it has been suggested that strontium in LSCF acts as a nucleating agent for the formation of deposits[48].

Various attempts have been made to get around these problems. Electrical polarisation can promote the de-segregation of strontium[41, 42]; acid-etching can attenuate the passivating outer layer, though clearly is impractical for use on a working SOFC[40, 43]; various coatings have been applied to steel interconnects in an attempt to prevent Cr vaporisation[49]. An alternative method would be to look for an entirely new cathode material that is more resistant to these deleterious effects. The current generation of high-performing materials adopt the perovskite structure, so a reasonable starting point could be to consider materials of this structure with different constituent elements. However, the breadth of the periodic table provides for a huge variety of potential materials and it can be difficult to know which element to substitute for another in the search for improvement. Serra et al. have looked at perovskites with as many as seven different metal ions, for example La$_{0.8725}$Pr$_{0.0725}$Sm$_{0.29}$Ba$_{0.145}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-δ}$ [50]. With so many compositional degrees of freedom any improvement seen in such perovskites would be hard to ascribe to a particular cause. Synthesising and testing many new compositions is a labour- and time-intensive exercise. Various techniques have been developed to overcome this problem, including robotic automation of sol-gel synthesis[51], automation of a continuous hydrothermal flow reactor for synthesis[52] and use of high-throughput powder X-ray diffraction at the Diamond Light Synchrotron for material analysis[53]. Whilst these are elegant solutions to some of the problems it is not possible to automate every necessary step along the path to developing a new cathode material. Also it seems
likely that any increases in performance based on modifications of known materials will be only incremental[54]. Researchers are therefore starting to look away from traditional perovskite-structured oxides in the search for a step-wise improvement in materials properties.

2.3.3 Alternative structure types for SOFC cathodes

The fundamental requirement for a high-performance SOFC cathode material is good mixed ionic-electronic conductivity. Moving on from perovskite, a variety of materials belonging to other structure types have been screened for this. A major family of these are the Ruddlesden-Popper (R-P) phases. This thesis is chiefly concerned with such materials so they will be reviewed in detail. Other structure types considered as SOFC cathodes include pyrochlores, phases with tetrahedrally-coordinated cobalt, composites with the fast-ion conductor BIMEVOX, bismuth ruthenates, rutiles, spinels, and more. These have been comprehensively covered by the author in a contribution towards a recent review article[55]; the interested reader is directed towards this.

2.4 Ruddlesden-Popper phases as SOFC cathodes

R-P phases have the generic formula (ABO$_3$)$_n$AO. These phases are related to the perovskite structure as they consist of $n$ perovskite-like layers; ABO$_3$, separated by single rock salt-like layers; AO. Typically phases with $n = 1, 2,$ and $3$ can be synthesised by traditional ceramic techniques[56]. These structures are shown in Figure 2.4. Higher-order phases can be reached via layer-by-layer deposition methods[57]. $n = \infty$ corresponds to infinitely thick perovskite layers, i.e. the perovskite structure itself.

Interest in these phases was motivated by the discovery of MIEC in the $n = 1$ phase La$_2$NiO$_{4+\delta}$ (L2N1) at temperatures relevant to IT-SOFCs[59, 60]. Before this time R-P phases had predominantly been studied at low temperatures for interesting magnetic effects[61, 62], as well as superconductivity[63]. The ionic conductivity in L2N1 was found to be greater than LSCF[60]; 0.02 vs. 0.003 Scm$^{-1}$ at 700 °C[64]. The realisation of this potential was a catalyst for a great deal of research into R-P phases as SOFC materials.
2.4.1 Ionic conductivity in L2N1

It is accepted that the superior ionic conductivity in L2N1 stems from its oxygen-hyperstoichiometry. The amount of excess oxygen is quantified by the parameter $\delta$. Literature values for this show some variation depending on the synthetic route used; typically the range is from 0.14 – 0.25[65-68]. Déomurgues et al. carried out a detailed study of the crystal structure of L2N1 from $0.0 \leq \delta \leq 0.25$ using X-ray and neutron diffraction[68]. Low $\delta$ values were reached by heating under reducing atmosphere; high values by electrochemical oxidation. They found that oxygen excess is accommodated as interstitials which reside in the LaO rock salt layers of the structure. This has since been confirmed by further neutron studies[66, 69], and modeled in computational space[70, 71]. The interstitial content will also be affected by the intrinsic Frenkel disorder[64];

$$O_0^x \leftrightarrow V_0^{**} + O_1^{**}$$  \hspace{1cm} \text{Equation 2.3}

where $O_0^x$ represents an oxygen ion on the site adjacent to the LaO layers; $V_0^{**}$ an oxygen vacancy on this site; and $O_1^{**}$ an interstitial oxygen in the LaO layer.

The early work on L2N1 includes much discussion on the nature of the ionic conductivity. Kharton et al. suggest that this will consist of contributions from both oxygen interstitials as well as vacancies [59, 72], with the proposal that the activation energy for interstitials will be larger than for vacancies. Bassat et al. carried out a detailed study on single crystals.
of L2N1[64]. They used secondary-ion mass spectrometry (SIMS) to carry out isotopic-exchange depth profiling (IEDP). In this way they measured the oxygen diffusivity parallel and perpendicular to the $(a,b)$ plane (NB: the LaO layers in the structure run parallel to the $(a,b)$ plane, perpendicular to this is the $c$ axis, cf. Figure 2.4). Significant anisotropy was found, with conductivity parallel to $(a,b)$ 1-2 orders of magnitude higher than perpendicular. Interestingly, the activation energy parallel was higher than perpendicular; 0.9 vs 0.25 eV. This anisotropy has since been confirmed by studies on epitaxial thin films of L2N1 grown in different orientations[73]. Discussing the conductivity mechanisms, Bassat states that $O^{i'}_1$ are confined to the LaO rock salt layers due to their size. Therefore they can only contribute to conductivity along these layers, i.e. parallel to $(a,b)$. This means that conductivity along the $c$ axis must involve oxygen vacancies. Hence the lower activation energy in this direction confirms Kharton’s suggestion that the activation energy for vacancies is lower than for interstitials. Given that the conductivity along the $(a,b)$ plane is much higher than along the $c$ axis, and $O^{i''}_1$ are confined to the LaO layers in this $(a,b)$ plane, it is evident that it is the interstitial oxygen content in L2N1 that provides for its high ionic conductivity.

Minervini and co-workers [71] undertook atomistic modeling on oxygen migration in L2N1 and predicted significant anisotropy, agreeing with the experimental work. An interstitialcy mechanism is suggested along the LaO layers, with contributions from both mono- and divalent oxygen ions, $O^{i'}_1$ and $O^{i''}_1$. Subsequent density functional theory modeling by Frayret et al. [74] claims to rule out the presence of $O^{i'}_1$, and this has been accepted in a more recent atomistic study by Chroneos et al. [75]. Similar to Minervini, Chroneos predicts anisotropy and an interstitialcy mechanism in the $(a,b)$ plane.

The maximum entropy method (MEM) has been applied to neutron diffraction data collected on $(Pr_{0.5}La_{0.1})_2(Ni_{0.74}Cu_{0.22}Ga_{0.05})O_{4+δ}$, an $n = 1$ R-P phase believed to behave similarly to L2N1 [76]. This method allows for oxygen migration pathways to be probed using experimental data rather than computational techniques. Nuclear density is found to link interstitial sites in rock salt layers to nearby occupied sites, agreeing with the predicted interstitialcy mechanism. The bottleneck for this pathway decreases with increasing temperature. Atomistic modelling on $Pr_2NiO_{4+δ}$ has predicted a remarkably similar pathway[77], these are shown in Figure 2.5.
Another important property of L2N1 is the magnitude of the conductivity of dense polycrystalline samples compared to single crystals. This is compared by Bassat in Figure 2.6. Self-diffusion in dense ceramic L2N1 is almost as high as the maximum anisotropic value. This indicates that the isotropic ionic conductivity in polycrystalline R-P phases is not significantly limited by the low conductivity along the c axis; rather it approaches the high value parallel to (a,b). If this is the case for layered oxides in general then this is an important result. It is difficult to envisage a single-crystal cathode hence polycrystalline samples must exhibit high conductivity to be good electrode materials.

From the above it is seen that ionic conductivity in L2N1 and related \( n = 1 \) R-P phases has been studied by a wide variety of methods and is a generally well-understood phenomenon.

**Figure 2.5:** Interstitialcy pathway for ionic diffusion in \( n = 1 \) R-P phases as predicted by atomistic simulation on \( \text{Pr}_2\text{NiO}_{4+\delta} \) by Parfitt *et al.* [77], and shown experimentally by MEM applied to neutron diffraction data for \( (\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Ga}_{0.05})\text{O}_{4+\delta} \) by Yashima *et al.* [76]. O1: equatorial oxygen site in \( \text{BO}_6 \) octahedra; O2: apical oxygen site in \( \text{BO}_6 \) octahedra; O3: interstitial site in AO rock salt layer.
### 2.4.2 Other properties of L2N1

Turning attention to the other properties of L2N1, its TEC is of the order of $13 \times 10^{-6} \text{ K}^{-1}$ [58, 78] which is a good match with common SOFC electrolytes. Thermally, Montenegro-Hernández et al. have demonstrated the stability of the phase at 700 and 900 °C for 72h [79], however Amow did detect slight decomposition towards higher-order phases after 2 weeks at 900 °C [58]. Given that the target operating temperature for IT-SOFCs is well below 900 °C this is not considered preventative. Reactivity has been observed with YSZ and CGO electrolytes [79, 80] however this does not occur with LSGM [81]. Electrically, L2N1 behaves as a semiconductor. From 200 – 700 °C conductivity is broadly constant, going through a maximum at approx. 400 °C with values from 60 – 80 Scm$^{-1}$ [58, 78]. This falls short of the target of 100 Scm$^{-1}$.

### 2.4.3 Electrode performance of L2N1

A variety of studies have been carried out on the electrode performance of L2N1. When these have been extended across a variety of electrodes lower ASRs have been found using LSGM over both YSZ and CGO [82, 83]. This is consistent with the reactivity seen between L2N1 and YSZ/CGO but not LSGM. With this in mind it seems sensible to confine further research to LSGM, or perhaps consider using it as interlayer to prevent reaction. A variety of literature data are summarised in Figure 2.7. From this it is evident that the performance to date of L2N1 and related materials is relatively poor, which could be
related to the low electronic conductivity of the phase. Despite this, the properties of L2N1 are still considered attractive enough to encourage persistence and further investigation.

2.4.4 Improvements on L2N1
A variety of doping strategies have been used in an attempt to improve the performance of L2N1, with some benefit found [82, 83]. Also, the use of $n = 1$ R-P phases with alternative lanthanide ions has been considered. The praseodymium and neodymium analogues are known to have slightly higher electronic conductivity than lanthanum, whilst maintaining high ionic conductivity [78]. Nd$_2$NiO$_{4+\delta}$ possesses similar thermal stability to L2N1, however Pr$_2$NiO$_{4+\delta}$ decomposes during annealing at 700 °C [79], making its future as a cathode material questionable. Nd$_{1.6}$Sr$_{0.4}$NiO$_{4+\delta}$ has shown promising results [84] indicating the potential of this approach. Sayers et al. recently tested graded L2N1 cathodes [85, 86]. They found that a porous L2N1 cathode could be improved with the addition of a compact L2N1 interlayer between electrolyte and porous layer, with the ASR reduced from 7.4 to 1.0 $\Omega$cm$^2$ at 700 °C. The suggestion is that the compact interlayer improves the overall electrode/electrolyte contact. Sayers also comments that improved current collection enhances the electrode performance of L2N1, further indicating that poor electronic conductivity limits the performance of this phase. From Figure 2.7 it can be see that Sayers’ grading approach leads to some of the lowest ASRs to date for R-P phases in the IT-SOFC region, highlighting the potential of this microstructural engineering.

As discussed above, the formation of a composite is an established means for improving the performance of traditional perovskite cathode materials LSM and LSCF. These are combined with a material of high ionic conductivity, with the compromise of lower electronic conductivity in the composite compared to the bulk perovskite. Given the widespread use of this method it is surprising that little work has been published applying this to R-P phases. The bulk properties of a phase must be taken into account when considering a composite. In the case of L2N1, this is a material with excellent ionic conductivity, and one certainly would not want to lower its electronic conductivity any further. Therefore a sensible approach here would be to make a composite with a phase with high electronic conductivity. Chen and co-workers have studied LSCF+L2N1 composites, however this was geared around the properties of the perovskite and the addition of L2N1 actually resulted in increased ASRs over pure LSCF [87]. The ideal composite should give better performance than the single phases of all its constituents. It is clear that there is scope for more research to be undertaken with a view to improving on R-P phases by the formation of a composite.
Figure 2.7: log(ASR) vs. 1000/T for various R-P phases, with comparison to state-of-the-art LSCF+CGO composite. 0.15 $\Omega$cm$^2$ target indicated.

An alternative to $n = 1$ phases is to consider higher-order phases. For the La-Ni R-P family electronic conductivity is known to increase with $n$ [58, 88]. For La$_3$Ni$_2$O$_{7-\delta}$ ($n = 2$; L3N2) and La$_4$Ni$_3$O$_{10-\delta}$ ($n = 3$; L4N3) this is above the 100 Scm$^{-1}$ target at relevant temperatures. Attention must be drawn to the oxygen stoichiometry in these phases; they are both hypostoichiometric; i.e. they are minus $\delta$ as opposed to the plus $\delta$ seen in L2N1. This suggests that there will be no significant concentration of oxygen interstitials in the LaO layers, rather that oxygen vacancies will be the predominant defect. This has ramifications with respect to potential ionic conductivity in these phases; the interstitialcy mechanism discussed previously will not be valid. Whether L3N2 or L4N3 possess significant ionic conductivity has yet to be established. Such measurements require fully-dense samples; despite cold isostatic pressing to 300 MPa these have yet to be fabricated [58]. The thermal stability of these materials is understood to be greater than L2N1, no impurity phases have been detected after isothermal treatment at 900 °C for 2 weeks [58]. These properties
appear promising, so a small number of investigations into the electrode performance of these phases have recently been presented. Amow has indicated that the performance of L3N2 and L4N3 electrodes is slightly improved over L2N1 [58]. The magnitude of the quoted ASRs is somewhat high (≈ 1 Ωcm² for L4N3 at 800 °C) but is consistent within the study. Takahashi has also compared L3N2 and L4N3 to L2N1 and found improvement[88]. Lou has demonstrated promising performance for L3N2 cathodes, 0.39 Ωcm² at 750 °C [89]. Given the relative lack of knowledge of the transport properties of L3N2 and L4N3 these improvements are typically simply ascribed to the increased electronic conductivity over L2N1. The precise mechanism aside, these limited reports indicate the promise of higher-order R-P phases, and it is clear that more research is required in this area.

2.5 Percolation theory
Some of the electrodes tested in this thesis will be composites. When considering the properties of a composite it is self-evident that the way in which the constituent phases are arranged will have an effect on the electrode performance. Considering a composite of a pure-electronic conductor mixed with a pure-ionic conductor, it is clear that the magnitude of the different forms of conductivity will depend on the interpenetration of the two phases. A model describing this is effective medium percolation theory (EMPT). Percolation generally applies to the movement of fluids through porous solids, but in EMPT this is extended to include the electrical properties of porous composites of two solid phases. The full details of this are discussed by Wu et al. [90] and explored for LSCF+CGO composites by Dusastre and Kilner[37]. The essential aspects are summarised below.

The model is based on a composite of three phases, 1, 2 and 3, with volume fractions for each, p₁, p₂, and p₃, obeying the following relation;

\[ p_1 + p_2 + p_3 = 1 \]  

Equation 2.4

If 1 and 2 are taken to be making up a porous composite p₃ can be said to be p, the non-conductive porosity of this composite. From this the relative volume fractions are;

\[ x_n = \frac{p_n}{(1 - p)} \]  

Equation 2.5

where \( x_n \) is the relative volume fraction of phase n. For a biphasic composite it is necessary that;

\[ x_1 + x_2 = 1 \]  

Equation 2.6
therefore;

\[ p_1 = (1 - p)(1 - x_2) \]  
\[ p_2 = (1 - p)x_2 \]  

Equation 2.7

Equation 2.8

The effective electronic conductivity of the composite, \( \sigma_{e,\text{comp}} \), is given by;

\[ \sigma_{e,\text{comp}} = \frac{F_{e,1} + \sqrt{(F_{e,1})^2 + F_{e,2}}}{4} \]  

Equation 2.9

where \( F_{e,1} \) and \( F_{e,2} \) represent the functions;

\[ F_{e,1} = 3(1 - p)[(1 - x_2)\sigma_{e,1} + x_2\sigma_{e,2}] - (\sigma_{e,1} + \sigma_{e,2}) \]  

Equation 2.10

\[ F_{e,2} = 4\sigma_{e,1}\sigma_{e,2}[3(1 - p) - 1] \]  

Equation 2.11

where \( \sigma_{e,1} \) and \( \sigma_{e,2} \) are the electronic conductivity of phases 1 and 2 respectively.

Similarly the effective ionic conductivity of the composite, \( \sigma_{i,\text{comp}} \), is;

\[ \sigma_{i,\text{comp}} = \frac{F_{i,1} + \sqrt{(F_{i,1})^2 + F_{i,2}}}{4} \]  

Equation 2.12

where \( F_{i,1} \) and \( F_{i,2} \) represent the functions;

\[ F_{i,1} = 3(1 - p)[(1 - x_2)\sigma_{i,1} + x_2\sigma_{i,2}] - (\sigma_{i,1} + \sigma_{i,2}) \]  

Equation 2.13

\[ F_{i,2} = 4\sigma_{i,1}\sigma_{i,2}[3(1 - p) - 1] \]  

Equation 2.14

where \( \sigma_{i,1} \) and \( \sigma_{i,2} \) the ionic conductivity of phases 1 and 2 respectively.

\( \sigma_{\text{amb}} \) is the ambipolar conductivity of the composite, this being the simultaneous transport of both ions and electrons as well as the separate contributions of each. It is approximated to;

\[ \sigma_{\text{amb}} \approx \frac{\sigma_i\sigma_e}{\sigma_i + \sigma_e} \]  

Equation 2.15

The EMPT model allows for the prediction of ionic and electronic conductivity for a composite of given porosity, provided the fundamental conductivities of the constituent phases are known. It is predicted that there is a certain minimum volume fraction required for a component to contribute significantly towards the conductivity; this is known as the percolation limit and depends on the porosity. An example is given in Figure
2.8, the vertical regions corresponding to the percolation limit for the electronic-conducting part of an electronic-ionic composite. The consequences of this are that the MIEC properties of a composite electrode can be greatly affected by both microstructure and composition.

![Effective composite electronic conductivity modelled for an example porous electronic-ionic conducting composite using EMPT. Adapted from Wu et al. [90].](image)

**Figure 2.8:** Effective electronic conductivity modelled for an example porous electronic-ionic conducting composite using EMPT. Adapted from Wu et al. [90].

### 2.6 Summary

The types of material commonly used in the three main components of SOFCs have been reviewed. For the electrolyte, YSZ has been the choice for many years; however it has recently been supplanted by materials that function better at lower temperatures. The anode is typically a cermet of nickel and the electrolyte material. The cathode has traditionally involved the pure-electronic conductor LSM for HT-SOFCs, but for IT-SOFCs MIEC materials are needed. LSCF is a current state-of-the-art MIEC cathode, which is further improved by forming composites with CGO. Problems with the cathode still abound, particularly performance degradation during operation. For LSCF this is linked to dopant segregation forming a passivating surface layer, and chromium poisoning being exacerbated by nucleating agents present in the material. This has led to alternative phases and structure types being studied. Some phases belonging to the Ruddlesden-Popper family have shown promising fundamental properties, in particular the ionic conductivity of L2N1. The electrode performance of this phase to date has been poor, with suggestions that this is due to its limited electronic conductivity. A variety of doping
strategies have been used in an attempt to improve the performance of L2N1 but these have not led to significant improvements.

Alternative means for improving electrode performance are the formation of composite or functionally graded electrodes. Many reports have applied these methods to standard perovskite materials; however there is a significant gap in the literature over the utilisation of these on alternative structure types. There is one report on LSCF+L2N1 composites, however this was geared around the properties of the perovskite and did not show any improvements in polarisation resistance. Graded L2N1 electrodes have been considered and the promise of this approach demonstrated.

From the reviewed literature it is evident that there is still great scope for further research into R-P phases as SOFC cathodes. This is particularly apparent in the areas of composite and graded cathodes, as well as the use of higher-order phases. This thesis will present work in these areas.
References

Chapter 3 - Characterisation of SOFCs

An SOFC *in operando* is a complex entity with many different processes occurring throughout the range of materials involved. The majority of analytical techniques available to the scientist are *ex situ*; these are often carried out under conditions atypical for SOFC materials due to the specific requirements for each technique. This means that the relevance of data obtained in this manner can be questionable. Typically there is an inherent assumption that no significant changes occur for the materials between experimental and operational conditions. This will not be valid for all cases. The work of Cheng *et al.* gives an excellent demonstration of the potential for errors related to this assumption[1]. They studied sulphur poisoning of Ni-YSZ cermet anodes using both *in situ* Raman spectroscopy and *ex situ* X-ray diffraction, and found notable differences in the data obtained. Samples for *ex situ* study were produced by exposure to an H$_2$S-poisoned hydrogen fuel at high temperature followed by slow cooling to room temperature. Results on these indicated the presence of various nickel sulphide species. From this one could conclude that these are responsible for the anode poisoning. However, *in situ* testing found no such species at high temperature; they were only observed during the slow cooling process therefore requiring different interpretation. Cheng comments; "*ex situ* experiments should be carried out with great caution to prevent any artifacts induced by sample preparation". Researchers are increasingly looking to *in situ* techniques to further understand SOFCs. Relevant advances made in this area are now reviewed; for a further discussion of some of these techniques the interested reader is referred to the recent article by Brett *et al.*[2].

3.1 Thermal imaging

SOFCs operate at high temperature and the distribution of heat could affect performance. Brett *et al.*[3] have used thermal imaging cameras to follow temperature changes as a function of electrical load changes on a single cell. This was achieved to an accuracy of 0.1 °C with a spatial resolution of 0.5 mm. Test Ni+CGO|CGO|CGO+LSCF cells were studied with the thermal camera directed at the cathode side. Changes were observed in the temperature distribution between open-circuit and a load of 0.2 V, and the effect this could have on the polarisation resistance was considered. Brett and Clague[4] also used this technique to examine the effect of thermal stress. This was simulated by blowing cold nitrogen onto a hot working cell. Thermal gradients of up to 9 °Cm$^{-1}$ were applied to an electrolyte-supported cell without causing cracking.
3.2 Raman spectroscopy

Raman spectroscopy is finding a growing number of uses for in situ studies on SOFCs. It relies on the absorption of electromagnetic radiation around the visible region, from infrared to ultraviolet. Adequate intensities are achieved by the use of laser light, and the wavelength can be varied to probe different species. Pomfret et al. [5] found that the energy of the Raman band from YSZ shifts with respect to temperature and used this to determine the absolute temperature of exposed YSZ surfaces to within 25 °C. Maher et al. [6] analysed CGO and YSZ electrolytes by in-situ Raman spectroscopy and were able to follow absolute temperature changes to a similar degree of accuracy but also relative temperature changes to within 1 K. The absolute temperature determination is much less accurate than the thermal imaging method used by Brett [3] but has better spatial resolution, of the order of a micron.

The technique can also be used to supply chemical information. Maher et al. observed the reduction of CGO when heated under hydrogen at 600 °C [6]. Pomfret et al. followed NiO/Ni redox chemistry in a Ni-YSZ cermet under various fuel mixes, as well as following carbon deposition on such an anode [5]. Pomfret has carried out further such studies on the anode, analysing the carbon deposits formed during oxidation of butane and carbon monoxide [7], and extending this to alternative hydrocarbon fuels [8]. Sulphur poisoning is another process than can lead to losses of performance at the anode. As already discussed, this has been probed by Cheng et al. [1].

Raman spectroscopy has also been applied to SOFC cathodes. Abernathy et al. [9] studied reactions above 500 °C between silver used to enhance LSM cathodes and chromium vapour, the aim being to simulate poisoning from a Cr-containing interconnect. They found that Ag/Cr species deposit on the surface of the cathode which would lower its catalytic activity. They conclude that one should avoid using chromium-containing interconnects in conjunction with a silver-containing cathode.

This spectroscopy does have some challenges with respect to its application to SOFCs. Typical commercial Raman microscopes were not designed with such high temperatures in mind. For high quality data the Raman objective lens should be close to the tested sample, of the order of 10 mm, but not at excessive temperature. Considering this, Brightman and co-workers [10] have recently developed a sample stage for heating test cells to ≈ 600 °C whilst maintaining a cool exterior. Their design also has the advantage of...
the ability to collect AC impedance data simultaneously with Raman data. They demonstrated its capability by following the common NiO/Ni redox process at the anode.

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

XPS allows for chemical information to be gained on the near-surface region of a material via the detection of emitted photoelectrons. These electrons scatter strongly from gas molecules so historically this technique has required high vacuum conditions. Many of the important processes occurring in an SOFC involve the gas/electrode interface which clearly will behave differently under high vacuum. However, recent advances have allowed XPS to be carried out at ‘near-ambient’ pressures of the order of $10^2$ Pa, both at synchrotron sources[11] and using smaller in-house equipment[12]. The pressure gap between this and operating pressures (standard atmospheric pressure ≈10$^5$ Pa) must still be considered. Huber et al. studied the effect of polarisation on strontium segregation at 600 °C in LSM[13] and LSCrM[14]. In situ XPS was used to probe the relative cation composition in the near-surface region under different applied voltages. They found that cathodic bias leads to de-segregation of strontium from the surface hence activation of the cathode. In these studies they also carried out SIMS measurements as soon as possible after polarisation, terming this “quasi in situ” SIMS. Whether the use of the term in situ here is valid is open to debate.

### 3.4 Scanning photoelectron microscopy (SPEM)

SPEM is similar to XPS in that it relies on emitted photoelectrons; therefore it has the same pressure considerations. For SPEM these electrons are used for lateral elemental mapping of the near-surface of a material. It has been used to study LSM on YSZ under near-ambient pressure and found that under cathodic polarisation at 650 °C manganese species spread onto the YSZ surface, extending the active area for the ORR[15]. SPEM also finds uses following in situ morphological changes at electrodes[16].

### 3.5 X-ray diffraction (XRD)

Sorby et al. carried out synchrotron in situ XRD on LSM cathodes on YSZ under different polarisations at 850 °C[17]. They found changes in lattice parameters and peak widths for LSM but not for YSZ. In context with Huber’s XPS findings this could indicate cation diffusion is facilitated by polarisation[13, 14]. Given the widespread use of XRD throughout the ceramic fraternity it is surprising that not more work has been published using in situ diffraction techniques applied to SOFCs.
3.6 X-ray absorption near-edge structure (XANES)

XANES can provide chemical information on a material. This occurs via the interaction of X-rays with electrons at different energy levels in a material, the same fundamental processes occurring in XPS but with incident X-rays at much higher energy. The information in XANES is carried in transmitted or fluorescent X-rays; these are not strongly affected by gas molecules. This means that XANES can be carried out at genuine ambient pressure, a clear advantage over XPS. XANES is a technique of great importance to this thesis so a detailed description of the processes occurring is given in the next chapter. Briefly, XANES data can be used to probe the oxidation state of species present in a material. For SOFC applications this is useful as materials often are made of a variety of different elements with different variable oxidation states. These states play a key role in the fundamental properties of SOFC materials.

The majority of XANES experiments applied to SOFC materials to date have been \textit{ex situ}. Braun \textit{et al.} [18] studied commercial Ni cermet anodes at room temperature after operating under different sulphur exposures, and found a variety of sulphur species. However one must be careful when interpreting these data given the differences seen between \textit{in situ} and \textit{ex situ} results on sulphur-poisoned anodes found by Cheng [1]. Braun did not consider such possible discrepancies. Room temperature \textit{ex situ} studies have been carried out on the valence of the transition metal at different $\delta$ in the MIEC anode materials $\text{Sr}_2\text{Mg}(\text{Mo,W})\text{O}_{6.5}$ and $\text{Sr}_2\text{Mg}(\text{Mo,Nb})\text{O}_{6.5}$ [19]; similar work has been done on barium cerate proton-conducting perovskites [20]. Kakinuma \textit{et al.} [21] have studied the cathode material $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ by manganese and iron K-edge absorption. They first obtained a calibration line from data obtained on $\text{La}_{0.6}\text{Sr}_{0.4}\text{MO}_3$ and $\text{LaMO}_3$ ; the valance of $M$ being 3.4 and 3 respectively. They found the valence of both Mn and Fe in $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ to be above 3.0. This indicates a lack of oxygen vacancies meaning that the material will not be mixed-conducting. Soldati \textit{et al.} [22] studied cobalt and iron absorption edges for LSCF samples \textit{ex situ} after various reducing and oxidising heat treatments; they found the redox processes to be reversible.

A limited \textit{ex situ} XANES study has been published on L2N1 samples at different oxygen stoichiometry [23]. The nickel K-edge was found to shift to lower energy as the oxygen content is reduced, indicating a reduction in the nickel oxidation state. However in this work no efforts were made to calibrate the K-edge position to the oxidation state, so only a qualitative conclusions can be drawn.
Moving on from room temperature *ex situ* experiments, there have recently been studies carried out at high temperatures. Itoh *et al.* [24] collected *in situ* data on the cobalt and iron K-edges in LSCF powders during reduction at IT-SOFC temperatures. They found that cobalt reduces more readily than iron and attempted to quantify this using a calibration line generated from the edge positions of compounds with specified oxidation state. However, the calibration used for iron was:

\[
\text{edge position in eV} = 7113.45 + 3.65 \times \text{valence} \quad \text{Equation 3.1}
\]

This would imply an edge position of 7113.45 for iron metal, whereas the standard literature value is 7112.0 eV[25]. This discrepancy leads to questions over the assignment of formal valence in Itoh's study.

Improving on this Hagen *et al.* have developed equipment for studying symmetrical cells at high temperature[26], with their setup also allowing for simultaneous AC impedance studies and polarisation. Studying LSCF on YSZ electrolyte they observed a greater reduction in the K-edge position for cobalt than for iron between room temperature and 600 °C, implying a greater reduction in the cobalt oxidation state, similar to Itoh's results. No changes in the XANES data were observed during polarisation at these temperatures.

### 3.7 Summary

There has been a recent concerted effort amongst the community to develop improved *in situ* characterisation methods. XANES is identified as a powerful technique; it is unique in that it can give chemical information on a material in a non-destructive manner at ambient pressure. Therefore it is surprising that so little *in situ* work has been carried out on SOFC materials by this method. There is a clear need for further work in this area.

In general, the main challenge faced during *in situ* characterisation is imitating the demanding conditions of an operating fuel cell. Primarily this is the high temperature required for adequate oxygen reduction and transport kinetics. This temperature plays a central role in defining materials selection criteria; hence the first step in *in situ* work tends to be enabling data collection at these temperatures. SOFC performance also depends on a subtle interplay of a variety of factors beyond temperature; these include atmosphere, microstructure, the interface between different components, and electrical polarisation. Accounting for these considerations whilst remaining at high temperature poses increasing challenges in terms of equipment design. The form of the sample itself must also be considered. It is often relatively straightforward to test a material in isolation, yet this is clearly a gross simplification over the form the material would be in an
operating device. For example an SOFC cathode is typically a thin porous layer deposited on a dense electrolyte. If the material is tested in isolation, e.g. as a powder or a sintered pellet, it is difficult to take into account the effect of porosity, the interface with the electrolyte, or the sintering conditions used during fabrication; assumptions need to be made over these. Therefore it is advantageous to test a cathode directly, not just to test the material from which it is fabricated. These problems have been overcome to a greater or lesser degree in the reviewed literature. In particular the work of Brightman [10] and Hagen [26] is highlighted. They used different techniques, Raman and XANES spectroscopy respectively, but both developed novel equipment to take test cells to appropriate temperature whilst collecting in situ data. During this thesis similar work has been undertaken. This approach is a step towards an ultimate goal of collecting data on an SOFC in operando.
References

Chapter 4 - Experimental methods

A variety of experimental methods and analytical techniques have been used during this research. The aim of this chapter is to give a detailed description of these, along with a discussion of the theoretical background where necessary.

4.1 Materials synthesis

Different processes can be utilised to synthesise fuel cell materials. Those relevant to this work are discussed.

4.1.1 Solid-state synthesis

The simplest method of synthesising ceramic materials is known as solid-state synthesis. Typically this involves three steps, the first being accurate weighing of calculated stoichiometric amounts of starting materials. For simplicity these precursors are usually binary oxides or carbonates of the desired metallic element. Care must be taken to ascertain the correct relative formula mass (RFM) of these. This can be affected by adsorbed species such as water or carbon dioxide, so where necessary precursors are heated to remove these prior to weighing. Weighing was carried out to an accuracy of 0.0001g using a Sartorius ED224S Balance. The second step of solid-state synthesis involves intimately mixing the starting materials and is usually carried with an agate pestle and mortar; volatile solvents such as acetone or ethanol can be used to speed homogenisation. The resulting powder can be pressed into a pellet where necessary. In the third step this precursor mixture is calcined at a set temperature typically derived from literature work on such compounds. This takes place below the melting point of the precursors but at a sufficiently high temperature for facile cation diffusion. Provided the mix is homogeneous the most thermodynamically stable oxide should result. In many cases this will be kinetically stable during radiative cooling to room temperature (RT), however when necessary materials can be quenched to preserve a metastable product. Powder X-ray diffraction, discussed later, should then be carried out to check for a pure product. This is often readily achieved to a yield approaching 100%. Steps two and three can be repeated if any impurities are detected. If this fails to lead to improvement possible sources of error include inaccurate weighing of precursors, impure precursors, or incorrect calcining temperatures.

Advantages of solid-state synthesis include its simplicity and variability. Many mixed-metal oxides can be easily synthesised in an atmosphere of laboratory air by this method. With the use of reactive atmospheres the technique can be extended to form compounds
of other anions such as nitriles [1]. As such this method is often the first port-of-call for the scientist looking to produce small batches of material for proof-of-concept studies.

4.1.2 Solution-gel synthesis

A modern technique for ceramic synthesis is the solution-gel method, commonly known as sol-gel, or the Pechini method. This is named for Maggio Pechini, who patented this as a method for forming thin-film capacitors. He utilised alpha hydroxy acids and a poly hydroxy alcohol to form a resin with metal-cation solutions, which is then combusted leaving the desired product[2]. The method used in this thesis differs little from his work. The first step is the formation of cation solutions of known concentration; relevant metal nitrates are dissolved in deionised water and the concentration found by ICP-AES (inductively-coupled plasma atomic emission spectroscopy, discussed later). Calculated stoichiometric amounts of these are mixed and an excess of citric acid (an alpha hydroxy acid) and poly ethylene glycol (PEG – a polymer of a poly hydroxy alcohol) is added. The solution is stirred on a hotplate at approx. 90 °C until a dry resin is formed. This is decomposed at 300 then 600 °C to remove any organic species and the resulting powder calcined at the desired temperature.

The full details of the wet chemistry occurring during the formation of the resin are complex and can depend on many variables. These include the nature of the organic chemicals used, their ratios, the counter ions present in the metal cation solutions and the temperature at which the solution is heated. The full details of these are beyond the scope of this thesis; the interested reader is referred to the text by S. Sakka [3]. The essential concepts of the method are the formation of a complex between the ‘solution’ of metal cations and organic acid anions. This is polymerised and gains in viscosity via the poly hydroxy alcohol to form the ‘gel’ phase. Warming evaporates excess solvent leaving behind a foam-like metal-organic resin. Thermal decomposition of this leaves behind a fine powder of the desired metal oxide. This is summarised in Figure 4.1.

![Figure 4.1: Schematic of sequential processes occurring during the Pechini sol-gel method. Adapted from [3].](image-url)
4.1.3 Spray Pyrolysis

In this technique a solution is ejected from a nozzle towards a heated surface. Droplets form from the nozzle and can react to form the desired product either during their passage towards the surface, on the surface itself, or inside the surface after diffusion into it. Typically this method is used to produce a thin film on a substrate [4]; however the surface can be designed as a rotating chamber allowing for the production of bulk materials. With respect to this work, spray pyrolysis was the method used industrially by the manufacturers of some of the commercial powders used.

4.2 Test cell fabrication

A method of studying SOFC electrodes is via the fabrication of a test cell. These can be single cells complete with anode, electrolyte, and cathode, or more simply, symmetrical cells consisting of the electrode material in question deposited on each side of an electrolyte. Typically the electrolyte makes up the bulk of the thickness of a symmetrical cell and provides its mechanical stability. As such these cells can be referred to as electrolyte-supported symmetrical cells. Advantages of symmetrical cells over single cells include ease of fabrication and simplified data analysis. This derives from only needing to be concerned with the processes occurring in one electrode material, rather than having to separate anode from cathode. All cells tested in this thesis were symmetrical cells.

4.2.1 Electrolyte fabrication

The materials of interest in this thesis are cathode materials. These were studied as electrolyte-supported symmetrical cells for which standard solid-oxide electrolytes were used; the rationale being that analysis will be simplified if the properties of the electrolyte are already understood. The electrolyte used was $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM8282, hereafter abbreviated as LSGM). To ensure uniformity this was obtained from a commercial source (Praxair Speciality Ceramics) and processed in the same manner each time. Symmetrical cells require dense pellets of the order of 1.5 mm thickness. To achieve this, commercial powders were uniaxially then isostatically pressed to 300 MPa, then sintered at 1450 °C × 8 hours. Densities were then tested via the Archimedes method (discussed later) and confirmed to be at >95 % of the theoretical value.

4.2.2 Electrode ink fabrication

Once uniform electrolyte pellets have been fabricated the next step is to deposit electrode materials on to them. This is done via the formation of an ‘ink’. This consists of powders of the electrode material in question dispersed in an ink ‘vehicle’, a viscous organic liquid
acting as solvent and binder. The nature of the organic part can be varied considerably, even including additions as esoteric as icing sugar[5] or fish oil[6]. Water-based inks have also been developed for SOFC cathodes [7]. In general the manufacture of inks is known to be somewhat of a ‘dark art’ and often receives little attention in SOFC electrode literature. An ink vehicle was chosen from a commercial source (Fuel Cell Materials Ink Vehicle 311006) to ensure uniformity. The bulk of this is made up from terpineol, an unsaturated organic alcohol that exists as a mix of structural isomers. Electrode inks were made using a regime developed in the Fuel Cells Group at Imperial College, known to give good results for these materials[8];

- Desired amounts of as-synthesised electrode powder ball-milled for 24h using zirconia balls in ethanol as a solvent
- Wash powder from zirconia balls using more ethanol, allow solvent to evaporate
- Mix powder with ink vehicle in a 2:1 ratio by mass
- Three-roll mill using an Exakt 80E
- Collect finished ink
- Store in refrigerator to reduce volatility of organic part

4.2.3 Ink deposition

To deposit the inks onto electrolytes two methods were used, brush coating and screen printing. Cells were then sintered to promote electrolyte/electrode adherence in a manner described in the relevant experimental chapters.

4.2.3.1 Brush coating

A simple means of depositing an ink onto an electrolyte pellet is to apply a thin layer by hand using a fine brush. These pellets are then dried in an oven at approx. 100 °C, causing the organic solvent to evaporate. This leaves behind a layer with limited mechanical stability. This stability is sufficient to allow the pellets to be inverted for deposition onto the other side, forming a symmetrical cell. Further layers can be applied to the oven-dried ones, allowing thicker electrodes to be fabricated.

4.2.3.2 Screen printing

A more involved method of ink deposition is screen printing. This requires a thin screen with a mesh aperture the desired dimensions of the electrode. An electrolyte pellet is positioned under this aperture and ink is forced across the mesh using a ‘squeegee’. Where it crosses the aperture the ink passes through the mesh onto the pellet, depositing a thin uniform layer. As with brush coating, these layers can be dried in an oven before inversion
to complete the symmetrical cell. Advantages of screen printing over brush coating include more uniform deposition, and the ability to produce a thinner layer.

4.3 Materials characterisation

A variety of techniques were used to study synthesised materials and fabrication symmetrical cells. These are described below.

4.3.1 X-ray diffraction

4.3.1.1 Theoretical background

X-ray diffraction (XRD) is an analytical technique used to give information on the crystallographic structure of a material. A crystal is made up of a regular periodic arrangement of atoms in space. An incident X-ray beam is scattered by the electrons on each atom, giving rise to many secondary waves. As a consequence of the structural periodicity, constructive interference takes place at certain scattering angles, $2\theta$, as described by W.L. Bragg[9];

$$2d_{hkl} \sin \theta = \lambda$$  \hspace{1cm} \text{Equation 4.1}

where $d_{hkl}$ is the distance between Miller planes passing through the crystal structure; this is defined by the Miller indices, $h$, $k$, and $l$, and the unit cell parameters. $\lambda$ is the wavelength of the incident radiation.

The intensity of the diffracted beams, $I_{hkl}$, is measured by the diffractometer as a function of $2\theta$. The unit cell parameter can be obtained from the position of the peaks in the pattern and the magnitude of $I_{hkl}$ gives information about the positions of the atoms within the unit cell. This is because $I_{hkl} \propto |F_{hkl}|^2$. $F_{hkl}$ is the structure factor, calculated as follows;

$$F_{hkl} = \sum_{j=1}^{\text{atoms}} f_j \exp\left[2\pi i (hx_j + ky_j + lz_j)\right]$$  \hspace{1cm} \text{Equation 4.2}

where $f_j$ is the atomic scattering factor for the $j^{\text{th}}$ atom, and $x_j$, $y_j$, and $z_j$ are its fractional coordinates.

X-rays interact with electrons and $f_j$ is proportional to the number of electrons on the atom, meaning that heavier elements give rise to more intense peaks in the pattern. It can hence be hard to observe light elements in the presence of heavy. In the context of the elements used in this research, this means the contribution towards a Bragg peak by
oxygen is hard to assign. \( I_{hl} \) is also proportional to other parameters which depend on the experimental setup; these are accounted for in the data analysis.

**4.3.1.2 Experimental considerations**

X-rays are generated by accelerating a beam of electrons towards a copper target. This beam has enough energy to ionise electrons from the K (1s) shell, creating a vacancy. Electrons from the 2p or 3p levels drop to fill this vacancy and emit X-rays of the energy equal to the drop, known as \( K_\alpha \) and \( K_\beta \) respectively. \( K_\alpha \) is the most intense emitted and is split into two, \( K_{\alpha 1} \) and \( K_{\alpha 2} \). This is due to spin-orbit coupling splitting 2p into two different energy levels, known as \( ^2P_{1/2} \) and \( ^2P_{3/2} \). As a consequence of the different occupancies of these levels \( K_{\alpha 1} \) is twice as intense as \( K_{\alpha 2} \). To simplify data analysis monochromatic X-rays are desirable. \( K_\beta \) radiation is easily filtered using the metal one to the left in the periodic table (the ‘Z-1 rule’), in this case nickel. Filtering \( K_{\alpha 2} \) from \( K_{\alpha 1} \) is more difficult due to their similar wavelengths \( (K_{\alpha 1} = 1.54056; \ K_{\alpha 2} = 1.54439 \ \text{Å}) \). This can be achieved using an arrangement of curved single crystals known as a Johansson Monochromator[10] but this comes with the cost of lowered X-ray intensity. Typical laboratory diffractometers use both \( K_{\alpha 1} \) and \( K_{\alpha 2} \) and the researcher is relied on to account for this in data analysis. Theoretically, at all angles each allowed reflection will result in a diffraction peak from \( K_{\alpha 1} \) and another from \( K_{\alpha 2} \). In practice, at low angles these are merged together and at high angles \( K_{\alpha 2} \) peaks are easily identified as being just to the right of a \( K_{\alpha 1} \) peak (higher \( 2\theta \)) and half as intense.

XRD is a non-destructive technique that can be applied to a wide variety of samples. For this thesis powders were mounted on a zero-diffraction plate. This is fabricated from single-crystal silicon cut parallel to a specific Miller plane such that no diffraction from it will occur over the tested angular range. Pellets and symmetrical cells were mounted ‘as-is’ on a small amount of putty, with care being taken to ensure they were flat. Diffraction patterns were collected on a PANalytical X’Pert Pro MPD using Ni filtered Cu \( K_\alpha \) radiation with tube voltage/current at 40 kV/40 mA. Initial analysis was carried out using X’pert Highscore software. This includes within it a database, managed by the International Centre for Diffraction Data (ICDD), containing a large number of XRD patterns. The positions and relative intensities of observed peaks are compared with this database and good matches are highlighted. This provides a facile means of identifying a phase, provided it has previously been reported and is entered into the database. For more detailed analysis of XRD patterns Rietveld refinement was carried out.
4.3.1.2.1 Rietveld refinement

Rietveld refinement was developed in the 1960s [11] and is used to analyse powder diffraction data. First a structural model for the phase must be postulated and the diffraction pattern for this calculated. This is then compared to the observed data, and the model refined to improve the match between the two. Creating the initial model requires some prior knowledge; the composition of the sample should be known and a reasonable estimate of the expected structure must be made. This is achieved by peak-matching to the ICDD database as discussed above. The Rietveld refinements presented in this thesis were carried out using the General Structure Analysis System (GSAS)[12] facilitated by EXPGUI software[13]. This uses a whole-pattern method, i.e. the entire observed angular region is used in the refinement, not just the regions of Bragg peaks. Hence a function must be used to represent the background in the theoretical model; in this research a Chebyshev polynomial of the first kind was used. Various other functions and parameters are varied to account for the information in \( I_{\text{obs}} \) which depends on the experimental geometry.

Fitting calculated data to observed is achieved via a minimisation function \( M \) reached by a method of least squares;

\[
M = f_h \sum_n M_h
\]

Equation 4.3

where \( M_h \) represents a particular minimisation contribution and \( f_h \) its weight.

For powder diffraction data the intensity, \( I_{\text{obs}} \), is recorded in the pattern at increments of \( i \) over the angular range. All values of \( I_{\text{obs}} \) contribute to the minimisation thus;

\[
M_{\text{powder}} = \sum_i w_i (I_{\text{obs}} - I_{\text{calc}})^2
\]

Equation 4.4

where \( w_i \) is a weighting factor ensuring that no single point dominates the refinement; and \( I_{\text{calc}} \) is the calculated intensity at the \( i \)th step.

The quality of the fit of calculated data to observed data is quantified by various parameters. \( \chi^2 \) is the 'goodness of fit';

\[
\chi^2 = \frac{M}{(N_{\text{obs}} - N_{\text{var}})}
\]

Equation 4.5

where \( N_{\text{obs}} \) the total number of points in the observed data; and \( N_{\text{var}} \) the number of variables used in the least squares fit.
There is also the residual $R_p$ and the weighted residual $R_{wp}$. GSAS outputs these both for all points, \textit{i.e.} including the background function, and for only those points that contribute towards Bragg peaks. The former can give values artificially low, so in this thesis residuals given do not include the background contribution:

$$R_p = \frac{\sum_i \left| \frac{I_{obs} - I_{calc}}{I_{obs}} \times \frac{I_{obs} - I_{back}}{I_{obs}} \right|}{\sum_i |I_{obs} - I_{back}|}$$

Equation 4.6

$$R_{wp} = \sqrt{\frac{\sum_i w_i \left( \frac{|I_{obs} - I_{calc}| \times |I_{obs} - I_{back}|}{I_{obs}} \right)^2}{\sum_i w_i (I_{obs} - I_{back})^2}}$$

Equation 4.7

where $I_{back}$ is the background intensity at the $i^{th}$ step.

These parameters allow for the quality of different refinements to be compared. For an individual refinement the plotted difference line, $I_{obs} - I_{calc}$, gives a visualisation of the fitting. This can be highly informative; it can help isolate peaks from impurity phases present, and identify regions of the postulated XRD pattern that do not fit well the observed data.

\textit{N.B.} schematics of crystal structures used in this thesis were produced using VESTA [14] unless otherwise stated.

4.3.2 Scanning Electron Microscopy

4.3.2.1 Theoretical background

Scanning electron microscopy (SEM) is used to obtain high-magnification images. Electrons are thermionically emitted from a filament and accelerated to a typical energy of 20 keV. This beam is focussed on the sample in question and interacts with it in a manner that depends on the atomic number of elements present. This results in the scattering of high-energy electrons, an elastic process, and the generation of lower-energy secondary electrons, an inelastic process. Both of these can be detected; this is known as back-scattered electron imaging (BEI) and secondary electron imaging (SEI) respectively.

4.3.2.2 Experimental considerations

To prevent the build-up of a static charge samples studied by SEM must have an electrically conductive surface and be grounded. For insulating samples this is achieved by
mounting on a metallic stub using conductive carbon tape and sputter-coating a thin layer of gold onto the surface of the sample. The interface between different ceramic layers of a device is of importance to the SOFC researcher; for this work this corresponds to the electrode/electrolyte region of a symmetrical cell. To access this test cells were sectioned using a Buehler IsoMet low-speed saw, or fractured by sharp impact using hammer and chisel. As such SEM is an inherently destructive technique; samples prepared for imaging cannot be analysed subsequently by other methods. An electron beam is required so the majority of microscopes operate under high-vacuum; a significant pressure gap therefore exists between the conditions required for SEM and those of an SOFC in operando. This is a common feature with ion and electron beam techniques and must be considered during data analysis. SEM data in this thesis were collected using either a JEOL 5610 LV or a JEOL 6010 LA, both in SEI mode.

### 4.3.3 Total conductivity testing

#### 4.3.3.1 Theoretical background

The van der Pauw technique can be used to measure the lateral conductivity of a flat sample of any shape [15, 16]. Taking a square sample, one can make electrical contacts at each corner. Defining these as 1, 2, 3 and 4, one can obtain two characteristic resistances $R_A$ and $R_B$, as shown in Figure 4.2.

Van der Pauw has shown that:

$$\exp\left(-\pi d \frac{R_A}{\rho}\right) + \exp\left(-\pi d \frac{R_B}{\rho}\right) = 1$$  

Equation 4.8

where the sample has a thickness $d$, found by post-test SEM analysis; and resistivity $\rho$, found by solving this equation numerically using a least-squares method.

#### 4.3.3.2 Experimental considerations

The total conductivity of SOFC cathodes is an important property. Typically bulk material conductivities are explored via the fabrication and testing of a dense bar of cathode material, however it is clear that this arrangement bears little resemblance to a fuel cell. Cathodes are designed to be thin and porous so attempts should be made to test them as such. To enable this, 5×5mm square layers of the electrode inks were screen-printed onto dense LSGM pellets and sintered using the same regime as the symmetrical cells. Screen printing was chosen as the deposition method to ensure consistency between the different materials. These squares were mounted in a spring-loaded holder as described by
Esquirol [17]. This provided the electrical connections shown in Figure 4.2 and was positioned inside a tube furnace.

Data were obtained over a similar temperature range to that used for ACIS. The contribution towards the conductivity from the dense LSGM pellet was assumed to be negligible, as were any differences in the tortuosity and porosity of the electrode layers. Numerical solutions for the resistivity were found using MATLAB [18].

Figure 4.2: Electrical contacts that define two characteristic resistances for total conductivity measurements on square electrodes. Dark grey = screen-printed electrode; light grey = LSGM substrate.

4.3.4 AC Impedance Spectroscopy

4.3.4.1 Theoretical background

The majority of people are familiar with the inherent ability of materials to resist the flow of current. This is the concept of resistance which is quantified using Ohm’s law, \( R = \frac{V}{I} \), where \( R \) is the resistance of a component, \( V \) the voltage across it and \( I \) the current. This simple relationship is typically valid for materials under a direct current, but this is not necessarily the case for materials under an alternating current. This is accounted for by the concept of impedance; this being the resistance to the flow of an alternating current. The impedance \( (Z) \) of a sample is probed by AC Impedance Spectroscopy (ACIS). Analogous to Ohm’s law, impedance is defined as;

\[
Z = \frac{V(t)}{I(t)}
\]

Equation 4.9

where \( V(t) \) and \( I(t) \) are the voltage and current expressed as a function of time.

The application of a voltage of amplitude, \( E_0 \), and frequency, \( \omega \), results in a current of different amplitude, \( I_0 \), that is shifted in phase, \( \varphi \). Hence the impedance resulting from a sinusoidal voltage can be represented as;
This can be re-written to split the impedance into real ($Z'$) and complex ($Z''$) parts:

$$Z = Z_0 \left( \cos(\varphi) + j \sin(\varphi) \right)$$  \hspace{1cm} \text{Equation 4.11}$$

$$Z' = |Z| \cos(\varphi)$$  \hspace{1cm} \text{Equation 4.12}$$

$$Z'' = |Z| \sin(\varphi)$$  \hspace{1cm} \text{Equation 4.13}$$

where $j$ is the complex quantity $\sqrt{-1}$, and $|Z|$ is the magnitude of the impedance.

This leads to a typical method of presenting impedance data, the Nyquist plot, as shown in Figure 4.3. Here the real and complex parts of the impedance are plotted against each other on square 1:1 axes. A limitation of this is that the frequency data contained within the impedance are not shown explicitly, although the Nyquist plot can be annotated to include them. An alternative representation is the Bode plot where the natural logarithm of the frequency is plotted against either the phase shift ($\varphi$) or the modulus of the impedance ($|Z|$). Examples of these are shown in Figure 4.4.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{Nyquist_plot.png}
  \caption{Example of a Nyquist plot of impedance data. Inset is the equivalent circuit used to generate it.}
  \label{fig:nyquist}
\end{figure}

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>$R = 30 , \Omega$</td>
</tr>
<tr>
<td>$R_2$</td>
<td>$R = 15 , \Omega$</td>
</tr>
<tr>
<td>$R_3$</td>
<td>$R = 15 , \Omega$</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$C = 1 \times 10^{-5} , F$</td>
</tr>
<tr>
<td>$\text{CPE}_1$</td>
<td>$Q = 5 \times 10^{-2} , F$; $n = 0.75$</td>
</tr>
</tbody>
</table>

\textbf{Table 4.1:} Values for equivalent circuit used to generate Figure 4.3 and Figure 4.4
Figure 4.4: Bode plots generated for the same equivalent circuit as Figure 4.3 and Table 4.1.

Data obtained from ACIS are information-rich; this is due to the different processes occurring and length scales present. These mean that the impedance of SOFC materials is dependent on the frequency of the alternating current. This can be varied over many orders of magnitude, typically of the order of $10^6 - 10^{-2}$ Hz, allowing for the contributions of different aspects of a material towards its properties to be explored. Data obtained on SOFC materials at relevant temperatures typically appear as a series of arcs when represented on a Nyquist plot. Data at low $Z'$ are from the high-frequency range of the applied voltage, moving to lower frequency as $Z'$ increases (cf. Figure 4.3). The difference between the high- and low-frequency intercepts of an arc with $Z'' = 0$ represent the contribution of this arc to the overall resistance of the tested material. To gain further insight into the processes occurring ACIS data can be modelled using a combination of electrical components. This is known as the equivalent circuit model (ECM). Arcs on a Nyquist plot can be modelled using a combination of a resistor (R) in parallel with a capacitor (C). Such an RC element results in a semi-circular arc whose intercepts span the
resistance $R$. However, ACIS data on real systems typically is of the form of a depressed semicircle. These are modelled by replacing the capacitor with a constant-phase element (CPE). A CPE can be thought of as an imperfect capacitor and is defined by two parameters: $Q$, the pseudo-capacitance; and $n$, a parameter related to the depressed nature of the arc. If $n = 1$ then the CPE is behaving as a pure capacitor. If $n \neq 1$ then an equivalent capacitance, $C$, can be calculated from;

$$C = \frac{(RQ)^{\frac{1}{n}}}{R}$$

Equation 4.14

$R$ being the resistance of the resistor in parallel with the CPE.

This equation is commonly used in the literature, however care must be taken over interpretation of values derived from it. Shoar Abouzari et al. comment that they may be invalid unless $n$ or $RQ$ are close to unity[19].

By using a series of $R$ and $R$/CPE components the researcher can build up a model to represent their ACIS data (cf. Table 4.1), bearing in mind that an arc may consist of more than one $R$/CPE component. Once $C$ values have been found these components can be assigned to particular phenomena occurring in the cell. Irvine et al. suggest typical capacitances for various common processes[20]. Care must be taken over this approach as ECM modelling is phenomenological. This means that more than one ECM could accurately represent the data. Furthermore, the physical meaning of some components commonly used, include the CPE, is still not entirely clear[21].

For SOFC cathodes tested as symmetrical cells the polarisation resistance ($R_p$) is a key property. This can be found from summing the $R$ values for $R$/CPE components assigned to the electrode. For a typical cell at operating temperature often just one arc (or a superposition of arcs) is present, resulting from the electrode. This leads to a very simple method of finding $R_p$: the difference between the arc intercepts at $Z'' = 0$. This demonstrates the convenience of the Nyquist plot as a means of presenting ACIS data. Combined with the dimensions of the cell $R_p$ can be used to calculate the area-specific resistance (ASR) for the cathode material;

$$\text{ASR} = \frac{R_p \times A}{2}$$

Equation 4.15

where $A$ is the area of each electrode, and dividing by two accounts for the cell symmetry.
4.3.4.2 Experimental considerations

For the SOFC researcher ACIS is a technique of great value. SOFCs are electrochemical devices so it is only natural that one wishes to gain information on the electrical properties of relevant materials. One of the main advantages of ACIS is flexibility; data can be collected on a single material, a symmetrical cell, or a complete anode/electrolyte/cathode cell. All that is necessary is to provide electrical connections from the sample in question to a frequency response analyser (FRA). Custom equipment can be designed to provide these connections under a variety of conditions including different fuels, atmospheres, temperatures, and polarisations. Hence ACIS can be considered an in situ technique as the experimental conditions can be chosen to mimic that of an operating SOFC.

The bulk of the ACIS data for this thesis were obtained using a Solartron 1260a Impedance/Gain-Phase Analyser. In some cases alternative equipment was used, a Voltalab 80 PGZ 402 Universal Potentiostat or an Ivium Compactstat. Depending on the temperature and material a range of frequencies from $10^6$ – $10^2$ Hz were used, with an AC amplitude of 25 mV. Equivalent-circuit modelling was carried out using ZView version 3.3c (Scribner Associates).

4.3.4.2.1 Two-electrode testing

A standard method of collecting data on the electrode properties of a potential SOFC cathode material is to carry out two-electrode testing on a symmetrical cell. To achieve this connections are made from each side of the cell to the FRA; these act as working and counter electrode and are identical. This is enabled by the use of custom-built alumina sample holders, as shown in Figure 4.5. These are positioned inside a tube furnace to reach the desired testing temperature.

![Figure 4.5: Schematic of custom-built sample holders for two-electrode ACIS testing. Outer tube slides over inner tube to locate symmetrical cell.](image-url)
4.3.5 X-ray absorption near-edge structure

Previously the interaction of X-rays of relatively long wavelength with the structural periodicity of a crystal structure has been detailed, this being X-ray diffraction. X-rays however cover a broad region of the electromagnetic spectrum, and at shorter wavelengths their interaction with matter can lead to further insights beyond diffraction patterns. The way X-rays of shorter wavelength are absorbed by matter can be explored in what is known as X-ray absorption spectroscopy (XAS). An aspect of XAS of great value to this thesis is X-ray absorption near-edge structure (XANES), which will now be discussed.

4.3.5.1 Theoretical background

The Beer-Lambert law is concerned with the absorption of light as it passes through a material. It can be formulated as:

\[ I_t = I_0 \exp(-\mu t) \]  

Equation 4.16

where \( I_t \) is the intensity of light transmitted through a material of thickness \( t \); \( I_0 \) is the intensity of the incident light; and \( \mu \) the absorption coefficient of the material.

This formula is equally applicable to X-rays as it is visible light. Over most of the X-ray spectrum, simplifying for an elemental substance, the absorption coefficient can be approximated as:

\[ \mu \approx \frac{\rho Z^4}{AE^3} \]  

Equation 4.17

where \( \rho \) is the sample density; \( Z \) and \( A \) the atomic and mass numbers; and \( E \) the X-ray energy.

At certain energies \( \mu \) does not follow this relationship and the absorption is much stronger. This is known as an ‘absorption edge’. These occur when the X-ray energy is equal to the binding energy of a core electron in the sample. At these energies X-ray photons are much more likely to be absorbed, resulting in the excitation of said electron to a higher energy level. XANES is concerned with how the absorption changes with energy in the region near these absorption edges. Once a photon has been absorbed the atom is left in an excited state. These have limited lifetimes and can decay by a variety of processes. A common means for this is an electron from an outer shell dropping to fill the hole in the core shell. This releases a photon in a process known as X-ray fluorescence. Hence XANES data can be obtained from measuring the intensity of the radiation transmitted through a sample, known as transmission geometry, or the X-rays emitted
from a sample, known as fluorescence geometry. From the Beer-Lambert law transmission data are represented as;

\[
\mu(E) \propto \ln \left( \frac{I_0}{I_t} \right) \quad \text{Equation 4.18}
\]

and fluorescence data as;

\[
\mu(E) \propto \frac{I_f}{I_0} \quad \text{Equation 4.19}
\]

where \( I_t \) is the intensity of the fluorescent radiation.

The binding energy experienced by an electron is due to the electrostatic attraction to the nucleus it orbits, hence this depends on the number of protons in the nucleus. This means that elements have characteristic binding energies for their core electrons, so by judicious choice of X-ray wavelength the researcher can chose which element in a material they wish to study. Of course there are multiple electrons orbiting a nucleus, these shield each other from the electrostatic attraction. The level of this shielding will depend on the number of electrons in the atom, \( i.e. \) its oxidation state. A higher oxidation state means fewer electrons, therefore a greater attraction between the remaining electrons and the nucleus. This means the binding energy will be greater hence absorption edges will be at higher energy. The magnitude of this effect is much smaller than that of changing the number of protons in the nucleus, \( i.e. \) going from one element to another. Hence the variation due to oxidation state is seen as a subtle adjustment to the characteristic absorption edges of an element. This leads to one of XANES main uses: a non-destructive means of probing the redox chemistry of materials.

Some consideration must be given to the state of the excited electron. Orbitals that this can be promoted to are governed by various selection rules. An X-ray photon carries with it one unit of angular momentum; the quantum number \( \ell = 1 \). For a core electron in an \( s \) shell \( \ell = 0 \). Angular momentum must be conserved over the whole photon absorption/electron excitation process. Hence \( s \) electrons can only be promoted to orbitals where \( \ell = 1 \), these being \( p \) orbitals. In practise however there is mixing between orbitals meaning that \( d \) orbitals can gain \( p \) character, allowing some \( s \) electrons to be promoted to these levels. The degree of this mixing can depend on the geometry around the atom in question. For the materials used in this thesis the redox chemistry of transition metals present were of chief concern. Such elements typically have empty \( d \) orbitals that are accessible due to the aforementioned mixing giving them some \( p \) character. Excitation of
1s electrons into these results in a small feature before the main absorption edge; this is known as a 'pre-edge'. The main absorption edge is from fully-allowed transitions to empty states of much stronger \( p \) character. At higher energies these are a continuum of loosely-bound states. Electrons in these can interact with neighbouring atoms before returning. These 'backscattering' events affect the final state of excited electrons and are manifested as oscillations in the absorption at energies above the main absorption edge. These are dealt with as part of extended x-ray absorption fine-structure (EXAFS) spectroscopy. XANES is typically considered to be data within \( \approx 30 \) eV of the absorption edge; energies above this are the EXAFS region. These features are demonstrated in Figure 4.6. For further information the interested reader is referred to the excellent short report on the fundamentals of X-ray absorption spectroscopy by Newville[22].

![Typical K-shell XAS data demonstrating XANES and EXAFS regions, and a pre-edge feature.](image)

**Figure 4.6:** Typical K-shell XAS data demonstrating XANES and EXAFS regions, and a pre-edge feature.

### 4.3.5.2 Experimental considerations

XANES requires X-rays of high energy to excite core electrons; high resolution and tunability to allow specific elements to be probed; and high intensity for fast data acquisition. To meet these criteria XANES data are collected using synchrotron light in the vast majority of cases. Because of the high energy and intensity of these X-rays they are not absorbed strongly by air, or other gases. This means that XANES data are easily obtained at ambient pressure and can be analysed without any pressure gap considerations. This is a clear advantage over alternative techniques for probing the redox chemistry of elements such as X-ray photoelectron spectroscopy (XPS), which typically
requires high vacuum. Even modern ‘pseudo-ambient’ XPS systems only operate at approx. 50 mbar [23]. The relaxed requirement over pressure gives great flexibility to XANES experiments; with the development of suitable equipment XANES can be considered a true in situ technique.

As discussed previously XANES can be explored in both transmission and fluorescence geometry. For the former clearly the transmitted light must be of adequate intensity to be easily detected, and also there must be a distinguishable difference between incident and transmitted intensity. Samples containing a high concentration of the probed element may absorb too strongly in their pure form. In these cases it is standard procedure to lower the concentration by mixing intimately with a lightly-absorbing inert compound, typically hexagonal boron nitride (h-BN). The ratio of sample:h-BN can be varied until a suitable transmitted intensity is observed. For fluorescence geometry the intensity of the detected radiation can be varied simply by moving the detector closer or further from the irradiated sample. Fluorescence geometry is more flexible than transmission; elements in low concentration can be probed more readily and there is no requirement for the sample to allow any transmitted light or otherwise. This makes it amenable to testing thin films on dense substrates. A schematic of transmission and fluorescence geometries is given in Figure 4.7.

![Figure 4.7: Schematic of transmission (I\textsubscript{t}) and fluorescence (I\textsubscript{f}) geometries used for XANES spectroscopy.](image)

A typical addition to transmission geometry is shown – an internal reference spectrum is collected simultaneously to the sample of interest. This is normally chosen to be a metal foil of the same element as the one being probed. The edge position found for the reference can be calibrated to the literature value, and the same shift applied to the sample scan. This helps to correct any possible errors made calibrating the beamline.
XANES data in this thesis were obtained on beamline X10C at the National Synchrotron Light Source, Brookhaven National Laboratory. Where custom equipment was used to mount samples this will be detailed in the relevant chapters. Data were analysed using the Athena GUI[24] for IFEFFIT software[25]. $\mu(E)$ was normalised such that the edge step occurs from 0 – 1 arbitrary units. This is achieved by fitting a 'pre-edge' line to the data before the absorption edge (N.B. This is not to be confused with any pre-edge features – one does not depend on the other), and a 'post-edge' polynomial to the data after the edge. The energy difference between these at the absorption edge, $\Delta \mu E_0$, is then normalised to be from 0 – 1. This is represented in Figure 4.8. The precise position of the absorption edges is of interest. To ensure repeatability these were selected as at the maximum in the first derivative of the normalised data: a point of zero-crossing in the second derivative of these data. Where necessary a 3-point smoothing algorithm included in Athena was applied.

![Figure 4.8: Unnormalised XANES data from Figure 4.6, showing pre- and post-edge lines.](image)

### 4.3.6 Archimedes density testing

Finding the density, $\rho$, of ceramic pellets was achieved using the Archimedes principle. When a body is immersed in fluid it will displace a certain weight of fluid that would occupy the volume of the body. The body experiences a buoyant force equal to this weight of fluid. The density of a pellet can hence be obtained from its weight in both air and fluid, which is typically chosen as distilled water. Prior to weighing in distilled water the pellet is immersed in this medium under vacuum; this ensures that any open pore network is filled. High-accuracy equipment is used to obtain the parameters for the equation;
\[
\rho(\text{experimental}) = \rho(g) + \frac{\rho(fl) \times W(a)}{D(W(a) - W(fl))}
\]

where \(\rho(g)\) and \(\rho(fl)\) are the densities of air and water under testing conditions; \(W(a)\) and \(W(fl)\) are the weight of the pellet in air and when immersed in fluid; \(D\) is a correction for the water displaced by the wires of the weighing assembly.

The experimental density is compared to the theoretical density, the latter calculated from:

\[
\rho(\text{theoretical}) = \frac{n \times \text{RFM}}{V_C \times N_A}
\]

where \(n\) is the number of formula units in the unit cell; \(\text{RFM}\) is the relative formula mass of the material in units per mole; \(V_C\) is the unit cell volume calculated from standard parameters from the Inorganic Crystal Structure Database (ICSD); \(N_A\) is Avogadro's number.

For an SOFC electrolyte pellet the target is \(\rho(\text{experimental}) > 95\% \rho(\text{theoretical})\).

### 4.3.7 Electrode adherence testing

Any viable SOFC cathode material must demonstrate adequate mechanical stability. This includes adherence between cathode and electrolyte. After sintering electrode ink to electrolyte pellet the Scotch-tape test was carried out to confirm this. A piece of tape is pressed against the thin electrode layer then quickly removed. Ideally this will result in no visible change to the electrode, and no residue remaining on the sticky-side of the tape. Adhesion is also confirmed via SEM images of cross sections or fracture surfaces of symmetrical cells.

### 4.3.8 Iodometric titration

Iodometric titration is a method to determine the \(\text{Ni}^{3+}\) content of a sample. In an aqueous environment such ions act as an oxidising agent, hence their concentration can be determined by proxy of the concentration of aqueous iodine formed from the following reaction:

\[
2\text{Ni}^{3+} + 2\text{I}^- \rightarrow 2\text{Ni}^{2+} + \text{I}_2
\]

_N.B._ iodine in aqueous solution with excess \(\text{I}^-\) will in reality be in equilibrium with the triiodide ion, \(\text{I}_3^-\); this is simplified to \(\text{I}_2\) for clarity.
The presence of iodine is indicated by a dark colour with starch solution. The concentration is found by titration with a standardised sodium thiosulphate solution thus;

\[ \text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-} \]

Equation 4.23

the end point being a colour change from dark to clear. From these two equations it can be seen that the number of moles of Ni\(^{3+}\) in the starting solution is equal to the number of moles of S\(_2\)O\(_3\)^{2-} used in the titration. Therefore, to determine the Ni\(^{3+}\) content in a sample, a known mass is dissolved in aqueous acid, an excess of I\(^-\) ions added in the form of potassium iodide, and the resulting solution titrated against 0.1M Na\(_2\)S\(_2\)O\(_3\) solution (Sigma-Aldrich) using starch indicator. It is clear that this technique is an unavoidably destructive \textit{ex situ} process.

4.3.9 \textbf{Inductively coupled plasma atomic emission spectroscopy}

4.3.9.1 \textit{Theoretical background}

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is a highly sensitive technique used to determine the concentration of elements in a sample down to parts-per-million (ppm) levels. It works by stimulating electronic transitions in atoms which occur at energies characteristic for individual elements. To achieve this, an argon plasma is generated and maintained by electromagnetic induction. The sample is introduced as an aqueous mist and quickly gains energy from the plasma, becoming atomised. Electrons are repeatedly lost and gained from these atoms; this occurs only at discrete energy levels that are dependent on the identity of the atom. This means that light is emitted at specific wavelengths allowing for atomic identification. The intensity of this light depends on the concentration of each particular atom in the sample.

4.3.9.2 \textit{Experimental considerations}

ICP-AES equipment is designed to analyse aqueous samples. This means that any materials to be tested must first be completely dissolved in deionised water. This can limit the range of materials that can be tested; however aqueous acid can be used to encourage inorganic oxides – \textit{i.e.} typical SOFC materials – to form solutions.

The detectors used in the equipment are very sensitive and can therefore become saturated if the concentration of the sample is too high; they are intended for use and most accurate in the range of 0-20 ppm. This means that the sample in question must often be diluted significantly to put it in this range. An idea of the correct dilution level can be
found if the concentration of relevant atoms in the sample can be estimated by other means.

To calculate the concentrations of atoms in the sample 'standard' samples of known concentration must be tested first. Solutions containing the relevant elements at known concentration are purchased from a commercial source and diluted to 1, 5, and 20 ppm levels. These are tested along with deionised water (0 ppm); the emitted intensities from these should lie on a straight line. This provides a simple check as to whether the dilution processes have been carried out correctly. If the unknown sample has been diluted to the correct level then its intensity should fall on this calibration line allowing the concentration of the elements present to be found.

ICP-AES works on a parts-per-million scale. This is a dimensionless scale used to describe the mass of a solute in the mass of a solvent. If \( x \) is the mass in grams of an element in 1 litre of water then;

\[
\text{ppm} = \frac{x}{1000} \times 10^6
\]

Equation 4.24

1000g being the mass of a litre of water.

From this it can be shown that the molar ratio of two elements A and B in a solution is;

\[
\frac{\text{moles (A)}}{\text{moles (B)}} = \frac{\text{ppm (A)}}{\text{ppm (B)}} \times \frac{\text{RAM (B)}}{\text{RAM (A)}}
\]

Equation 4.25

where RAM is the relative atomic mass of the element.

ICP-AES data for this work were obtained using a Thermo Scientific iCAP 6300 Duo spectrometer.

4.3.10 Low-energy ion scattering

4.3.10.1 Theoretical background

Low-energy ion scattering (LEIS) is a technique that gives information on the elements present on the outer monolayer of a material. It is unique in that it is truly 'surface sensitive'; other techniques exist that are commonly referred to as such but these sample over many atomic layers\[26\]. LEIS works by firing low-energy noble gas ions (commonly He\(^+\) and Ne\(^+\)) at the material and measuring the energy of the resultant scattered ions. The energy of the scattered ions can be modelled mathematically;
\[ E_f = f(M_0, M_1, \theta) \times E_i \]

where \( E_f \) and \( E_i \) are the energies of the scattered (final) and primary (initial) noble gas ions; \( M_0 \) the mass of the noble gas ion; \( M_1 \) the mass of the atom struck; and \( \theta \) the angle at which this occurs.

For the purposes of this brief review the most important aspect of this equation is that \( E_f \) is proportional to the mass of the atom on the outer surface that is struck. The result of this is that peaks on a LEIS spectrum at different energies can be assigned to the presence of a particular element or isotope on the surface; this is shown in Figure 4.9. The positions of these peaks act as qualitative information on the elemental makeup of the surface. For quantitative information such as surface coverage and concentration one can compare the integrated intensities of the peaks with those collected for relevant ‘standard’ compounds. For example, the spectra of the binary A and B oxides would be of value in studying the surface of a material \( A_x B_y O_z \) by LEIS. This touches on another important advantage of the technique; it typically experiences no matrix effects. This means that the presence of other species on the surface does not alter the signal that one would expect to see from a particular element. For further details on this and other aspects of LEIS, the review by Brongersma et al. is recommended[27].

\[ \text{Figure 4.9: Diagram of the LEIS process: Incident noble gas ions (purple) are scattered from surface atoms (red, green, and blue) at an angle } \theta. \text{ Energy of scattered ion depends on mass of atom struck.} \]

\subsection*{4.3.10.2 Experimental considerations}

LEIS is capable of studying a wide variety of samples ranging from liquids to solids. With regard to ceramics, single crystals and dense sintered pellets can be studied as well as lightly-pressed powders. The roughness of the sample will affect the signal and should be considered during analysis. Figure 4.10 illustrates this; roughness can block the passage of scattered ions to the detector or even shield incident ions from areas of the surface. This would act to reduce the scattered yield. Alternatively the roughness could result in an artificially increased density of atoms at the surface and hence increase the signal.
As LEIS is such a surface-sensitive technique it is important that the surface being studied is clean. It quickly becomes apparent that a thin surface layer that blocks the expected LEIS signal is ubiquitous on many ‘as-prepared’ ceramics. This layer typically consists of adsorbed water and carbon dioxide, as well as a variety of uncharacterised organic species. These can be removed by atomic oxygen; this cleaning procedure is normally applied to samples before testing. Other cleaning treatments include heating, sputtering, and chemical methods. LEIS depends on ion beams so it must be carried out under high vacuum. Similarly to SEM this pressure gap should be considered when applying the findings of LEIS to the typical environment of an SOFC in operando.

LEIS data used in this thesis were obtained using an ION-TOF Qtac 100. The identity and energy of the primary noble gas ion beams are described in the relevant results chapter.

4.3.11 Material compatibility studies

An SOFC has large regions of interface between different types of inorganic material. During manufacture and operation it is desirable to avoid any reactions occurring at these interfaces. As such it is advisable to test materials for chemical compatibility with each other at an early stage of research. A simple method for this is mixing a small volume of one material with an equal volume of another, collecting an XRD pattern, sintering under the desired conditions, and then collecting another XRD pattern. Comparing the ‘before’ and ‘after’ patterns should reveal any compatibility issues that are present and aid in identifying what reactions may have occurred. With regard to testing novel cathode materials, such tests are typically carried out with a range of common electrolytes with a view to detecting any potential mismatches.
References

Chapter 5 - \( \text{La}_2\text{NiO}_{4+\delta} \) and \( \text{La}_4\text{Ni}_3\text{O}_{10-\delta} \) composite electrodes

5.1 Introduction
From the literature reviewed in Chapter 2 it is clear that L2N1 is thought to be a promising IT-SOFC cathode material. This is due to the high ionic conductivity of this phase at relevant temperatures [1, 2]. However, the electrode performance of this phase to date is yet to match the 0.15 \( \Omega \) cm\(^2\) target at these temperatures, and falls some way short of state-of-the-art LSCF+CGO composite cathodes (cf. Figure 2.7). This is believed to be due to the insufficient electronic conductivity of the phase. In spite of this, it is worth persisting with research in this area for a variety of reasons. The current generation of high-performance perovskite cathode materials have degradation problems and there is a growing consensus that alternative structure types should be considered as IT-SOFC cathodes[3, 4]. One such alternative is the layered Ruddlesden-Popper series, of which L2N1 is an \( n = 1 \) member. There have been a small number of studies into higher-order phases of this series, \( n = 2 \) or 3, which have indicated the promise of the area[5-7]. The fundamental properties of these are not yet fully understood, but they have shown better total conductivity than L2N1 [6, 7]. Therefore higher-order phases represent a large new area of compositional space which should be explored. Further to this, there are common strategies for improving electrode performance which have yet to be applied to L2N1. Doping to tailor materials properties is a typical means for this; indeed LSCF was developed in this manner as a modification to LSC. Various such strategies have been applied to L2N1 with little success[8-10]. Another method for improvement is the formation of composite cathodes; very little work has been published applying this to L2N1 or R-P phases in general. For a material with high electronic conductivity, such as LSCF, a composite of superior performance is formed when utilising a material with high ionic conductivity, such as CGO [11, 12]. Making a composite to improve L2N1 will require an alternative approach as this phase already has good ionic conductivity.

The motivations for this chapter are to develop improved IT-SOFC cathodes related to L2N1. It is hoped that these would show greater long-term stability than the standard perovskite materials. Considering the above, a logical approach is to further explore the feasibility of higher order R-P phases, and to look to improve on L2N1 by the formation of a composite. Of the higher-order phases the \( n = 3 \) phase L4N3 is chosen as it has the highest electronic conductivity of the La-Ni R-P series. Reflecting on the properties of
L2N1 and L4N3 it is apparent that they are good candidates for forming a composite, L2N1 with good ionic and L4N3 with good electronic conductivity. Therefore novel L2N1+L4N3 composite cathodes will be tested.

5.2 Preparation of materials

L4N3 was synthesised by the Pechini method described in the previous chapter (cf. 4.1.2) [13], similar to that used by Amow[6]. La(NO$_3$)$_3$.6H$_2$O and Ni(NO$_3$)$_2$.6H$_2$O were dissolved in deionised water to make solutions of concentration approx. 0.5 M, the precise molarities then found using ICP-AES. Stoichiometric amounts of these were stirred with calculated excesses of citric acid and ethylene glycol. Water was evaporated on a hotplate forming a foamy green gel. This was decomposed at 300 °C for 12 hours then 600 °C for 12 hours to ensure removal of all the organic components. The resulting powder was ground and sintered at 1050 °C for 48 hours under an atmosphere of static laboratory air (Table 5.1). This was then characterised by powder XRD and found to match with a standard pattern (PDF 00-050-0243, ICDD). XRD patterns for each stage of the synthesis are shown in Figure 5.1. No crystalline phases have been formed after the first decomposition stage; after subsequent heating at 600 °C for 12 hours the powder is loosely characterised as a mix of various La-Ni-O species; after final calcination at 1050 °C for 48 hours the powder is single-phase L4N3.

![Figure 5.1: XRD patterns for each stage of sol-gel L4N3 synthesis.](image-url)
An important factor during the synthesis is the La:Ni ratio. The phase diagram proposed by Zinkevich and Aldinger[14] demonstrates that L4N3 is the thermodynamic product of a 4:3 La:Ni ratio over a broad temperature range, 750 – 1150 °C (Figure 5.2), but that deviations from this ratio will result in impurities. NiO will be formed if too much nickel, or L3N2 if too little. During this research this was confirmed, a number of batches were found to contain either NiO or L3N2 impurities and were rejected from further use.

L2N1 was obtained from a commercial source (CerPoTech) where it is synthesised by spray pyrolysis. The XRD pattern of the as-received powder matches with a standard pattern (PDF 01-080-1910, ICDD). This material has been characterised previously by researchers at Imperial College[15]. The Pechini method was also extended to make the remaining two members of the La-Ni R-P series (L3N2 and L1N1) for subsequent surface studies (cf. Chapter 9). For L3N2 the final calcination was at 1100 °C for 48 hours; for L1N1 this was 800 °C for 14 hours. Synthesis conditions are summarised in Table 5.1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Synthetic route</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 1 ) L2N1</td>
<td>Spray pyrolysis, supplied by CerPoTech</td>
</tr>
<tr>
<td>( n = 2 ) L3N2</td>
<td>Pechini, 300 °C × 12h; 600 °C × 12h; 1100 °C × 48h</td>
</tr>
<tr>
<td>( n = 3 ) L4N3</td>
<td>Pechini, 300 °C × 12h; 600 °C × 12h; 1050 °C × 48h</td>
</tr>
<tr>
<td>( n = \infty ) L1N1</td>
<td>Pechini, 300 °C × 12h; 600 °C × 12h; 800 °C × 14h</td>
</tr>
</tbody>
</table>

Table 5.1: Synthesis details for materials used in this research

Figure 5.2: La-Ni-O phase diagram adapted from Zinkevich and Aldinger[14].

Figure 5.3 shows the diffraction patterns for these materials and illustrates some of the challenges posed by working within an R-P series. There are a large number of
overlapping peaks throughout the phases and some regions on the phase diagram where \( n = 1, 2, \) and \( 3 \) are all of similar stability. The most intense peaks however do not fully overlap and help identify each phase. These are at \( \approx 32^\circ \) and correspond to \((1 1 3)\) for \( \text{L2N1} \); \((1 1 5)\) for \( \text{L3N2} \); \((1 1 7)\) for \( \text{L4N3} \); and \((1 1 0)\) for \( \text{L1N1} \).

![Diagram showing XRD patterns for different phases](image)

**Figure 5.3**: XRD patterns for all La-Ni R-P phases. Materials synthesised as per Table 5.1.

### 5.2.1 Rietveld refinement

XRD patterns from the as-synthesised R-P phases were refined using the Rietveld method to help confirm phase identification. For the crystal structure of \( \text{L4N3} \) at room temperature different space groups have been proposed; \( Fmmm \) [16] is the aristotype, and the related \( Bmab \) [17] / \( Cmca \) [18] structures reflect rotations in the \( \text{NiO}_6 \) octahedra. These are depicted in Figure 5.4. Each of these models was tested, with the \( Fmmm \) model found to give the best fit to the observed data. The refinement according to this is shown in Figure 5.5. From the difference line it can be seen that the refinement is not ideal. This is due to the calculated model being unable to accurately match the observed peak intensity in all cases, as well as the positions of some of the peaks being slightly shifted. Synchrotron XRD data on \( \text{L4N3} \) refined to \( Bmab \) by Parker also shows a significant difference line [19], indicating the difficulties of obtaining a good structural model using X-ray data on these phases. Due to the low X-ray scattering of oxygen the fractional occupancy of these ions was not refined and was fixed at the stoichiometric value of \( \text{La}_4\text{Ni}_3\text{O}_{10} \). For \( \text{L3N2} \) a similar
variety of space groups are suggested \cite{17, 18, 20}, and again the highest symmetry \textit{Fmmm} gave the best fit. L1N1 was refined using \textit{R3c} as the accepted symmetry \cite{21}. The unit cell parameters for these fits compared to those from the best ICDD matches found using X’Pert Highscore are shown in Table 5.2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.4.png}
\caption{Schematic representation of different structures proposed for L4N3; \textit{Fmmm} from Zhang \cite{16} and \textit{Bmab} from Ling \cite{17}. In the \textit{Bmab} structure there is a rotational mode about the \textit{a} axis for the \textit{NiO}_6 octahedra. Green: lanthanum; blue: nickel; red: oxygen.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Phase & Space group & \textit{a} / Å & \textit{b} / Å & \textit{c} / Å & \textit{R}_{wp} \textsuperscript{†} \%
\hline
L3N2 & \textit{Fmmm} \cite{20} & 5.4016(4) & 5.4530(4) & 20.485(2) & 16.21 \%
00-050-0244 & \textit{Fmmm} & 5.4040 & 5.4540 & 20.5300 &
\hline
L4N3 & \textit{Fmmm} \cite{16} & 5.4147(6) & 5.4626(6) & 28.000(3) & 9.24 \%
00-050-0243 & \textit{Fmmm} & 5.4150 & 5.4670 & 27.9700 &
\hline
L1N1 & \textit{R3c} \cite{21} & 5.4576(8) & 5.4576(8) & 13.217(3) & 9.39 \%
01-088-0633 & \textit{R3c} & 5.4573 & 5.4573 & 13.1601 &
\hline
\textsuperscript{†} \textit{R}_{wp} values for regions of Bragg intensity
\end{tabular}
\caption{Unit cell parameters obtained from Rietveld refinement compared to ICDD entry with best match found using X’Pert Highscore. The standard deviation for the refined cell parameters is shown in brackets.}
\end{table}
Figure 5.5: Rietveld refinement of as-synthesised L4N3 according to \textit{Fmmm} structure proposed by Zhang [16]. Tick marks: observed data; red: calculated data; green: background function; blue: difference line; pink bars: calculated peak positions.

5.3 Material stability

The thermal stability of L2N1 and L4N3 has been established [6, 22]. Studies on L2N1 and a variety of electrolytes have found that using LSGM gives the best performance [8, 9]. The lack of reactivity between L2N1 and LSGM has been demonstrated [23], however reactivity has been observed between L2N1 and CGO or YSZ [22, 24]. Hence LSGM was the electrolyte used throughout this research. To confirm the compatibility of L4N3 with LSGM a 50:50 wt.% mix of these materials was annealed at 1000 °C for 4 hours and 700 °C for 4 hours. The aim of this was to simulate the conditions of sintering electrode ink to electrolyte pellet, and subsequent electrochemical testing. Figure 5.6 presents XRD patterns for as-mixed and annealed samples, with no reactivity evident. With the compatibility of L4N3 and LSGM confirmed, next the stability of L2N1 with L4N3 had to be tested. For a composite to be a viable electrode the two phases must not react during sintering or testing. As before, a 50:50 wt.% mix was annealed at 1000 and 700 °C for 4 hours. The subsequent diffraction pattern (Figure 5.7) shows slight peak broadening but no evidence of the formation of any impurity phases. This was deemed acceptable so tests on L2N1+L4N3 composites proceeded.
Figure 5.6: Reactivity test for a 50:50 wt.% mix of L4N3 and LSGM powders intimately ground using an agate pestle and mortar. XRD patterns are compared for as-mixed powder, and powder after annealing at 1000 °C × 4h then 700 °C × 4h. No evidence for new phases observed.

Figure 5.7: Reactivity test for a 50:50 wt.% mix of L2N1 and L4N3 powders intimately ground using an agate pestle and mortar. XRD patterns are compared for as-mixed powder, and powder after annealing at 1000 °C × 4h then 700 °C × 4h. No evidence for new phases observed.
5.4 Symmetrical cells

5.4.1 Preparation

Electrode inks and dense LSGM pellets were prepared as described in Chapter 4. For the composite inks 40:60, 50:50 and 60:40 L2N1:L4N3 wt.% ratios were made. Inks were brush-coated onto the pellets and sintered at a range of temperatures for 4 hours, electrode adherence checked using the Scotch tape test. For L2N1 and composite inks 1000 °C gave good adhesion, however for L4N3 1200 °C was required. Aguadero et al. also used 1000 °C × 4h for L2N1 [9], however Amow et al. sintered at just 900 °C for both L2N1 and L4N3 [6]. This indicates that the composition of the electrode ink could play an important role in adhesion. The sintering conditions used for symmetrical cells in this research are summarised in Table 5.3.

<table>
<thead>
<tr>
<th>Electrode ink composition</th>
<th>Sintering regime</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% L2N1</td>
<td>1000 °C × 4 hours</td>
<td>L2N1</td>
</tr>
<tr>
<td>60 wt.% L2N1 + 40 wt.% L4N3</td>
<td>1000 °C × 4 hours</td>
<td>60:40</td>
</tr>
<tr>
<td>50 wt.% L2N1 + 50 wt.% L4N3</td>
<td>1000 °C × 4 hours</td>
<td>50:50</td>
</tr>
<tr>
<td>40 wt.% L2N1 + 60 wt.% L4N3</td>
<td>1000 °C × 4 hours</td>
<td>40:60</td>
</tr>
<tr>
<td>100% L4N3</td>
<td>1200 °C × 4 hours</td>
<td>L4N3</td>
</tr>
</tbody>
</table>

Table 5.3: Electrode details and nomenclature for symmetrical cells tested. Adherence between electrode and LSGM electrolyte was confirmed by the Scotch tape test.

5.4.2 Characterisation and discussion

5.4.2.1 XRD on as-sintered electrodes

Figure 5.8 presents XRD patterns collected for the electrodes after sintering compared to the powder patterns for L2N1 and L4N3. For L4N3 extra peaks are present in the electrode pattern over the powder pattern. These peaks can be assigned to the formation during the sintering process of lower-order R-P phases and nickel oxide. This behaviour can be explained using the La-Ni-O phase diagram proposed by Zinkevich and Aldinger [14] shown in Figure 5.2. Heating L4N3 to 1200 °C takes it into a region of L3N2 + NiO and very close to a region of L2N1 + NiO, agreeing well with what is seen in the diffraction pattern.
Figure 5.8: XRD patterns for powders compared to as-sintered electrodes. Marked peak in L4N3 electrode pattern is from NiO.

The pattern from the as-sintered L2N1 electrode matches that of the powder. This is as expected given the phase diagram; L2N1 should be stable at all temperatures between 800-1400 °C and L2N1 is known to be unreactive with LSGM even after 50 hours at 1000 °C[23]. For L2N1+L4N3 composite electrodes no reactivity was observed on sintering as expected from the reactivity tests. The diffraction patterns for these are a linear combination of the powder patterns for the two materials. Across the range of the compositions, 60:40 - 50:50 - 40:60, XRD patterns show the expected concurrent drop in intensity of L2N1 peaks and increase in L4N3 peaks. This is easily seen in the first two peaks, the (111) reflections for each phase. The integrated intensities of these peaks are as expected across the changing L2N1:L4N3 ratio, as shown in Figure 5.9 and Table 5.4. The phase diagram in Figure 5.2 has no two-phase L2N1-L4N3 region and predicts that L3N2 would form from a mix of the two at 1000 °C. This was not observed in this work, which indicates that the sintering time and interface between the phases was not sufficient to result in reactivity within the detection limit of XRD.
Figure 5.9: (1 1 1) reflection for L4N3 (23.4 °) and L2N1 (24.2 °). Relative intensity shifts are as expected due to the changing L2N1:L4N3 ratio.

<table>
<thead>
<tr>
<th>L2N1:L4N3 ratio</th>
<th>L2N1 (1 1 1) peak intensity / arb. units</th>
<th>L4N3 (1 1 1) peak intensity / arb. units</th>
<th>Intensity ratio normalised to 50:50 ratio</th>
<th>Expected ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>60:40</td>
<td>833</td>
<td>275</td>
<td>1.54</td>
<td>1.50</td>
</tr>
<tr>
<td>50:50</td>
<td>731</td>
<td>371</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>40:60</td>
<td>608</td>
<td>469</td>
<td>0.66</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 5.4: Integrated peak densities for L2N1 and L4N3 (1 1 1) peaks. The relative intensities of the peaks are as expected given the changing L2N1:L4N3 ratio in the composite electrodes.

5.4.2.2 Total Conductivity of electrode layers

A rationale behind testing higher-order R-P phases is that their better electronic conductivity should lead to better performance than L2N1. Forming an L2N1+L4N3 composite is also geared towards forming an electrode with better conductivity. The typical method for testing this property is to fabricate dense bars of electrode material and measure the voltage across these with applied current. However, it is clear that this arrangement bears little resemblance to that of an SOFC electrode. These are designed to be thin and porous, not thick and dense, meaning that data from a dense bar may not be entirely relevant to an SOFC. This could be particularly apparent for testing composite electrodes where the percolation of one phase within the other will play a key role in the electrochemical performance. The microstructure of the electrode will affect this interpenetration of phases. Hence a dense composite bar could be far removed from a thin porous composite layer. With this in mind the lateral conductivity of thin porous La-Ni R-P electrodes was tested in the manner described in the previous chapter (cf. 4.3.3).
sintering conditions for the electrode layers were identical to those for the symmetrical
cells.

The temperature dependence of the total conductivity ($\sigma_{tot}$) is displayed in Figure 5.10. The $n = 3$ phase L4N3 has higher conductivity than the $n = 1$ phase L2N1; it is well-established that $\sigma_{tot}$ in (LaNiO$_3$)$_n$LaO increases with $n$ [6, 7]. Values for L4N3 were 20 Scm$^{-1}$ at 400 °C increasing to 30 Scm$^{-1}$ at 700 °C. It must be recalled that the L4N3 electrode undergoes some decomposition towards L3N2 during sintering (cf. Figure 5.8). L3N2 has greater conductivity than L2N1 so it is not surprising that the L4N3 layer still maintains the highest conductivity despite the observed phase changes. Literature data from Takahashi [7] and Amow [6] on the conductivity of sintered bars of L2N1 and L4N3 give values approximately an order of magnitude larger than that presented here. It is as expected that a porous layer has lower conductivity than a compacted bar.

![Figure 5.10](image)

**Figure 5.10:** Total conductivity as a function of temperature for porous layers of La-Ni R-P materials. Layers deposited onto LSGM substrates by screen printing and sintering as according to Table 5.3.

Over the temperature range $\sigma_{tot}$ for each porous electrode follows the same trend; it is relatively constant up to 550 °C followed by an increase over the remainder. Again, comparisons are drawn with literature data on sintered bars. Takahashi and Amow have shown L4N3 to be a metallic conductor between 400 and 700 °C. For L2N1 there is less
consensus; Takahashi shows a semiconductor-to-metal transition at approximately 600 °C, but Amow and Aguadero [25] both show this at approximately 400 °C. Aguadero has noted that phase transitions in L2N1 are strongly dependant on the local atmosphere and that these affect the total conductivity of the material. The differences between these reports and the data on porous electrodes in Figure 5.10 highlight the importance of processing and microstructure in testing SOFC materials. Consistency in these greatly facilitates the comparison of datasets.

5.4.2.3 Electrochemical testing

ACIS measurements were carried out on symmetrical cells from 507 – 710 °C. A typical Nyquist plot at approx. 700 °C is shown in Figure 5.11. It was found that an equivalent-circuit model with two R/CPE components gave the best fit to the observed data across the tested temperature range.

![Typical Nyquist plot for composite symmetrical cell at approx. 700 °C, in this case a 50:50 cell at 707 °C. Circles: observed data; dashed line; fitted data.](image)

There is an inductive response at high frequencies due to the measuring apparatus; this was eliminated in the analysis. Values obtained from the ECM fitting are presented in Table 5.5 with equivalent CPE capacitances calculated using the equation in Chapter 4.3.4.1. The error values for the ASR are noted to be high; this is considered to be an artifact of the fitting process. This is demonstrated by testing to two different models, as shown in Figure 5.12 and Table 5.6.
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Temperature °C</th>
<th>$R_1$ (Ω)</th>
<th>CPE$_1$-Q (F)</th>
<th>CPE$_1$-n (F)</th>
<th>$C_1^\dagger$ (Ω)</th>
<th>CPE$_2$-Q (F)</th>
<th>CPE$_2$-n (F)</th>
<th>$C_2^\dagger$ (Ω)</th>
<th>ASR (Ω cm$^2$)</th>
<th>ASR error (Ω cm$^2$)</th>
<th>Weighted sum of squares$^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2N1</td>
<td>507</td>
<td>65.04</td>
<td>9.94×10$^{-3}$</td>
<td>0.71</td>
<td>8.34×10$^{-3}$</td>
<td>7.63</td>
<td>2.00×10$^{-1}$</td>
<td>1.04</td>
<td>1.97×10$^{-1}$</td>
<td>34.10</td>
<td>±5.61</td>
</tr>
<tr>
<td></td>
<td>609</td>
<td>7.26</td>
<td>9.69×10$^{-3}$</td>
<td>0.85</td>
<td>5.99×10$^{-3}$</td>
<td>0.81</td>
<td>3.69×10$^{-2}$</td>
<td>0.64</td>
<td>4.90×10$^{-3}$</td>
<td>3.79</td>
<td>±0.24</td>
</tr>
<tr>
<td></td>
<td>710</td>
<td>0.24</td>
<td>4.11×10$^{-3}$</td>
<td>0.89</td>
<td>1.71×10$^{-3}$</td>
<td>1.75</td>
<td>6.06×10$^{-3}$</td>
<td>0.87</td>
<td>3.02×10$^{-3}$</td>
<td>0.93</td>
<td>±0.06</td>
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<tr>
<td></td>
<td>60:40</td>
<td>507</td>
<td>42.42</td>
<td>8.46×10$^{-2}$</td>
<td>0.94</td>
<td>9.17×10$^{-2}$</td>
<td>29.63</td>
<td>4.43×10$^{-2}$</td>
<td>0.62</td>
<td>5.22×10$^{-2}$</td>
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<tr>
<td></td>
<td>609</td>
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<td>4.62×10$^{-2}$</td>
<td>0.90</td>
<td>3.21×10$^{-2}$</td>
<td>2.37</td>
<td>5.26×10$^{-2}$</td>
<td>0.61</td>
<td>1.36×10$^{-2}$</td>
<td>3.45</td>
<td>±1.41</td>
</tr>
<tr>
<td></td>
<td>710</td>
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<td>2.93×10$^{-2}$</td>
<td>0.75</td>
<td>9.07×10$^{-3}$</td>
<td>0.59</td>
<td>1.75×10$^{-2}$</td>
<td>0.69</td>
<td>2.20×10$^{-3}$</td>
<td>0.78</td>
<td>±0.22</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>504</td>
<td>16.02</td>
<td>5.28×10$^{-2}$</td>
<td>0.53</td>
<td>4.54×10$^{-2}$</td>
<td>53.04</td>
<td>5.08×10$^{-2}$</td>
<td>0.81</td>
<td>6.40×10$^{-2}$</td>
<td>32.40</td>
</tr>
<tr>
<td></td>
<td>606</td>
<td>5.43</td>
<td>4.21×10$^{-2}$</td>
<td>0.51</td>
<td>2.28×10$^{-2}$</td>
<td>0.58</td>
<td>8.68×10$^{-2}$</td>
<td>0.59</td>
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<td>0.12</td>
<td>3.80×10$^{-4}$</td>
<td>1.07</td>
<td>6.98×10$^{-4}$</td>
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<td>±0.04</td>
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<td></td>
<td>40:60</td>
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<td>43.37</td>
<td>8.18×10$^{-2}$</td>
<td>0.91</td>
<td>9.23×10$^{-2}$</td>
<td>31.74</td>
<td>4.63×10$^{-2}$</td>
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<td>5.66×10$^{-2}$</td>
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<td>609</td>
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<td>2.92×10$^{-1}$</td>
<td>1.00</td>
<td>2.92×10$^{-1}$</td>
<td>5.80</td>
<td>4.22×10$^{-2}$</td>
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<td>2.30×10$^{-2}$</td>
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<td>0.53</td>
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<td>207.70</td>
<td>4.10×10$^{-2}$</td>
<td>0.91</td>
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<td>1.12×10$^{-1}$</td>
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<td>9.08×10$^{-2}$</td>
<td>0.94</td>
<td>7.97×10$^{-2}$</td>
<td>3.02</td>
<td>3.03×10$^{-2}$</td>
<td>0.77</td>
<td>1.46×10$^{-2}$</td>
<td>2.03</td>
<td>±1.10</td>
</tr>
</tbody>
</table>

$^\dagger$ Capacitances calculated using Equation 4.14
$^\ddagger$ Proportional to percentage error between observed and calculated data points

Table 5.5: ECM fitting for composite electrode ACIS data across IT-SOFC temperature range.
Figure 5.12: ECM fitting using different models on 50:50 cell at 504 °C. Circles: collected data; dashed lines: fitted data according to $R_sR_1/CPE_1$ (red) and $R_sR_1/CPE_1R_2/CPE_2$ (blue).

<table>
<thead>
<tr>
<th>Model</th>
<th>ASR / $\Omega cm^2$</th>
<th>ASR error / $\Omega cm^2$</th>
<th>Weighted sum of squares$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_sR_1/CPE_1$ (red)</td>
<td>35.19</td>
<td>±0.37</td>
<td>$3.31 \times 10^{-1}$</td>
</tr>
<tr>
<td>$R_sR_1/CPE_1R_2/CPE_2$ (blue)</td>
<td>32.40</td>
<td>±10.81</td>
<td>$4.00 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

$^+$Proportional to percentage error between observed and calculated data points

Table 5.6: ECM fitting from Figure 5.12.

The ECM with the single $R/CPE$ component results in an ASR with a much lower error than the model with two $R/CPE$ components, however, visually it is clear that this gives an inferior fit and overestimates the resistance. This is reflected in the weighted sum of squares, a value obtained from the difference between observed and calculated points, which is an order of magnitude higher for the single $R/CPE$ model. Introducing more $R/CPE$ or $R/C$ components to the $R_sR_1/CPE_1R_2/CPE_2$ model did not lead to significant improvements in the fit, and increased the uncertainty in the resistance. Therefore the $R_sR_1/CPE_1R_2/CPE_2$ model was accepted. Considering the suggested interpretations of capacitance given by Irvine et al.[26] the two $R/CPE$ elements reflect electrochemical reactions occurring at the electrode. Further interpretations were not attempted as some of the CPE exponents ($CPE-n$) for the composite electrodes showed significant deviation from unity. Shoar Abouzari et al. [27] warn that care should be taken over interpretation of capacitances calculated from these.
Figure 5.13: Arrhenius plot of log(ASR) vs. 1000/T comparing the performance of the symmetrical cells described in Table 5.3.

ASR values calculated from the $R_1 R_2/CPE_1 R_2/CPE_2$ model for each electrode are displayed in Figure 5.13. The composite electrodes and L4N3 had an activation energy of the order of 0.6 eV over the whole temperature range. L2N1 shows a change in gradient from 0.6 eV from 500 – 600 °C to 0.5 eV from 600 – 700 °C. The change in activation energy in L2N1 indicates a change in the electrode-limiting step. This could reflect modifications in the crystal structure of L2N1. This phase is known to undergo structural transitions at elevated temperature, and these are strongly dependent on the oxygen stoichiometry and surrounding atmosphere [25, 28], even with suggestions of biphasic mixes[15]. Similar changes in the activation energy of L2N1 electrodes have been observed before[8, 29] but are not present in all studies. The activation energy values found in this study are in a similar region to those found by Aguadero et al. for L2N1 on LSGM [9], but again differ from other cases. These variations emphasise the importance of processing, microstructure, and experimental conditions on the properties of SOFC electrodes. The change in activation energy in the L2N1 electrode is considered likely to be a phenomenon related to the electronic conductivity of the phase. This is evidenced by the observation from this research that addition of L4N3, a phase with much higher electronic conductivity, suppresses the activation energy change. Further to this, Sayers has shown
that the addition of a platinum current-collecting layer to L2N1 also results in the suppression of this change in gradient[29].

From 500 – 600 °C the performance of the composite electrodes is comparable to L2N1; however from 600 – 700 °C it is superior due to the change of activation energy in L2N1. Comparisons are drawn between Figure 5.13 and the total conductivity data in Figure 5.10. Below 600 °C the total conductivity for the composites is similar to that of L2N1; above 600 °C this increases faster in the composites than for L2N1. This means that by 700 °C the total conductivity of the pure L2N1 electrode is markedly inferior to the composite electrodes. Here the advantage of the composite is highlighted. It is believed that the good ionic conductivity of L2N1 is maintained over the whole temperature range, and that the addition of L4N3 enhances the total conductivity. This suppresses the change in gradient seen in the L2N1 impedance data leading to improved performance above 600 °C. From the different ratios explored a 50:50 wt.% composite gave the lowest ASRs.

The L4N3 electrode was found to be inferior to both L2N1 and L2N1+L4N3 composites. It has been shown that this electrode is no longer single phase due to the high sintering temperature required for adherence. This could explain the high ASR however Figure 5.10 shows that this electrode still has the greatest total conductivity. Compared to the data presented by Amow for an L4N3 symmetrical cell on LSGM [6], the ASRs found here are actually lower, e.g. 2.23 vs. 6.30 Ωcm² at approx. 700 °C. The better performance shown by Amow of L4N3 over L3N2 and L2N1 is consistent within that study, but the absolute ASRs for all three electrodes are notably high compared to other work on these phases (cf. Figure 2.7). The performance of the 50:50 composite electrode developed here is a significant improvement on the early work of Amow and co-workers.

Some consideration must be given to the current-collection arrangement used in the ACIS experimental setup. Connections to the FRA were made by pressing a fine platinum mesh onto each electrode of the symmetrical cell (cf. Figure 4.5). These meshes did not cover the entire surface area of the porous ceramic electrodes, and clearly the open nature of a mesh means that the contact between the platinum and ceramic will not be continuous. This has potential implications with regard to the current pathways through the ceramic. An assumption made in calculating the ASR for the porous ceramic electrodes was that the current propagates laterally along the full surface area, meaning that the electrochemical response of the full body of the electrode is what is being measured by the technique. The electronic conductivity of the R-P phases used in these electrodes is relatively low (cf.
Figure 5.10) which may invalidate this assumption. If that is the case then this would imply that the only active pathways through the electrode are small regions around the areas directly in contact with the platinum current collector, and that the remainder of the electrode is unperturbed. The ACIS data presented in this section therefore serve to explore the performance of the fabricated symmetrical cells ‘as-is’ as electrochemical devices, but may not necessarily be fully exploring the fundamental properties of the materials used to form their porous ceramic electrodes. This could be rectified by the application of a thin continuous layer of high electronic conductivity over the surface of the electrode, and pressing the platinum mesh of the ACIS setup onto this. Such a layer can be deposited by painting a thin coating of silver or platinum slurry, followed by sintering for adhesion. If this modification is made then care must be taken to deconvolute any effects of this layer, for example oxygen reduction catalysed by the metal, or any potential reactivity between the metal and ceramic.

5.4.2.4 Post-test microstructural analysis

Figure 5.14 shows SEM images of cross-sectioned symmetrical cells obtained after ACIS testing. It is to be noted that by this method one cannot definitively distinguish between the L2N1 and L4N3 constituting the composites. This is as expected given the nature of the physical processes occurring during image acquisition. From these images it can be seen that a reason for the performance enhancement of the composite electrodes over single phases is their improved microstructure. The L4N3 electrode has particles sized approx. 1.5 – 3.0 μm which are poorly connected. There also are a series of voids throughout its thickness which is consistent with the reported difficulty in sintering this phase[6]. The L2N1 electrode has finer particles than L4N3 at 0.5 – 1.5 μm. The interconnectivity between these remains poor, as is the connectivity to the LSGM electrolyte. The differing particle sizes observed between L2N1 and L4N3 will affect the percolation and interpenetration of the two phases as part of a composite, hence the performance of these electrodes. Figure 5.14c shows the microstructure for a 50:50 composite electrode. It presents a broader range of particle sizes than the single phase electrodes; 0.5 – 2.0 μm. Based on Figures 5.14a and 5.14b the largest and smallest particles in the composite electrode can be tentatively assigned as L4N3 and L2N1 respectively. The particle interconnectivity in the composite electrode is clearly improved over the single phases and this is a likely reason for the improved performance seen. The microstructure is still not ideal however; the connectivity to the electrolyte is not optimal which is reflected in the markedly depressed nature of the arcs in the Nyquist plots (cf. Figure 5.11).
Figure 5.14: SEM images of cross sections of symmetrical cells after testing. (a) L4N3 (b) L2N1 (c) 50:50.

5.4.2.5 Long-term electrode performance

5.4.2.5.1 IT-SOFC temperatures

Commercial SOFCs are designed to operate for substantial periods of time. It is difficult to study materials under these conditions in-house as there is no accepted accelerated testing method. During the studies described so far the symmetrical cells had not been at temperature for more than four hours. Further testing was therefore carried out under isothermal conditions for longer periods. It was hoped that this would give preliminary insights into the long-term stability of these La-Ni R-P electrodes. A 50:50 cell was tested at \( \approx 700 \, ^\circ C \) for 5 days with ACIS data collected every 30 minutes. Due to the large number of measurements the electrode contribution towards the impedance of the cell was modelled using a single R/CPE component to facilitate batch fitting the data. The evolution of the series and polarisation resistances are shown in Figure 5.15. Changes over an initial testing period can be normally attributed to the furnace and sample holder reaching thermal equilibrium; however the largest changes in \( R_s \) take place over an initial 16 hours. It seems unlikely that thermal equilibrium is not reached over this timescale.
The decrease in $R_s$ is therefore believed to reflect an improvement in the interface between composite electrode and the platinum mesh providing electrical contact to the FRA. Considering the polarisation resistance now, there is some oscillation over the testing period however the magnitude of this is small. For the first 38 hours $R_p$ increases whereas for the rest of the period there was a decrease. The overall change for the final 100 hours is a decrease in $R_p$ of 6%. This final trend is promising for these electrodes, however it must be stressed that the testing period is short in comparison to the desired operational life of an SOFC. A diffraction pattern was taken of the composite electrode after the isothermal test. This is presented in Figure 5.16 in comparison to the pattern before testing. There has been a shift in the relative intensities of the L2N1 and L4N3 peaks which corresponds to an increase in the proportion of L4N3. The microstructure after the isothermal test was not significantly different from an as-sintered cell (Figure 5.17); there has been no noticeable coarsening or sintering. These images again highlight the poor connectivity between the composite electrodes and LSGM electrolyte, and the broad particle size distribution likely arising from the starting L2N1 and L4N3 powders used to make the composite. These factors may limit the performance and are an area for further improvement. Without interim data it is difficult to explain the increase then decrease in $R_p$ over the testing period.
Figure 5.16: XRD patterns for 50:50 electrodes; as-sintered, and after isothermal testing at 707 °C for 5 days.

Figure 5.17: SEM images of cross sections of 50:50 symmetrical cells. (left) as-sintered; (right) after isothermal testing at 707 °C for 5 days.

5.4.2.5.2 HT-SOFC temperatures

Early-stage studies into these composite electrodes had included testing a symmetrical cell at approx. 900 °C, temperatures more appropriate for traditional HT-SOFCs. On visual inspection after testing marks were evident on the electrodes where the platinum mesh from the ACIS equipment (cf. Figure 4.5) had been in contact. These were not observed after testing to 700 °C. It was hypothesised that this was due to reactivity between the L2N1+L4N3 composite and platinum occurring at high temperatures, but not at
intermediate temperatures. This was not considered of paramount importance as the desired temperature range for modern SOFCs is somewhat lower than 900 °C, and these are unlikely to contain expensive platinum. Notwithstanding this, the phenomenon was explored further. Larger cells were fabricated with L2N1, 50:50, and L4N3 electrodes using the same sintering conditions as before (cf. Table 5.3), and tested isothermally for 5-day periods above 900 °C. The evolution of the resistances for these cells is presented in Figure 5.18.

**Figure 5.18:** Evolution of series and polarisation for large symmetrical cells under isothermal conditions at 910 °C. Dashed lines: $R_s$; filled lines: $R_p$.

It is clear that the trend for the 50:50 composite cell is different from L2N1 and L4N3. The latter two show an increase in $R_p$ over the final 100 hours of 5 and 34 % respectively, whereas the 50:50 cell has a decrease over this period of 43 %. The series resistance for the 50:50 cell shows a markedly slow decrease which does not appear to have reached completion even after 120 hours, over the final 100 hours the decrease is 28 %. For L2N1 and L4N3 the trend for $R_s$ is much flatter, decreasing by 2 and 3 % respectively. The differences in the magnitude of $R_s$ between the three cells reflect variation in the thickness of the electrolyte which was in the order 50:50 > L2N1 > L4N3, and irregularities in the shape of the cells.

On removing the cells from the testing apparatus it was visually clear where the Pt mesh had been in contact. For subsequent characterisation these larger cells were then sectioned into a region that had been in contact with platinum, and a region that had not. The rationale behind this was to separate the effect of platinum contact and high temperature from the effect of high temperature in isolation. XRD patterns were collected
for these two regions and are displayed for the 50:50 electrode in Figure 5.19. Significant differences are evident between these and were similarly seen between the two regions of the L2N1 and L4N3 electrodes (Figure 5.20). For the region in contact with platinum X’pert Highscore found a good match from the ICDD database with peaks from the phase La$_2$NiPtO$_6$ as reported by Ouchetto et al. [30]. This is the only study detailing this phase, and these peaks are indicated by black stars. La$_2$NiPtO$_6$ is a double-perovskite with Ni and Pt occupying the B-site ordered in alternating layers of the crystal structure. Ouchetto synthesised this phase by a solid state method from La$_2$O$_3$, NiO and Pt metal sintered at 1000 then 1300 °C for a total of 10 days. It is therefore plausible that this has formed on the L2N1+L4N3 composite electrode when in contact with Pt metal at 910 °C for 5 days. The influence of the electrochemical testing may allow for phase-formation at the lower temperature. The XRD pattern also contains many peaks belonging to residual La-Ni R-P phases on the electrode. There is significant overlap between the peaks from La$_2$NiPtO$_6$ and La-Ni R-P phases, particularly for the strongest peak at $\approx 32^\circ$. This meant that Rietveld refinement was unable to give satisfactory fits for a combination of these phases. A further reason for this is that the stoichiometry in the double-perovskite is not known, and may be more accurately represented as La$_2$Ni$_{1-x}$Pt$_{1+x}$O$_{6-\delta}$. The diffraction pattern of La$_2$NiPtO$_6$ from the standardised ICDD data was modelled using GSAS and is displayed in Figure 5.19 for comparison, the agreement being visually clear. The Pt-free region has undergone decomposition away from the initial 50:50 L2N1+L4N3 composite. The majority phases are still L2N1 and L4N3 however there are likely contributions from L3N2 and L1N1. As for the Pt-contact region, the large number of overlapping peaks makes Rietveld refinement a difficult process. There were some peaks in the pattern that do not belong to La-Ni-O phases. These are indicated with purple stars in Figure 5.19; the two strongest at 28.8 and 29.9° are also evident in the Pt-contact region. No single entry into the ICDD database used by X’Pert Highscore matches these peaks; however a combination of different entries for lanthanum oxides is informative. Consulting the literature it becomes apparent that a variety of different diffraction patterns have been reported for La$_2$O$_3$, and that non-stoichiometric phases have received little attention beyond thermodynamic modelling [31, 32]. These peaks are therefore tentatively assigned as belonging to a binary lanthanum-oxygen compound La$_x$O$_y$. These phenomena described for the 50:50 electrode were repeated in the L2N1 and L4N3 electrodes as shown in Figure 5.20; La$_2$NiPtO$_6$ is formed when in contact with platinum, and the R-P phase undergoes some decomposition.
Figure 5.19: Top: XRD patterns for 50:50 electrode after isothermal testing at 910 °C. Patterns collected for region that had been in contact with platinum electrodes, and region that had not. Peaks indicated black: La$_2$NiPtO$_6$, indicated purple: tentatively assigned as La$_x$O$_y$. Bottom: Modelled diffraction pattern for La$_2$NiPtO$_6$ using crystallographic data from Ouchetto et al. [30].

The reactivity of L2N1 with platinum has been considered before by Sayers using in situ high temperature XRD up to 1000 °C [15]. In that work a direct reaction between the two is not considered, rather the hypothesis is that platinum catalyses phase changes from L2N1 to the higher order phases L3N2 and L4N3. Interestingly, no evidence is seen of any lanthanum oxide species which would be required to balance the cation ratio of such reactions. Close inspection of Sayers’ data shows that it is consistent with the formation of a small amount of La$_2$NiPtO$_6$ as well as L3N2 and L4N3.
Figure 5.20: XRD patterns for L2N1 (top) and L4N3 (bottom) electrodes after isothermal testing at 910 °C. Patterns collected for region that had been in contact with platinum electrodes, and region that had not. Peaks indicated black: La$_2$NiPtO$_6$; indicated purple: tentatively assigned as La$_x$O$_y$.

5.4.2.5.3 Further comments

The electrochemical properties of SOFC cathodes are known to evolve at operating temperatures even without any chemical reactivity. For example, Chiba and co-workers have shown that the performance of the perovskite cathode LaNi$_{0.6}$Fe$_{0.4}$O$_3$ improves over the first ≈ 100 hours of operation, a so-called 'burn-in' phenomenon [33, 34]. This is assigned to various sintering processes improving the current collector/electrode and
electrolyte/electrode connectivity, as well as improving conductive pathways within the electrode. These affect both the series and polarisation resistances. Considering the phenomena seen in Figure 5.15 and Figure 5.18 and the timescales over which they progress it is likely that these processes are occurring in the La-Ni R-P electrodes. The effects at 900 °C are more pronounced in the 50:50 composite electrode than the single phase L2N1 or L4N3 symmetrical cells, despite the fact that all three undergo similar reactivity with the platinum mesh current collector. Here the differences between composite and single phase electrodes are highlighted. The performance of a composite will be strongly dependent on the interface between the two phases within it, and this could be improved by sintering at this high temperature. It is noted that XRD reveals significant phase decomposition occurs in the region free from platinum, yet this does not appear to have a deleterious effect on polarisation resistance.

From these isothermal tests it is clear that great care must be taken if using La-Ni R-P electrodes at 900 °C, and if platinum is used in the experimental setup this must be accounted for. The performance at 700 °C was promising, and is a more appropriate experiment given the current efforts to develop low-cost SOFCs operating in the intermediate-temperature range.

5.4.3 Percolation

The properties of the L2N1+L4N3 composite should be considered with respect to the percolation theory (EMPT) discussed in Chapter 2.5. This allows for the effective ionic and electronic conductivity of a porous two-phase composite to be calculated, provided the relevant fundamental properties are known. This brings with it some issues with respect to this particular composite – the properties of L2N1 are established however this is not the case for L4N3, and a consistent comparison of the electronic properties of these has yet to be published. Both Amow[6] and Takahashi[7] agree that $\sigma_e$ for L2N1 at 700 °C is approx. 50 Scm$^{-1}$, however they disagree over L4N3 quoting 90 and 200 Scm$^{-1}$ respectively. Neither of their tested samples will have approached theoretical density so the actual conductivity of L4N3 is expected to be higher.

Using the values from Takahashi, the electronic conductivity of the composite ($\sigma_{e,comp}$) is modelled in Figure 5.21. This demonstrates that the difference between the electronic conductivity of L2N1 and L4N3 from these literature values is not sufficient to form a sharp percolation limit. Therefore the electronic conductivity over the composite range tested, $0.4 \leq x_{L4N3} \leq 0.6$, is not expected to show a significant stepwise change. This is confirmed in the lateral conductivity data presented in Figure 5.10.
Figure 5.21: Effective electronic conductivity for L2N1+L4N3 composites with different porosities as a function of L4N3 volume fraction. Modelled using EMPT from Wu [35] and data from Takahashi [7].

Considering the ionic conductivity now, Bassat gives \( \sigma_i = 2 \times 10^{-2} \text{ Scm}^{-1} \) for L2N1 at 700 °C [36]. No research has been published on \( \sigma_i \) for L4N3 to date so suggesting any values would be pure speculation. What does seem likely however is that the ionic conductivity of L4N3 is less than that of L2N1. If the opposite then L4N3 would have truly remarkable fundamental properties and would be expected to show excellent electrode performance as a single-phase cathode. This research has indicated that this is not the case. The EMPT model can however still be used to make a prediction: for a sharp percolation limit to be present the ionic conductivity of L4N3 must be at least two orders of magnitude lower than L2N1. Figure 5.22 demonstrates this concept for a given porosity of 0.25. The position of any percolation limit present will depend on this porosity. The relative particle sizes of the constituent phases in a composite will affect their percolation and interpenetration. It can be visualised that at a given volume fraction the percolation of identically-sized particles will be different from that of particles with substantially different sizes. Figure 5.14 demonstrates that the L2N1 and L4N3 used in this research do have different particle sizes; whether this is sufficient to significantly affect the properties of the composite electrodes is a subject for further investigation. Efforts made to control the particle sizes could also affect the porosity of the composite. Based on a simple ‘counting squares’ approach, the porosity in the composites is estimated at approximately

\[
\text{Porosity} = \frac{\text{Volume of voids}}{\text{Total volume}}
\]
30%. The EMPT modelling demonstrates that this parameter is key to the position of a possible percolation limit in the ionic conductivity at a particular L2N1:L4N3 ratio.

![Figure 5.22](image.png)

**Figure 5.22**: Effective ionic conductivity for a porous L2N1+L4N3 composite with porosity = 0.25 as a function of L4N3 volume fraction. Modelled for ionic conductivity of L4N3 ranging from $2 \times 10^{-2}$ - $2 \times 10^{-7}$ Scm$^{-1}$.

### 5.5 Comparison to existing La-Ni R-P electrodes

The ASR values for the 50:50 L2N1+L4N3 composite, the best-performing electrode so far, are lower than those quoted for L2N1[37, 38]; a copper-doped phase La$_2$Ni$_{1.6}$Cu$_{0.4}$O$_{4.8}$[9]; L3N2 [5]; and the various La-Ni electrodes discussed in Tarancon's recent review[3] (cf. Figure 2.7). This improvement is believed to arise from the good mix of ionic conductivity from L2N1 and electronic conductivity from L4N3. Without detailed studies on the fundamental properties of L4N3, in particular its ionic conductivity, it is difficult to say why the 50:50 ratio in particular gives the best performance. A further reason for the lower ASRs is the improved microstructure of the composites. This stems from the materials properties of L4N3, a phase that sinters poorly. This leads to poor properties for L4N3 in isolation but provides for good interconnectivity in a composite.
5.6 Summary

L2N1 and L4N3 have been tested as SOFC cathodes, both single-phase and composite. During synthesis, stability testing, and symmetrical cell fabrication the La-Ni-O phase diagram (cf. Figure 5.2) was validated. The importance of the correct La-Ni ratio during synthesis is highlighted, as is the decomposition of L4N3 at 1200 °C. No reactions were observed at 1000 °C between L2N1, L4N3 and LSGM. The total conductivity of the electrode layers was as expected given the nature of the two phases and their ratios in the composite. Between 600 and 700 °C the conductivity for the composite electrodes improves at a greater rate than for monophasic L2N1. This is an important feature when considering the ASRs for these electrodes; from 500 – 600 °C L2N1 is comparable to the composites, whereas from 600 – 700 °C the composites show markedly improved performance. This enhancement is ascribed to the better conductivity of the composites as well as their improved microstructure. It must be noted that this microstructure is still not considered ideal, particularly in terms of the connectivity between the composite electrode and LSGM electrolyte. The optimal L2N1:L4N3 ratio was found to be 50:50, and the performance of this electrode compares well to published literature results on comparable R-P phases. Longer-term stability at 700 °C was confirmed by isothermal testing and a promising trend of decreasing ASR with time was observed. At 900 °C there is an effect of the platinum used in the ACIS setup which should be accounted for in further research into these phases.
References

Chapter 6 - Functionally graded La$_2$NiO$_{4+\delta}$ and La$_4$Ni$_3$O$_{10-\delta}$ electrodes

6.1 Introduction

In the previous chapter the performance of composite L2N1+L4N3 electrodes was found to be superior to that of the respective single phases [1], and compared well to published research on comparable R-P electrodes. This was a promising result; however the polarisation resistances seen were still short of the 0.15 $\Omega$cm$^2$ target at IT-SOFC temperatures. In particular the poor connectivity between composite electrode and LSGM electrolyte was identified as a limiting factor. The aim of this chapter was therefore to further improve on the electrode performance whilst remaining in the La-Ni R-P family.

A strategy that has seen significant performance enhancements for traditional perovskite materials is the fabrication of functionally graded electrodes. These utilise layers with different compositions, each geared towards a certain role in the electrode. A typical advantage of this is the accommodation of large TEC strains between electrolyte and cathode materials. This is overcome by a gradual change in composition over the graded layers [2-4]. This however is not a problem for the materials used in this study – L2N1 and L4N3 are well matched with the LSGM electrolyte used[5]. Therefore the application of functional grading in this chapter is geared towards improving the electrode electrochemically and microstructurally. For the former it is known that polarisation resistances can be improved by having a composition with high ionic conductivity adjacent to the electrolyte, and grading to a composition with greater electronic conductivity as the thickness of the electrode is increased[2-4, 6]. For the R-P phases used here this would correspond to a greater L2N1 content grading to a greater L4N3 content. Microstructurally, different approaches have been explored. One can fabricate the layer adjacent to the electrolyte to have a smaller particle size, with a view to maximising the electrocatalytically active area in this region [3, 7]. Alternatively, deposition conditions can be optimised to improve the electrolyte/electrode contact, at the possible expense of a non-ideal particle size distribution. This has been successfully used to improve the performance of single-phase L2N1 electrodes [8-10] and is the approach chosen here; functionally graded electrodes will start with a thin compact L2N1 layer. The bulk of the electrode will be made up of the porous L2N1+L4N3 composite used in the previous chapter. It is here that the bulk of the oxygen reduction and incorporation is assumed to occur. The outer region will be a porous L4N3 layer. This is designed to increase the
electronic conductivity, acting as a current-collector, whilst not blocking gas transport to the rest of the electrode. A schematic of this design is presented in Figure 6.1; this will be tested using the range of L2N1+L4N3 composites used in the previous chapter. The properties of these functionally graded electrodes are then explored at the various grading stages.

![Schematic of graded electrode](image)

**Figure 6.1**: Schematic of graded electrode; a: LSGM electrolyte; b: thin L2N1 layer; c: porous L2N1+L4N3 composite layer making up the bulk of the electrode; d: thin L4N3 current collector

### 6.2 Symmetrical cell preparation

The electrode inks and LSGM pellets were the same as used in the previous chapter. A uniform thin L2N1 layer was deposited by screen printing. This was sintered at 1300 °C for 4 hours to promote adherence to the LSGM pellet as well as densification. Thicker porous composite layers were brush coated onto these and sintered at 1000 °C for a further 4 hours, and then a L4N3 layer was screen printed and sintered at 1200 °C for a final 4 hours. These stages are summarised in Table 6.1. Some characterisation was carried out between these steps and is detailed below.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Fabrication method</th>
<th>Sintering conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>a LSGM electrolyte</td>
<td>Powder isostatically pressed</td>
<td>1450 °C × 8h</td>
</tr>
<tr>
<td>b compact L2N1</td>
<td>screen printed</td>
<td>1300 °C × 4h</td>
</tr>
<tr>
<td>c porous L2N1+L4N3 composite</td>
<td>brush coated</td>
<td>1000 °C × 4h</td>
</tr>
<tr>
<td>d porous L4N3</td>
<td>screen printed</td>
<td>1200 °C × 4h</td>
</tr>
</tbody>
</table>

**Table 6.1**: Fabrication method and sintering conditions for functionally graded symmetrical cells. These electrodes are denoted as L2N1|xy|L4N3, where xy represents the wt.% ratio used in the porous L2N1+L4N3 composite layer.
6.3 Results and discussion

6.3.1 XRD patterns for each grading stage

XRD patterns collected as-sintered after each stage of the grading process are displayed in Figure 6.2. For the initial L2N1 layer this was consistent with the starting powder apart from a small peak at 2θ = 30.7 °. This peak does not correspond to any binary or ternary La-Ni-O phase in the ICDD database, and neither could it result from the LSGM pellet underneath. As such, it remains unidentified.

The addition of the composite layer to the graded cells was as expected; the pattern is a linear combination of L2N1 and L4N3. Upon sintering the final L4N3 layer, completing the grading process, some phase-changes are evident towards L3N2 and nickel oxide. This is due to the high sintering temperature of 1200 °C required for this layer to adhere to the rest of the electrode. The phase changes within L4N3 are entirely consistent with the previous chapter and explained by the phase diagram suggested by Zinkevich and Aldinger[11] (cf. Figure 5.2 and Figure 5.8).

![Figure 6.2: XRD pattern for each stage of the grading process. Marked peaks are: a - unknown; b - L3N2; c – NiO.](image-url)
6.3.2 Electrochemical performance for the complete graded electrode

ACIS measurements were carried out on symmetrical cells from 500 – 700 °C. Typical Nyquist plots are shown in Figure 6.3, along with the ECM used to fit the data. There is an inductive response at high frequency from the measuring apparatus; this was not included in the analysis. It was found that a single R/CPE component fitted the electrode arc most appropriately. The contributions from the different layers in the electrode could not be deconvoluted from these electrochemical measurements.

Figure 6.3: Typical Nyquist plots at 500, 600, and 700 °C, in this case for a symmetrical cell with graded L2N1|50:50|L4N3 electrodes. Circles: collected data; dotted lines: fitted data. Inset shows the equivalent circuit model used for fitting.

Table 6.2 shows the data obtained from ECM fitting of the ACIS data and Figure 6.4 shows an Arrhenius plot, including comparison to the best-performing ungraded composite from the previous chapter. The slopes for the graded cells in this figure are constant with activation energies of 0.52 eV. This indicates unchanging electrode kinetics over the temperature range. Using a 50:50 composite in the graded electrodes gave the best performance. This is consistent with the previous chapter where a 50:50 ratio proved to be the optimal composite for an ungraded electrode. It is evident that that graded electrodes gave better performance than ungraded, and that this is particularly apparent at the lower-end of the temperature scale.
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Temperature</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>CPE&lt;sub&gt;1&lt;/sub&gt;-Q</th>
<th>CPE&lt;sub&gt;1&lt;/sub&gt;-n</th>
<th>C&lt;sub&gt;1&lt;/sub&gt;†</th>
<th>ASR</th>
<th>ASR error</th>
<th>Weighted sum of squares‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2N1</td>
<td>60:40</td>
<td>L4N3</td>
<td>500</td>
<td>40.97</td>
<td>7.48×10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.83</td>
<td>9.33×10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>19.22</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>5.82</td>
<td>9.59×10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.84</td>
<td>8.60×10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>2.73</td>
<td>±7.02×10&lt;sup&gt;-3&lt;/sup&gt;</td>
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<td></td>
<td>700</td>
<td>1.30</td>
<td>1.16×10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.84</td>
<td>8.22×10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.61</td>
<td>±2.13×10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>2.17×10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>L2N1</td>
<td>50:50</td>
<td>L4N3</td>
<td>500</td>
<td>33.22</td>
<td>6.61×10&lt;sup&gt;-2&lt;/sup&gt;</td>
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<td>15.59</td>
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<tr>
<td></td>
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<td>4.87</td>
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<td>0.85</td>
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<td>4.21×10&lt;sup&gt;-2&lt;/sup&gt;</td>
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<td></td>
<td>700</td>
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<td>6.47×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>L2N1</td>
<td>40:60</td>
<td>L4N3</td>
<td>498</td>
<td>51.78</td>
<td>7.13×10&lt;sup&gt;-2&lt;/sup&gt;</td>
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<td></td>
<td>598</td>
<td>6.96</td>
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<td>9.43×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

†Capacitances calculated using Equation 4.14
‡Proportional to percentage error between observed and calculated data points

**Table 6.2:** ECM fitting for graded electrode ACIS data across IT-SOFC temperature range.
Figure 6.4: log(ASR) vs. 1000/T for graded symmetrical cells from this study, with comparison to ungraded composite 50:50 cell from previous chapter.

Figure 6.5: Nyquist plots comparing electrode performance of ungraded 50:50 electrode at 504 °C with graded L2N1|50:50|L4N3 electrode at 500 °C. Data normalised to zero series resistance to aid comparison. Circles: collected data; dotted lines: fitted data.

Figure 6.5 compares the data at 500 °C for an ungraded composite 50:50 symmetrical cell with a graded L2N1|50:50|L4N3 symmetrical cell. As well as having a lower polarisation resistance, the graded electrode arc is closer to a true semicircle than the composite. This indicates that the microstructure of the graded electrode is superior; this will be discussed
in detail later. The shapes of the arcs are manifested in the exponents, \( n \), of the CPEs used in the ECM fitting. These are presented in Table 6.2 for these graded electrodes and Table 5.5 for ungraded. \( n = 1 \) corresponds to a perfect capacitor and \( n < 1 \) indicates deviations from ideality\[12\]. For the graded cells \( n \) was of the order of 0.85 whereas for the composites some CPE components had \( n < 0.6 \). Equivalent capacitances for the graded cells can be calculated with some confidence given the high value of \( n \); these were of the order of \( 10^{-2} \) F which corresponds to electrochemical reactions occurring at the electrode \[13\].

6.3.3 Electrochemical role of each layer

![Arrhenius plot](image)

**Figure 6.6**: log(ASR) vs. 1000/T demonstrating the performance at each stage of the grading process for an L2N1|50:50|L4N3 electrode.

Figure 6.6 shows the electrode performance at each stage of fabrication. This gives insight into the electrochemical role of the different layers in the graded electrodes. Data were obtained for the compact L2N1 layer, after the addition of the thick composite layer, and after the thin L4N3 layer completing the grading process. The L2N1 layer on its own provides a poor electrode. From the SEM images in Figure 6.7 (further discussed later) it is seen that this is too thin and has insufficient porosity to give good performance in isolation – it is known that an optimal electrode requires a sufficient thickness\[14, 15\]. There are two regions in the Arrhenius plot for this layer; a change of gradient is apparent
from 0.44 eV between 500 and 600 °C, to 0.15 eV between 600 and 700 °C. Similar behaviour was noted in the previous chapter for a thicker more porous L2N1 electrode, and indicates a change in the electrode-limiting step (cf. Figure 5.13), believed to be due to the electronic conductivity of the phase. The next step in the grading regime is adding the thick porous composite layer. This improves the electrode performance and suppresses the change in gradient, meaning that the performance enhancement is largest at the high-end of the temperature range. The enhancement is assigned to the increased electrode thickness and porosity giving a much larger region for oxygen reduction and incorporation, as well as the inherently better properties of an L2N1+L4N3 composite over pure L2N1 as demonstrated in the previous chapter. Adding a thin L4N3 layer completes the grading and gives a further performance enhancement, acting as a current collector. Total conductivity in these R-P phases is known to increase with $n$ [5, 16], and it has been shown that this is maintained in porous electrode layers (cf. Figure 5.10), so it is consistent that an outer L4N3 layer lowers the polarisation resistance.

The possible implications of insufficient current collection were discussed for the ungraded composite electrodes in the previous chapter, and similar effects are likely to be occurring for these graded electrodes. Again it must be stated that current collection was only achieved by pressing a platinum mesh to the porous ceramic electrodes. The electronic conductivity increases with each successive layer in the graded structure so it is likely that the propagation of the signal from the FRA increases, and a greater region of the electrode is being activated as these are built up. This is a probable factor contributing to the reduction in polarisation resistance observed over the grading process. Current collectors are known to improve electrode performance and have been utilised with these La-Ni R-P materials before [8, 9, 17]. However, in those cases the collector was a layer of platinum; due to the expense of this element it is unreasonable to expect that a commercial SOFC could utilise such a modification. Hence the L4N3 layer used as a current collector in this case is considered to be much more realistic with regard to viable devices, i.e. the data shown here represent the electrochemical properties of the completed graded electrodes as-fabricated. To fully explore the properties of each individual layer separate experiments could be performed on these, with the addition of a metallic current collector to avoid any differences in the size of the activated region of the ceramic electrode.

6.3.4 Post-test microstructural analysis

Figure 6.7 presents SEM images of a graded electrode cross-section obtained after electrochemical testing. In this case a L2N1|50:50|L4N3 was chosen; these data are representative for the other composites used.
Figure 6.7: SEM images of L2N1|50:50|L4N3 electrode deposited on LSGM electrolyte. a: LSGM; b: L2N1; c: 50:50; d: L4N3. Upper image shows whole cross-section; lower shows the LSGM|L2N1|50:50 region at higher magnification. Images obtained after electrochemical testing up to 700 °C.

The thin L2N1 layer – ‘b’ in Figures 6.1 & 6.7 – is clearly distinguishable from the rest of the electrode and is approximately 5 μm thick. It is well-adhered to the LSGM electrolyte and shows excellent interconnectivity. The L2N1+L4N3 composite making up the bulk of the electrode – ‘c’ in Figures 6.1 & 6.7 – is well-adhered to the thin L2N1 layer and again is highly interconnected. One cannot distinguish between L2N1 and L4N3 in the composite layer which is as expected given the nature of the physical processes occurring during image acquisition. The outer L4N3 layer can be identified by a slight change in microstructure. In the previous chapter a difference was noticeable between L4N3 and
composite electrodes, the former presenting a broader particle-size distribution and a series of voids throughout its thickness (cf. Figure 5.14). These features are apparent in the outer 10 μm of the graded electrode – ‘d’ in Figures 6.1 & 6.7 – allowing it to be tentatively assigned as the L4N3 current collector. The compact L2N1 layer has larger particles than the composite layer; approx. 3 μm vs. approx. 1 μm. This layer is also less porous, estimated at 20 % compared to 30 % for the composite. This is a feature of the sintering conditions and materials chemistry. Over the course of the grading process the L2N1 layer will have been sintered at 1300, 1000, then 1200 °C for 4 hours each; the composite layer at 1000 then 1200 °C for 4 hours each (cf. Table 6.1). It is the high temperature of the initial 1300 °C sintering that promotes grain growth and densification in the L2N1 layer. In the finished graded electrode the role of this is to increase the number of electrolyte/electrode contact points and as such it is ideal that L2N1 densifies as seen. This allows for excellent connectivity to the LSGM electrolyte, and it can be seen from Figure 6.7 that the subsequent composite layer adheres very well to L2N1. Compared to the previous chapter on non-graded composite electrodes, the overall contact between the composite layer and LSGM is better when mediated by the thin dense L2N1 layer. As such this could be described as an ‘interlayer’. These are thin layers between two phases in an SOFC that provide an overall performance enhancement. Often the function of these is to prevent deleterious reactivity between phases, for example a CGO interlayer avoids contact between YSZ and LSC[18] or LSCF [19-21]. In the case of the graded La-Ni R-P cathodes developed in this work reactivity with the electrolyte is not believed to be an issue, so the interlayer is focussed on improving the electrolyte/electrode connectivity. L2N1 is a novel material to use as an interlayer and could have some advantages over CGO. The presence of catalytically-active nickel and appreciable mixed ionic-electronic conductivity in L2N1 means that this interlayer will provide reactive sites for oxygen reduction and incorporation, as well as improving the conductive pathway between porous electrode and electrolyte. These sites will not be present in a CGO interlayer. It would therefore be of value to test dense L2N1 interlayers with traditional SOFC cathode materials. The final sintering step at 1200 °C does not lead to noticeable densification for the composite or the L4N3 layer; porosity remains high in the latter, estimated at above 40 %. This is a feature of the materials chemistry of L4N3; it is known to resist densification even with isostatic pressing and sintering[5]. The presence of this phase in the composite layer maintains the desired porosity during fabrication. The current-collecting layer should not be such that it blocks gas transport to the bulk of the electrode; Figure 6.7 demonstrates that this is the case for the outer L4N3 layer. The microstructure of this could however still be improved upon in terms of pore and particle size distribution.
6.3.5 Long-term electrode performance

As discussed in the previous chapter, it is desirable to gain preliminary insight into the longer-term performance of SOFC electrodes. Given the reactivity with platinum that had been noted at \( \approx 900 \, ^\circ \text{C} \) for the ungraded composite electrodes (cf. Figure 5.19), testing was limited to \( \approx 700 \, ^\circ \text{C} \) in this case.

![Figure 6.8](image_url)

**Figure 6.8:** Evolution of series and polarisation resistances for graded L2N1|50:50|L4N3 symmetrical cell under isothermal conditions at 710 \(^\circ\text{C}\).

![Figure 6.9](image_url)

**Figure 6.9:** XRD patterns for L2N1|50:50|L4N3 electrodes; as-sintered, and after isothermal testing at 710 \(^\circ\text{C}\) for 5 days.
Figure 6.8 shows the evolution of the resistances for an L2N1|50:50|L4N3 cell at 710 °C over a 5 day period, with ACIS data obtained every 30 minutes. The initial decrease in $R_p$ can be attributed to sintering improving the interfaces within the graded electrode. Over the final 100 hours this resistance increases by 5%. This mirrors the increase seen in $R_s$ and could indicate a worsening of the contact between the outer layer of the graded electrode and the platinum mesh used in the ACIS setup. Figure 6.9 shows the XRD pattern after isothermal testing. No significant changes are observed, however it should be noted that this pattern will be dominated by the contribution from the outer L4N3 layer. This may mask any potential processes occurring in the composite and L2N1 layers below. The increase in polarisation resistance indicates that further work may be required to optimise the long-term stability of these graded electrodes.

6.4 Comparison to existing electrodes

Considering the graded electrode as a whole, it is believed that ionic conductivity increases with each layer closer to the electrolyte ($\sigma_{\text{L2N1}} > \sigma_{\text{composite}} > \sigma_{\text{L4N3}}$), and total conductivity increases with each layer away from the electrolyte ($\sigma_{\text{tot L4N3}} > \sigma_{\text{tot composite}} > \sigma_{\text{tot L2N1}}$). As discussed, this is the ideal arrangement for a graded electrode, helping to explain the high performance seen. The performance of the ungraded composites from the previous chapter already was amongst the best-in-class, it is therefore notable that the graded electrodes improve on this. Figure 6.10 compares the best composite and best graded electrodes from this thesis with published values for various other electrodes belonging to this class of material. The relatively low polarisation resistance obtained from this research is evident.

Over a parallel timescale to this work Hildenbrand et al. [10] developed similar cathodes consisting of thin dense L2N1 layers deposited by PLD topped by a thicker porous screen-printed L2N1 layer. The similarities between these two-layer electrodes and the graded electrodes of this research mean that a more detailed comparison between the two should be carried out. Hildenbrand used PLD then sintered at 1000 °C to form a 400 nm thick fully dense L2N1 interlayer, then screen printed and sintered at 1000 °C a thick porous L2N1 layer to form an overall electrode thickness of $\approx 50 \mu$m. Figure 6.10 reveals that these gave excellent performance; surpassing the graded L2N1+L4N3 electrodes at all tested temperatures. This is believed to be due to the superiority of a PLD-deposited L2N1 interlayer vs. a screen-printed L2N1 interlayer. If the prime function of this interlayer is to improve the overall electrolyte/electrode contact then it is clear that this will be maximised if full density is achieved. The SEM images shown by Hildenbrand demonstrate
that this is the case for a 400 nm thick PLD L2N1 layer and that this is continuous along the electrolyte. It would be of value to see how the subsequent porous L2N1 layer connects to this interlayer; however such images are not supplied in the paper.

Figure 6.10: log(ASR) vs. 1000/T for best performing composite and graded electrodes from this research, compared to various literature reports on similar R-P materials.

Hildenbrand and co-workers propose an electrode pathway involving oxygen dissociation over the large surface area of the porous layer sustaining a flow of ions to the dense interlayer, both via incorporated and surface species. There is an ancillary contribution from oxygen incorporation occurring directly on the interlayer surface. This is similar to the mechanisms discussed above and is depicted in Figure 6.11. This mechanism serves to explain the lower ASR found by Hildenbrand and demonstrates that PLD is the optimal in-house method for fabricating a thin dense layer. Compared to the screen-printed L2N1 interlayer, the PLD L2N1 interlayer is approximately three orders of magnitude thinner, and is fully dense rather than porous. It would be interesting to use this method to modify the graded electrodes of this chapter, i.e. making an electrode with dense PLD-L2N1|porous 50:50 L2N1+L4N3 composite|L4N3 layers. It is anticipated that this would give even better performance than the pure-L2N1 electrodes of Hildenbrand. Be that as it may, it is questionable whether PLD could be applied to any eventual need for full scale
production. The screen printing method used in this research would be more applicable, and alternative methods could be explored.

Figure 6.11: Schematic comparing electrode pathways for porous L2N1 cathode and porous cathode with dense interlayer. The hatching of the L2N1 grains indicates the random orientation of the 2D ionic-conduction planes. Adapted from [10].

Metal-organic chemical vapour deposition has been demonstrated for L2N1 before [22] and could show promise. Hildenbrand also compared the impedance of two-layer electrodes with simple single-layer porous L2N1 electrodes. The electrode arcs on Nyquist plots for the former were much closer to capacitive behaviour than the latter, with CPE exponents from ECM fitting close to unity. This mirrors the comparisons drawn between porous L2N1+L4N3 composite electrodes and graded L2N1|L2N1+L4N3|L4N3 electrodes discussed above (cf. Figure 6.5) and again serves to illustrate the similar nature and importance of the L2N1 interlayers used in these works. It is seen that these modifications lead to remarkably low ASRs. What is also clear is that these values, irrespective of how well they compare within their class of material, are still short of the state-of-the-art LSCF+CGO cathode as well as the 0.15 Ωcm² target. However, these La-Ni R-P materials do have a potential advantage over standard perovskite cathodes in that they have no dopant on the A-site. The fundamental properties of LSCF depend on strontium doping for oxygen vacancies; however, as discussed in Chapter 2.3.2, this doping is believed to accelerate cathode degradation. This is due to dopant segregation leading to a surface-passivating layer, as well as strontium being a nucleating agent for chromium poisoning. L2N1 and L4N3 do not require any doping for the presence of ionic charge carriers (interstitials or vacancies) so it could be expected that they would be more resistant to degradation.
Furthermore, it is believed that cathode materials free of strontium would be more tolerant towards Cr poisoning[23]. This gives reason for continued research in these alternative cathode materials.

6.5 Summary

Functionally-graded L2N1/L4N3 electrodes consisting of three layers have been fabricated;

- A thin compact L2N1 layer adjacent to the electrolyte. This improves the electrolyte/electrode contact, facilitating the transport of O\textsuperscript{2-} to the electrolyte.
- A thicker porous L2N1+L4N3 composite, for which a 50:50 wt.% mix gave the best performance. It is here that the bulk of the oxygen reduction and incorporation is thought to occur.
- A thin outer layer of porous L4N3 acting as a low-cost current collector.

The lowest ASRs were for a L2N1|50:50|L4N3 electrode and represent performance amongst the best-in-class for these La-Ni R-P phases. Particularly notable was the large improvement at lower temperatures (500 – 600 °C) of the graded electrodes compared to un-graded composite electrodes from the previous chapter. The use of L2N1 as a novel interlayer phase was identified as an area for further research. Isothermal testing revealed that the long-term stability of these electrodes may require further optimisation.
References

Chapter 7 - *In situ* characterisation of La-Ni Ruddlesden-Popper phases

7.1 Introduction

The previous two chapters have described investigations exploring the potential of La-Ni R-P phases as SOFC cathodes. A parallel goal of this research was to also explore novel *in situ* characterisation techniques for SOFC cathodes. This chapter and the following will detail the advances made in this area.

The good ionic conductivity of L2N1 is dependent on its mobile interstitial oxygen ions which have therefore been the subject of much research. Interstitial ions are a manifestation of oxygen hyperstoichiometry which is quantified by the parameter $\delta$. This has been probed by a variety of different methods such as thermogravimetric analysis (TGA)[1, 2]; coulometric titration[3]; iodometric titration[4] and ranges from $0.14 \leq \delta \leq 0.25$ at room temperature. The interstitial ions have been shown by neutron diffraction to reside in the rock salt layers of the $n = 1$ R-P structure[5]. The nature of the structure itself has also been subject to much debate, seeming to have been answered by an *in situ* neutron diffraction experiment between 25 and 800 °C by Skinner[6], who found an orthorhombic $Fmmm$ structure at 25 – 150 °C and a tetragonal $I4/mmm$ structure above this. From this it would seem that oxygen stoichiometry in L2N1 is well understood, however the relevance of much of the discussed work with respect to the properties of the material as an SOFC cathode are questionable. It is clear that $\delta$ changes with temperature, and may also be affected by the thermal history of a sample. Therefore $\delta$ found *ex situ* at room temperature by laboratory means is likely to be somewhat different from the $\delta$ under operating conditions. Skinner’s neutron study does give insight at IT-SOFC temperatures, but was carried out under vacuum so is still not ideal. Much less work has been published on L4N3. Typically oxygen hypo stoichiometry is observed here with $\delta$ found at room temperature to be 0.22 by TGA[7, 8], however one earlier study found $\delta$ to be -0.02 by iodometric titration[9] suggesting that $\delta$ can vary markedly. *In situ* data on this phase is yet to be presented. It is clear that questions still remain over La-Ni R-P phases and their oxygen non-stoichiometry, particularly how they behave under IT-SOFC conditions.

Further to this, there are still unresolved questions over how oxygen non-stoichiometry is charge compensated by the materials electronically. A variety of plausible defect mechanisms exist (Table 7.1). Minervini *et al.*[10] modelled these using atomistic
computer simulations and calculated that both mono- and divalent oxygen could exist as interstitial species, designated $O'_i$ and $O''_i$ in Kröger-Vink notation. However, density-functional theory modelling by Frayret et al.[11] claims to rule out the possibility of $O'_i$ and this has been accepted by subsequent theoreticians[12]. If correct this would preclude mechanisms A, B and D. For low $\delta$ values Minervini predicts the charge-compensating holes will reside purely on nickel sites (mechanisms B and C). This corresponds to the partial oxidation of nickel from Ni$^{2+}$ to Ni$^{3+}$. For higher $\delta$ values the electron holes are predicted to be on a mix of nickel and oxygen sites (mechanism F). Both cases imply that samples of L$_2$N$_1$ with different $\delta$ values should have different average nickel oxidation states, with a higher oxidation state expected for higher $\delta$.

<table>
<thead>
<tr>
<th>Compensation mechanism</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A $1/2O_2 + O'_O \rightarrow 2O'_i + V''_O$</td>
<td></td>
</tr>
<tr>
<td>B $1/2O_2 + Ni^{3+}_{Ni} \rightarrow O'<em>i + Ni^{3+}</em>{Ni}$</td>
<td></td>
</tr>
<tr>
<td>C $1/2O_2 + 2Ni^{3+}_{Ni} \rightarrow O''<em>i + 2Ni^{3+}</em>{Ni}$</td>
<td></td>
</tr>
<tr>
<td>D $1/2O_2 + O''_O \rightarrow O'_i + O''_O$</td>
<td></td>
</tr>
<tr>
<td>E $1/2O_2 + 2O''_O \rightarrow O''_i + 2O''_O$</td>
<td></td>
</tr>
<tr>
<td>F $1/2O_2 + Ni^{3+}_{Ni} + O''_O \rightarrow O''<em>i + Ni^{3+}</em>{Ni} + O''_O$</td>
<td></td>
</tr>
</tbody>
</table>

**Table 7.1:** Plausible charge compensation mechanisms for oxygen hyperstoichiometry in L$_2$N$_1$.

Charge compensation for oxygen hypo stoichiometry in L$_4$N$_3$ is a simpler case than for hyperstoichiometry in L$_2$N$_1$. Ni$^{3+}$ is the only species present in L$_4$N$_3$ that can readily be reduced so the expected mechanism is;

$$O'_O + 2Ni^{3+}_{Ni} \rightarrow V'_O + 2Ni^{3+}_{Ni} + 1/2O_2 \uparrow$$

Equation 7.1

As with L$_2$N$_1$ this indicates that samples of L$_4$N$_3$ with different $\delta$ should have a different average nickel oxidation state. Given the key role of cation valence in compensation for oxygen non-stoichiometry in these compounds it is surprising that only limited investigations into the nickel oxidation state have been carried out. As discussed, Minervini considers Ni$^{3+}$ in L$_2$N$_1$ during simulations[10], however direct experimental evidence is scarce. Interpretations have been attempted of Ni-O bond-length data obtained from neutron diffraction [6, 13]; however these will reflect a summation of competing factors. La-O bonds found by this method change in length under different conditions yet lanthanum is generally considered to be purely La$^{3+}$ in these phases. This indicates that care should be taken over inferring data on the nickel oxidation state from Ni-O bond length variance.

A method that can give direct information on the valence of an element is XANES. This is based on the principle that the position of an absorption edge will depend on the oxidation
state of the element in question, as described in Chapter 4.3.5. In order to find the oxidation state for an unknown material first one must find the K-edge positions for a variety of standard compounds of known oxidation state. This allows for the K-edge position for the unknown to be calibrated. This approach is well established for studies on nickel redox chemistry [14-16]. L2N1 has been studied before by XANES[17]; samples of varying δ, as found by iodometric titration, were prepared by different thermal treatments. The room-temperature nickel K-edge positions were shifted to lower energy for lower values of δ indicating the expected oxidation state change. However, only qualitative trends can be obtained from these data as they were not compared to any standard nickel compounds, furthermore measurements were only made at room temperature, limiting the relevance of the work to SOFCs. In this chapter the aim is to improve on this by studying L2N1 and L4N3 at room temperature and in situ at IT-SOFC temperatures, and comparing these data to compounds of known oxidation state. A broader goal is to demonstrate the application of in situ XANES measurements on SOFC materials as a proof-of-concept for potential further experiments.

7.2 Results and discussion

7.2.1 Standard nickel compounds

To calibrate the position of the nickel K-edge appropriate standards were selected for Ni (0), (II), and (III). Ni (0) was naturally nickel foil, Ni(II) was green nickel oxide, and for Ni(III) the perovskite LaNiO₃ as synthesised in Chapter 5 was used. The Ni³⁺ content in LaNiO₃ was confirmed using iodometric titration. For XANES measurements powder samples were diluted with h-BN and data were collected in transmission geometry as described in earlier (cf Figure 4.7). Data were background-subtracted and normalised using the Athena GUI[18] for IFEFFIT software[19]. In the beam setup an internal reference nickel foil spectrum was collected simultaneously to the sample of interest. This was calibrated against the known position of the Ni(0) K-edge, 8333.0 eV[20], and the same shift applied to the sample scan. Data were obtained every 0.2 eV around the region of the nickel K-edge, and edge positions deemed to be at a maximum in the first derivative of normalised absorbance. The nickel standards data are displayed in Figure 7.1 and Figure 7.2 and are best fitted by a quadratic polynomial. O’Grady et al. have published similar work studying nickel battery electrodes where they also used standard compounds to quantify the oxidation state[14]. They chose to define the edge position as being at half the height of the normalised edge step, and from this found a straight-line relationship between position and oxidation state. However they also give the edge position at
maximum first derivative, the method used here, and found a polynomial relationship similar to that of this work. The edge positions of their Ni(II) and Ni(IV) standards sit just above the calibration polynomial used here and are shown in Figure 7.1. There is reasonable agreement considering the error in O’Grady’s study estimated at ±0.2 eV and in this work at ±0.1 eV. This gives evidence that the polynomial calibration seen in this research is an accurate means of determining the nickel oxidation state.

![Figure 7.1: Nickel oxidation state vs. K-edge position, as obtained from the maximum first derivative of normalised absorbance. Standards used in this study were Ni(0) foil, Ni(II)O, and LaNi(III)O₃; used by O’Grady were Ni(0) foil, β-Ni(II)(OH)₂, and BaNi(IV)O₃. Oxidation state for L2N1 and L4N3 assigned using calibration curve. Error estimated at ±0.1 eV, error bars within data points.](image)

7.2.2 Nickel oxidation state determination for L2N1 and L4N3 at room temperature

L2N1 and L4N3 were diluted in h-BN in the same manner as the standards. Their K-edges were found to sit between that of the nickel (II) and (III) standards as shown in Figure 7.2. For both compounds a small pre-edge feature at around 8335 eV is evident, appearing to be strongest for L4N3. Such a feature is not unusual for nickel and other transition metal compounds [14-16] and is due to ‘forbidden’ 1s – 3d transitions. These occur via p-d orbital mixing facilitated by distorted NiO octahedra. The presence of these is known from neutron diffraction [13], with greater distortion for L4N3 than L2N1, explaining why the former has the stronger pre-edge.
Figure 7.2: Normalised XANES data obtained at room temperature in ambient atmosphere for Ni(0) foil, Ni(II)O, LaNi(II)O$_3$, L2N1, and L4N3.

The calibration curve was used to assign the ambient oxidation state (Figure 7.1). For L2N1 this was 2.24, giving direct evidence for the presence of Ni$^{3+}$/Ni$_{Ni}$. This suggests that mechanisms B, C and F from Table 7.1 are plausible, as suggested by Minervini[10], however Frayret has since ruled out B[11]. In order to estimate the value of δ from this work the assumption that only compensation mechanism C is present is made. This is necessary as nickel XANES data do not probe the possible presence of O$_{2}^*$ or O$_{1}^*$. From this δ was estimated to be 0.12, which is slightly smaller than previous literature values of 0.14 – 0.25[1-4, 6]. However, if other compensation mechanisms were also present this would act to increase δ above the ‘C only’ value of 0.12, bringing it more in line with the literature range. The simulations indicate that mechanism F is the most likely candidate for this.

For L4N3 the oxidation state was assigned as 2.58. Using Equation 7.1 as the charge compensation mechanism δ is estimated to be 0.13, again somewhat smaller than found in previous studies[7, 8], although it is known that large variations in δ for this phase exist[9].
7.2.3 Nickel oxidation state determination for L2N1 and L4N3 *in situ* at IT-SOFC temperatures

Diluted samples of L2N1 and L4N3 were then mounted inside a furnace custom-designed for the beam hutch. This enabled *in situ* XANES data to be obtained at temperatures relevant to IT-SOFCs, in this case 650 °C, and for different atmospheres to be passed over the sample. L2N1 and L4N3 are potential cathode materials hence are likely to be at high temperature in an air atmosphere when *in operando*. For this study the use of atmospheres beyond air was therefore not a priority. However, a flow of nitrogen was passed over a sample of L2N1 during heating to demonstrate the ability of XANES to probe SOFC materials under a variety of conditions.

Figure 7.3 shows XANES data for the materials at room temperature and *in situ* at 650 °C. It is clear that the nickel K-edge shifts towards lower energy for both on heating, indicating a reduction in the nickel oxidation state. The calibration curve from Figure 7.1 was used to quantify this; values are presented in Table 7.2. For L2N1 the oxidation state reduces from 2.24 at 25 °C to 2.15 and 2.08 at 650 °C under air and N₂ respectively, for L4N3 from 2.58 at 25 °C to 2.42 at 650 °C under air.

![Figure 7.3: XANES data for L2N1 and L4N3 at room temperature (≈ 25 °C) and *in situ* at 650 °C.](image-url)
Demourges et al. have used iodometric titration to study the nickel oxidation state in L2N1 samples with different $\delta$[21]. Further to this room-temperature shifts in nickel K-edge positions have been observed in the XANES of similar samples[17]. The work presented in this chapter is the first time that changes to the nickel oxidation state have been observed \textit{in situ} in L2N1 and related R-P phases. A reduction in the nickel oxidation state in L2N1 implies fewer charge-compensating nickel holes and consequently fewer interstitial oxygen ions at IT-SOFC temperatures. Using the ‘C only’ assumption $\delta$ decreases to 0.08. It must be noted that the true value of $\delta$ may be slightly higher if mechanism $F$ is also present, however the trend of decreasing $\delta$ with increasing temperature is clear. L2N1 is known to be an excellent ionic conductor and it should be recalled that interstitial ions are believed to be the mobile species responsible for this. This indicates that greater control of the interstitial content could lead to higher performance for this phase as a cathode.

A nickel reduction for L4N3 has different implications than for L2N1 as $\delta$ is calculated to increase. It should be restated that L4N3 is $La_4Ni_3O_{10-\delta}$, an oxygen deficient phase, compared to the oxygen excess in L2N1 / $La_2NiO_{4+\delta}$. An increase in $\delta$ in L4N3 therefore means a greater number of oxygen vacancies and so its ionic conductivity may actually be better than anticipated. To date the ionic conductivity of this phase is yet to be reported.

The data presented so far were obtained from samples heated directly to 650 °C at 10 °Cmin$^{-1}$. To gain further insight into the kinetics of the nickel reduction fresh samples were subjected to a full heating/cooling cycle. The furnace was stepped in 100 °C increments during heating to 650 °C and cooling, and allowed to stabilise for 20 minutes at each temperature before collecting XANES data. The nickel K-edge positions found \textit{in situ} during the heating/cooling cycle are presented in Figure 7.4 and Table 7.3.
Table 7.3: Ni K-edge positions for L2N1 and L4N3 during heating/cooling cycle under an atmosphere of static laboratory air. Samples allowed to stabilise at each temperature for 20 minutes before data collection.

<table>
<thead>
<tr>
<th>Temp. / °C</th>
<th>L2N1 heat</th>
<th>L2N1 cool</th>
<th>L4N3 heat</th>
<th>L4N3 cool</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>8346.1</td>
<td>8346.1</td>
<td>8347.2</td>
<td>8347.1</td>
</tr>
<tr>
<td>150</td>
<td>8346.0</td>
<td>8346.0</td>
<td>8347.1</td>
<td>8347.1</td>
</tr>
<tr>
<td>250</td>
<td>8345.9</td>
<td>8346.0</td>
<td>8347.1</td>
<td>8347.0</td>
</tr>
<tr>
<td>350</td>
<td>8345.9</td>
<td>8346.0</td>
<td>8347.0</td>
<td>8346.9</td>
</tr>
<tr>
<td>450</td>
<td>8345.9</td>
<td>8345.9</td>
<td>8347.0</td>
<td>8346.9</td>
</tr>
<tr>
<td>550</td>
<td>8345.9</td>
<td>8345.9</td>
<td>8346.8</td>
<td>8346.9</td>
</tr>
<tr>
<td>650</td>
<td>8345.8</td>
<td></td>
<td></td>
<td>8346.7</td>
</tr>
</tbody>
</table>

†accurate to ±0.1 eV

The overall change is relatively small compared to the estimated error in the data. This means it is difficult to identify any clear trends beyond a shift towards lower energy as temperature is increased. The edge position returns to its initial value on cooling for L2N1, and within 0.1 eV for L4N3, i.e. within experimental error. This indicates that thermal cycling has little or no effect on these phases, a desirable property for any SOFC material.

Figure 7.4: Ni K-edge positions for L2N1 and L4N3 in situ during heating/cooling cycle under an atmosphere of static laboratory air. Samples allowed to stabilise at each temperature for 20 minutes before data collection.

Amow has published TGA traces obtained for L2N1 and L4N3 in air\[8\] (Figure 7.5); these can be compared to the XANES data also collected during heating in air. L2N1 showed an initial weight increase up to ≈350 °C, followed by a linear decrease up to 900 °C. One could
interpret the increase as extra oxygen being incorporated into the structure. If this was the case then one would expect to see a concomitant increase in the nickel oxidation state therefore K-edge position up to 350 °C. This was not seen in the XANES data which can be explained by the small magnitude of the TGA weight increase; 0.025%. Taking a reasonable starting L2N1 composition as La$_2$NiO$_{4.15}$ this increase would result in La$_2$NiO$_{4.156}$ i.e. a nickel valence change of 0.01, which is likely to be beyond the sensitivity of XANES measurements. Further TGA studies have been carried out by Sayers [22] and different behaviour was observed; a dependence on the synthetic route and thermal history of L2N1 was noted. These examples indicate that care must be taken over the interpretation of TGA traces, and serve to illustrate the importance of accurate in situ characterisation of SOFC materials. For L4N3 Amow found an approximately linear mass decrease from room temperature to 900 °C. This would seem to indicate a loss of oxygen which is consistent with the XANES data.

Figure 7.5: TGA data for L2N1 and L4N3 in air. Adapted from Amow[8].

7.3 Discussion

For the first time the oxidation state of nickel in R-P phases has been probed in situ at temperatures relevant to IT-SOFCs. In this case these data were correlated with the defect chemistry of the materials to confirm the nature of charge-compensation mechanisms for oxygen non-stoichiometry, and by extension how the concentration of ionic charge carriers will change with temperature.

Transition metal chemistry plays a central role in many of the processes occurring in an SOFC. The oxygen reduction and incorporation reaction is catalysed by the redox
chemistry of these metal cations, electronic conductivity proceeds via their partially-filled d-orbitals, and oxygen non-stoichiometry can be accommodated by changes to the average oxidation state. Hence it is imperative that methods are developed to study this chemistry in SOFC materials. In particular how this chemistry changes under SOFC operating conditions is of great importance. The work presented in this chapter therefore stands as important proof-of-concept on the uses of XANES to probe in situ redox chemistry in SOFC materials. L2N1 and L4N3 were ideal materials on which to demonstrate this technique; they show interesting and varied defect chemistry yet contain just the single redox-active element, nickel. This means that analysis at a single absorption edge is representative of the electrochemical state of the material. This is a simplification over studying materials with many such elements where coupled redox changes may occur. The unique advantage of the XANES technique is that it can be carried out at ambient pressure, and under different atmospheres given suitable equipment. This was demonstrated by heating L2N1 under nitrogen; a greater reduction was found than by heating under air (cf. Figure 7.3). Such ability is essential for improved in situ studies of SOFC materials, working towards eventual studies on SOFCs in operando. This is because processes occurring at the gas/solid interface are fundamental to the device. In the next chapter the techniques developed here are improved upon.

7.4 Summary

Nickel K-edge XANES has successfully been used to determine the nickel oxidation state in L2N1 and L4N3 powders in situ at room temperature and IT-SOFC temperature (650 °C). For both there is a reduction on heating. These data were correlated to the defect chemistry of the phases to gain insight into the changing concentrations of ionic charge carriers. From this it was shown that at operating temperature the number of interstitial oxygen ions in L2N1 will be reduced whereas the number of oxygen vacancies in L4N3 will be increased. The redox chemistry for both materials was followed over a full heating/cooling cycle from which it was seen that changes to the oxidation state are reversible. To demonstrate the capability of XANES to collect data under a variety of conditions, particularly atmospheric pressure using different atmospheres, L2N1 was heated under nitrogen and the oxidation state was found to reduce more than when heating in air.
References

Chapter 8 - Improved *in situ* studies on SOFC cathode materials: simultaneous XANES and ACIS on symmetrical cells

8.1 Introduction

The work described in the previous chapter was proof-of-concept that XANES can be used to explore SOFC materials *in situ* at high temperature. Since the publication of these data[1], related research has been carried out on the cathode material LSCF by Itoh *et al.* [2]. They probed the iron and cobalt K-edges as samples were reduced under low $pO_2$ at 900 and 1000 K, and found that cobalt showed the greatest reduction. Itoh’s work and that presented in the previous chapter were carried out at different light sources, but there is a striking similarity between them in the configuration of the beamline setup. In both cases the cathode materials were tested as powders diluted in $h$-BN and data obtained in transmission geometry. This arrangement is easily achieved and allows for existing beamline furnace equipment to be used; however it clearly bears little resemblance to the cathode of an SOFC. Whilst these methods have been invaluable for proving the relevant concepts, the value of carrying out further such studies is questionable. As discussed in Chapter 3 it is desirable to test a cathode directly, rather than just testing the material from which it is made. This avoids the need for many assumptions during data analysis.

A factor that has an effect on cathode performance is polarisation. A detailed electrical study into polarisation effects on La-Ni R-P phases has been carried out by Pérez-Coll *et al.* [3]. They observed that DC polarisation during ACIS testing leads to improved performance for L2N1 and L3N2 electrodes at high current fluxes. L3N2 is the $n = 2$ La-Ni R-P phase, it has similar defect chemistry to L4N3 studied in this thesis[4], so the two might be expected to behave similarly under polarisation. Pérez-Coll however does not put forward a mechanism to explain these findings. It is clear therefore that further work is required to understand how these phases behave as SOFC cathodes. Polarisation effects have been noted in other cathode materials and one of the proposed explanations for this involves redox behaviour of transition metal cations [5, 6]. If this mechanism is present in the La-Ni R-P phases it could be hoped that this is observable via nickel XANES data.

In this chapter equipment is developed to enable simultaneous XANES and ACIS data to be obtained *in situ* on symmetrical cells at high temperature under electrical polarisation. The motivations for this were twofold. Firstly, symmetrical cells are considered a good
representation of a real SOFC; this is why they are routinely tested by ACIS. Therefore XANES studies on them would be a stepwise improvement on the conditions used in the previous chapter. Secondly, the paper by Pérez-Coll leaves clear unanswered questions over the behaviour of La-Ni R-P phases under polarisation. In particular the redox chemistry of nickel under these conditions has not been explored.

8.2 Equipment development

In developing custom equipment various requirements had to be met. Key was the ability to heat a symmetrical cell to temperatures relevant to IT-SOFC materials (500 – 700 °C); to press a platinum mesh against the electrodes of the cell to provide electrical connections; and to position the cell in such a manner to allow for incident synchrotron light to impact upon one of the electrode layers. Heating was achieved using a circular IR heating element (Heraeus Noblelight Omega 80008212). This has an in-built gold reflector that directs the IR radiation towards its centre (Figure 8.1). IR heating is increasingly being used in such in situ rigs due to its compact nature and efficient heating[7]. Temperature control was managed by a standard Eurotherm unit. The internal diameter of the element was approx. 22mm; a Macor sample holder was machined to fit inside this (Figure 8.2). It consists of male and female sections designed such that the symmetrical cell and platinum meshes fit inside. The two parts screw together holding the meshes firmly against each side of the symmetrical cell, providing the electrical connections. Each end of the holder is open allowing for a thermocouple to be positioned close to one of the electrodes and X-rays to be incident on the other. The X-rays first had to penetrate the Pt mesh so this was chosen to be relatively coarse, with an open area of 62.7%. Pt wires were spot-welded to the meshes, run out the open ends of the holder, and connected to a Voltalab 80 PGZ 402 Universal Potentiostat such that the cells were tested in a two-electrode manner. The cells tested were similar to those from Chapter 5 (cf. Table 5.3); L2N1 and/or L4N3 electrodes deposited onto each side of LSGM pellets, approx. 11mm Ø×1.5mm thick, sintered at 1000 °C, or 1200 °C for L4N3.
Figure 8.1: Front-on view of sample holder held in alumina bricks. (1) insulating alumina brick; (2) IR element; (3) gold reflector in IR element; (4) Macor sample holder; (5) open part of sample holder, approx. 6mm across, exposing Pt mesh and electrode.

Figure 8.2: Diagram of sample holder. (1) Combined holder; (2) X-rays incident on exposed electrode; (3) fluorescent X-rays; (4) Open parts of machined Macor holder – screw thread visible; (5) Pt meshes and electrical connections; (6) symmetrical cell; (7) K-type thermocouple; (8) plan view of furnace in beam hutch demonstrating fluorescence geometry.
The sample holder was positioned inside the IR heating element, holding the symmetrical cell in the centre of the heated zone. The whole arrangement was supported in a cavity cut into insulating alumina bricks such that it was surrounded on 5 sides (Figure 8.1). On the final exposed face alumina plates were used to create an aperture such that the X-rays were not blocked but radiative heat loss from this face was minimised. The overall design was compact at approx. 150×80×80mm; this small size combined with the focussed IR element allowed for fast heating and cooling. Temperatures between 500 - 700 °C were readily reached in less than an hour and upon switching off the element the furnace cooled to room temperature on a similar timescale. For such a small furnace there is likely to be a significant thermal gradient. Hence the temperature read by a thermocouple positioned just behind the cell may not accurately reflect the temperature of the cell itself. To correct for this the furnace was calibrated. ASR values for a cell within it were compared with those obtained for the same cell using the in-house ACIS equipment (cf. Figure 4.5). An identical cell should display the same polarisation resistance when at the same temperature in different furnaces. By correlating the two data sets the temperature read by the thermocouple of the custom furnace was corrected to the temperature of the symmetrical cell in its centre.

XANES data were collected at beamline X10C at the National Synchrotron Light Source, Brookhaven National Laboratory, USA. All spectra were obtained in fluorescence geometry – this is a necessity given the opaque nature of the cells tested. Background subtraction and normalisation was achieved using the Athena GUI[8] for IFEFFIT[9] software. K-edge positions were deemed to be at a maximum in the first-derivative data; the precise position of this was found as a zero-crossing in the second derivative. A three-point smoothing algorithm included in Athena was applied to ensure consistency in the identification of this position. ACIS data were collected from 10,000 – 0.01 Hz with an AC amplitude of 25 mV. The effect of polarisation was tested from 0 – ±2.4 V. To facilitate comparison XANES and ACIS data collection times were designed to be the same at approximately 20 minutes per measurement.

Standard samples of L2N1 and L4N3 powders were also tested in fluorescence geometry. Previously only transmission data has been collected. These were prepared by mixing with hexagonal boron nitride and pressing into lozenges which were mounted in the furnace used in the previous chapter. All data were collected in an atmosphere of static laboratory air.
8.3 Results and discussion

8.3.1.1 XANES at room temperature

The room temperature nickel K-edge positions for the various symmetrical cell electrodes tested are presented in Table 8.1 and Figure 8.4 along with data for L2N1 and L4N3 powders diluted in h-BN. The edge positions for the single-phase electrodes were found to be shifted from the position of the respective powder. For L4N3 this is explained via the phase changes that were shown to occur on sintering this electrode (cf. Figure 5.8). Some decomposition occurs towards lower-order R-P phases and nickel oxide. This will decrease the nickel oxidation state and explains the lower K-edge position for the L4N3 electrode compared to powder. For L2N1 the electrode edge position is at higher energy than powder by 0.2 eV. This indicates a higher than expected nickel oxidation state here. A subsequent XRD pattern collected on this symmetrical cell revealed that the electrode had been contaminated by a small amount of higher-order phases, L3N2 and/or L4N3 (Figure 8.3). This explains the discrepancy between electrode and powder edge positions. To identify this cell it will subsequently be referred to as L2N1*. The edge positions for the composite electrodes were approximately as expected given their changing L2N1:L4N3 ratio.

![XRD_pattern](image.png)

**Figure 8.3:** XRD pattern for impure L2N1* symmetrical cell electrode. Marked regions are contributions from higher order La-Ni R-P phases.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Nickel K-edge position / eV†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
</tr>
<tr>
<td>L2N1 powder</td>
<td>8346.2</td>
</tr>
<tr>
<td>L4N3 powder</td>
<td>8347.4</td>
</tr>
<tr>
<td>L2N1* electrode</td>
<td>8346.4</td>
</tr>
<tr>
<td>60:40 electrode</td>
<td>8346.6</td>
</tr>
<tr>
<td>50:50 electrode</td>
<td>8346.8</td>
</tr>
<tr>
<td>40:60 electrode</td>
<td>8346.8</td>
</tr>
<tr>
<td>L4N3 electrode</td>
<td>8346.7</td>
</tr>
</tbody>
</table>

†accurate to ±0.1 eV

**Table 8.1:** Ni K-edge positions from fluorescence XANES at different temperatures for materials tested. Edge positions defined at maximum 1st derivative of normalised absorbance.

**Figure 8.4:** Ni K-edge positions from fluorescence XANES for powders and symmetrical cell electrodes at room and high temperatures.

There are discrepancies between the edge positions found via fluorescence geometry here and those found by transmission geometry in the previous chapter. An important difference between the two is that in transmission geometry a simultaneous reference nickel foil spectrum is obtained (cf. Figure 4.7). The edge position of this is calibrated to the stated value for nickel metal, 8333.0 eV, and this shift applied to the sample scan. This calibration is not available in fluorescence geometry. For this reason the oxidation state is not quantified from these fluorescence data by comparison to standard nickel compounds. What can still be seen qualitatively from the edge position is whether or not there has been oxidation (edge shift to higher energy) or reduction (edge shift to lower energy).

### 8.3.1.2 XANES at IT-SOFC temperatures

K-edge positions at elevated temperatures are summarised in Table 8.1 and Figure 8.4. The different electrodes behave similarly; typically from room temperature to 620 °C the
edge shifts towards lower energy by 0.2-0.3 eV implying a reduction in the nickel oxidation state. Some cells showed a further slight reduction between 620 and 670 °C. The exception was the L2N1* cell which showed no reduction at 620 °C, but by 670 °C a reduction of a similar magnitude to the other cells. Figure 8.5 shows XANES data for the 60:40 cell with the shift at high temperature evident. The sharp ‘glitch’ indicated in the figure is an artifact from the monochromator crystals. It was consistently at the same energy and indicates that the monochromator calibration is stable; similar behaviour has been reported previously on this beamline[10]. A pre-edge feature is visible at about 8334 eV; this is due to a ‘forbidden’ 1s → 3d transition as discussed in the previous chapter.

![Figure 8.5](image)

**Figure 8.5:** Nickel K-edge XANES data at room temperature, 620, and 670 °C for a 60:40 cell electrode. Data are representative of all electrodes tested. Inset shows the region of the edge step with the shift towards lower energy at high temperature clearly evident. Glitch marked is due to an imperfection in the monochromator.

Over the course of the electrical testing to be described below the cells were at elevated temperature for up to 4 hours with no change observed in the K-edge position over this period. Upon cooling to room temperature the K-edge positions returned to their pre-testing positions implying that the reduction at high temperatures is reversible. The behaviour of the electrodes is consistent with the data from the previous chapter on L2N1 and L4N3 powders[1] and corresponds to a reduction in the nickel oxidation state between room and high temperature. For the L2N1-part of the composite this shows that there will be fewer interstitial oxygen ions available for ionic conductivity whereas for L4N3 there will be a greater number of oxygen vacancies available. The performance of
the composite electrodes will be affected by a subtle interplay between these factors. That no shift in the K-edge is observed over the testing period is pleasing as durability is of paramount importance for SOFC materials. 'Cyclability' is also a desired property possessed by the materials demonstrated by the fact that the redox behaviour is reversible, i.e. the K-edges return to their pre-testing values on cooling.

**8.3.1.3 ACIS data at open-circuit voltage**

Figure 8.6 shows typical ACIS data at 620 and 670 °C presented on a Nyquist plot; these were for a 60:40 cell under open-circuit conditions and are representative for the rest of the electrodes. The background electrical noise evident in these data is due to the non-ideal environment at the synchrotron. Nevertheless, data were readily obtained and the electrode signal is strong. Due to this noise ECM fitting was not attempted; ASRs were calculated from the difference between estimated high- and low-frequency intercepts with \( Z'' = 0 \). Figure 8.7 compares these for the electrodes.

![Nyquist plot](image)

**Figure 8.6:** ACIS data for a 60:40 cell at 620 and 670 °C. Data normalised to zero series resistance.

The purpose of this part of the research was not to undertake a detailed electrochemical study of these electrodes as this has already been described in Chapter 5. The relative performance shown here is consistent with that work; composite electrodes are again shown to perform better than single-phase, with a 50:50 composite giving the lowest ASR. What is most important in this part of the thesis is the demonstration of combined XANES and ACIS studies *in situ* at high temperature, i.e. the data for Figure 8.5 and Figure 8.6 were collected simultaneously. To date there has only been one other report showing this capability, by Hagen *et al.* who published similar *in situ* data on LSCF at a parallel time to
this research[11]. The data presented here is the first time such measurements have been made on La-Ni R-P phases.

![Log(ASR) vs 1000/T for tested cells. ASR estimated from high- and low-frequency intercepts from Nyquist plots.](image)

**Figure 8.7:** log(ASR) vs 1000/T for tested cells. ASR estimated from high- and low-frequency intercepts from Nyquist plots.

### 8.3.1.4 **ACIS and XANES data under polarisation**

SOFCs are electrochemical devices and hence operate under polarisation, typically of the order of 1 V. To further simulate the conditions of an SOFC *in operando* similar polarisations were applied to the symmetrical cells during data collection. This caused a pronounced change in the ACIS data. Arcs for all the cells contracted and became more depressed, indicating reduced cell resistance. The largest effect was for L4N3 and is shown in Figure 8.8. The level of noise in the data increased markedly. This was particularly apparent at low frequencies where reliable data became hard to acquire. Pérez-Coll[3] comments that two-electrode measurements are not ideal for probing the effects of polarisation and that a three-electrode setup is preferred. The custom *in situ* furnace equipment developed here does not allow for such measurements.
**Figure 8.8:** ACIS data for L4N3 cell at 620 °C under open circuit and 1.4 V. Data normalised to zero series resistance. Inset: close-up of data at 1.4 V; points at frequencies below $10^0$ Hz omitted for polarised cell.

**Figure 8.9:** First derivative of normalised fluorescence for L2N1* cell at room temperature and 670 °C, under different polarisations. Dashed line is at 8346.4 eV, the K-edge position at room temperature. It is evident that the maximum of the first derivative is invariant with polarisation.
XANES data collected during polarisation showed no change from the open-circuit data for any of the cells. This was confirmed for the L2N1* cell up to ±2.4 V. It was thought plausible that perhaps the nickel reduction that occurs during heating supresses the possibility of any further redox changes due to an applied bias. ±2.4 V was applied to L2N1* at room temperature to test this theory, but again no change was seen in the K-edge position. Figure 8.9 displays the first derivative of the absorbance for these L2N1* XANES data. It is clear that the maximum in this, *i.e.* the Ni K-edge position, is invariant with polarisation. Consideration needs to be given to the penetration depth of the X-rays as this will be the region of the sample being probed by the technique. The attenuation length is defined as the depth into the material where the intensity of the X-rays has decreased to $1/e$ of the value at the surface, approx. 37%. The Beer-Lambert law can be written as;

$$I_x = I_o \exp(-\mu \rho x) \quad \text{Equation 8.1}$$

where $I_x$ is the intensity at depth $x$, $I_o$ the intensity at the surface, $\mu$ the mass absorption coefficient and $\rho$ the material density. From this the attenuation depth is;

$$x = \frac{1}{\mu \rho} \quad \text{Equation 8.2}$$

Using data from Henke *et al.* [12] and estimating that the porous electrode layer is 50% theoretical density the attenuation depth is calculated to be of the order of 10 μm. A further consideration is the utilisation length as predicted by the Adler model[13]. This is the distance beyond the TPB that effective oxygen reduction will take place (*cf.* Chapter 1.3.1). The significance of this is that at distances greater than this length from the electrolyte the model predicts that the electrode will not be reduced upon polarisation. Using values for $D^*$ and $k$ from Skinner and Kilner at 700 °C [14], with the typical values for $\epsilon$, $\tau$, and $\alpha$ given by Adler [13], the utilisation length for L2N1 is estimated to be of the order of 2 μm. The thickness of the tested electrodes was approx. 30 μm, meaning that the electrode region inside the utilisation length is not reached by the X-rays. Therefore a symmetrical cell with thin L2N1 electrodes was tested to ensure that this region was probed. This was prepared in the same manner as the initial layer from the functionally-graded electrodes tested in Chapter 6; it has electrodes approx. 5 μm thick. It was hoped that this could be tested at the same temperatures as the thicker cells, but unfortunately equipment failure prevented this. Room temperature XANES data were collected on this cell at open-circuit voltage and under polarisation, again with no change evident. These data lead to the conclusion that the bulk redox chemistry of nickel in these materials is
dominated by thermal effects. Similar behaviour was observed by Hagen for cobalt and iron redox chemistry in thin LSCF electrodes fully penetrated by the X-ray beam[11].

It must be noted again that the aim of this section is not to explore in detail the electrochemical properties of these electrodes. The goal was to demonstrate that polarisation does affect the performance, and to explore in situ any changes in redox chemistry linked to this. A detailed electrical study into polarisation effects on La-Ni R-P phases has already been carried out by Pérez-Coll et al. [3]. They observed that DC polarisation during ACIS testing leads to improved performances for L2N1 and L3N2 electrodes at high current fluxes, consistent with that seen here. No explanation has yet been put forward to explain these phenomena.

The effect of a polarisation on more traditional perovskite SOFC cathode materials has received significant attention in the literature. Performance changes have been noted and various mechanisms have been proposed to explain these. These involve;

(a) partial reduction of the transition metal cation, leading to an increased number of oxygen vacancies therefore facilitating oxygen incorporation[5, 6],

(b) microstructural changes in the electrode that may lead to improved oxygen diffusion[15, 16],

(c) cation diffusion leading to enhanced electrode properties at the surface[17-20].

Considering the R-P phases explored in this work, analogous mechanisms could take place. For L4N3, a phase containing a significant concentration of oxygen vacancies (a) would correspond to;

$$2\text{Ni}_{\text{ni,R-P}}^3 + \text{O}_{\text{o,R-P}}^2 + \text{V}_{\text{O,LSGM}}^\bullet + 2\text{e}^- \rightarrow 2\text{Ni}_{\text{ni,R-P}}^2 + \text{O}_{\text{o,LSGM}}^\times + \text{V}_{\text{O,R-P}}^\bullet$$  \[Equation 8.3\]

where $\text{Ni}_{\text{ni,R-P}}^3$, $\text{Ni}_{\text{ni,R-P}}^2$, $\text{O}_{\text{o,R-P}}^2$, and $\text{V}_{\text{O,R-P}}^\bullet$ respectively represent Ni$^{3+}$, Ni$^{2+}$, O$^2$, and oxygen vacancies present in the R-P phase, and $\text{V}_{\text{O,LSGM}}^\bullet$ and $\text{O}_{\text{o,LSGM}}^\times$ represent oxygen vacancies and O$^2$ in LSGM.

This mechanism would lead to improved performance in L4N3 – this phase has a large number of Ni$^{3+}$ ions available to be reduced and the creation of more oxygen vacancies should improve its cathode properties. However for L2N1 this is not the case. This phase has oxygen interstitials rather than vacancies so cathodic polarisation would reduce the concentration of these and impair the performance thus;
where $O'_{LR-P}$ represents an interstitial $O^{2-}$ in the R-P phase.

Mechanism (b) is considered unlikely as it is implausible that small microstructural changes in the electrode should be able to cause such significant changes to the electrode performance. When considering (c) the surface chemistry of the materials is an important factor. Low-energy ion scattering (LEIS) has revealed that L2N1 is terminated by a LaO layer [21]. In the next chapter it will be demonstrated that this is the case for the entire R-P series. Skinner [14], Bassat [22], and Smith [23] have all shown that the activation energy for oxygen surface exchange in L2N1 is significantly greater than for diffusion. Opposite results have been found for perovskite materials [24] containing oxygen vacancies. It has been proposed that the surface layer of LaO is the reason for the high activation energy seen for L2N1 [25]. Building on this with respect to mechanism (c), it is plausible that polarisation-induced cation diffusion brings some nickel to the surface of the La-Ni R-P phases, leading to improved oxygen reduction catalysis. However, such a mechanism would be expected to lead to some persistence in the performance changes upon removal of the polarisation; ions would relax back to their equilibrium position over time [17, 19]. Pérez-Coll observed no such persistence, seeming to eliminate mechanism (c).

This leads to a somewhat contradictory state. On the one hand various aspects of mechanism (a) make it seem the most likely explanation, yet on the other hand we observed no changes in the nickel K-edge position throughout our testing. This could be explained if any nickel redox activity is confined to a surface region of the material only when inside the utilisation length, rather than throughout the bulk. Changes here may be beyond the sensitivity of the XANES measurements made. It is apparent that a complete explanation for the behaviour of these La-Ni R-P phases under polarisation has yet to be reached. What this study proves is that the bulk nickel redox chemistry in these materials is dominated by thermal effects. Therefore any proposed contribution of nickel $2+$/3+ redox to the electrochemical performance of these cathodes under polarisation must occur only over a thin surface layer and not throughout the bulk of the material.
8.4 Application of *in situ* furnace equipment to further SOFC cathode materials

8.4.1 Introduction

So far the custom *in situ* furnace had only been used on the La-Ni R-P electrodes used throughout this thesis. These were chosen as they are model systems with only one multivalent element; however they are still relatively unusual as SOFC cathodes. To demonstrate the utility of this equipment and the potential for these combinatorial *in situ* measurements the next step was to study state-of-the-art cathode materials. As discussed in Chapter 2.3.2, LSCF is a perovskite-structured material that has been shown to be an excellent cathode when used in a composite with CGO[26, 27]. Barriers to the utilisation of these cathodes involve various degradation phenomena. These include SrO segregation to the surface forming a passivating layer [19, 20, 28, 29], and susceptibility to poisoning from chromium species originating from metallic interconnects[30]. The latter phenomenon is still not fully understood. Studying the effect of poisoning on electrochemical performance is naturally achieved via ACIS on poisoned cathodes; however studying the chromium species themselves is less straightforward. Chromium is thought to contaminate the cathode via gaseous Cr\(^{6+}\) species, CrO\(_3\) or CrO\(_4\)(OH)\(_2\), forming from Cr\(_2\)O\(_3\) scales on the surface of the metal[31]. These react with the cathode to form a variety of different species. The concentration of these is relatively low, Bucher found 4 atom-% Cr at the surface of a cathode contaminated from a metallic Cr source[32]. With regard to the identity of these species Horita suggests that Cr\(_2\)O\(_3\) forms at the TBPs and SrCrO\(_4\) forms on the cathode surface[33]. Numerous studies have observed SrCrO\(_4\) [34, 35], yet not all recent work takes this into account[36] indicating that there is still a lack of consensus over the nature of the deposited species. Poisoned cathodes are often analysed post-mortem *ex situ* using an acid treatment to access the relevant areas [34, 35, 37]. These conditions are decidedly atypical for an SOFC hence are not ideal for studying a phenomenon that only occurs during operation. Other studies simulate poisoning by artificially contaminating the cathode using a Cr-species such as Cr\(_2\)O\(_3\)[38] or Cr(NO\(_3\))\(_3\) solution[39], however how these react during testing has not been considered. From this brief review it is apparent that chromium poisoning of LSCF is still not fully understood, and that no *in situ* studies have been presented on the nature of the chromium deposits. Given that chromium poisoning only occurs during operation it would seem to be a phenomenon in particular need of *in situ* study. Therefore this represents an ideal area on which to demonstrate the utility of *in situ* XANES studies on SOFC electrodes to the wider community. To validate this capability a variety of questions will need to be answered;
a) The concentration of poisoning deposits is relatively low; can these be observed in situ by Cr K-edge XANES? A post-mortem ex situ XANES study on a poisoned solid-oxide electrolyser has shown that the technique is feasible.

b) Can the nature of the deposited species be verified i.e. can the presence of Cr$_2$O$_3$ or SrCrO$_4$ be shown?

c) For artificially-poisoned cathodes does the contaminating species undergo reactivity?

These were considered below.

### 8.4.2 Sample preparation

Artificially-poisoned symmetrical cells were prepared by Lee as according to her recent publication. Briefly, LSCF6428 ink is screen-printed onto dense CGO10 pellets and sintered at 1000 °C for 2 hours. Chromium poisoning is simulated by brushing a solution of Cr(NO$_3$)$_3$·9H$_2$O in ethanol over the electrodes. The concentration of chromium can be varied by the number of coats applied, and was checked by energy-dispersive X-ray spectroscopy (EDX). For her study Lee then sintered these as-poisoned electrodes at 900 °C for 2 hours. To test the effect of this Cr K-edge XANES data were obtained on both as-poisoned and poisoned-then-sintered electrodes. To explore a range of poisoning levels such samples were prepared with 1 and 8 wt.% Cr.

### 8.4.3 Results

#### 8.4.3.1 Preliminary studies

Artificially-poisoned cathodes were to be probed by XANES analysis at the Cr K-edge. For Cr$^0$ this is at 5989 eV. Consideration must be given to the other elements present in the sample as there is the possibility that absorption edges from these could interfere with the edge of interest. Edges from lanthanum in the LSCF cathode and cerium in the CGO electrolyte are in proximity to the Cr K-edge, La$^0$ L$_{II}$ = 5891 eV; La$^0$ L$_{III}$ = 6266 eV; Ce$^0$ L$_{II}$ = 6164 eV. These will be shifted to higher energy in ceramics reflecting the increased oxidation state. To check that Cr K-edge absorption could be seen fluorescence data were collected over a wide energy range spanning these edges, as shown in Figure 8.10. These were for pure LSCF and 8% Cr-poisoned LSCF symmetrical cells, and were normalised to the La L$_{III}$ edge step. It is clear that the Cr K-edge is not affected by the nearby lanthanide L-edges; however the pre- and post-edge regions do contain contributions from these. This indicates that care must be taken over normalisation of the Cr K-edge XANES in these electrodes.
Next it had to be verified that XANES could be studied for chromium concentrations appropriate for poisoned cathodes, so data were compared for 1% Cr-poisoned vs. 8% Cr-poisoned electrodes; Figure 8.11 shows that the lowest concentration does indeed give an adequate signal.

**Figure 8.10**: Normalised fluorescence for pure LSCF and 8% Cr-poisoned LSCF electrodes on CGO between 5750 and 6450 eV. Relevant absorption edges labelled. Data normalised so that the La $L_{II}$ edge step is from 0 – 1. LSCF composition is $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$.

**Figure 8.11**: Normalised Cr K-edge XANES for 8% and 1% Cr-poisoned LSCF
**8.4.3.2 Chromium species in artificially-poisoned LSCF**

XANES spectra were obtained for standard Cr compounds spanning a range of oxidation states; Cr foil, Cr$_2$O$_3$ and SrCrO$_4$. This was to help identify the chemical nature of the deposited Cr species by comparison. These are displayed in Figure 8.12. The large pre-edge at approx. 5995 eV from SrCrO$_4$ originates from transitions from 1s states to unoccupied 3d states. This is a well-established identifier for Cr$^{6+}$ species [40-42], however this feature is also present to a smaller degree for Cr$^{4+}$ species, including Sr$_2$CrO$_4$ [43].

![Figure 8.12: Chromium K-edges for standard compounds. Data were obtained in transmission geometry.](image)

To explore the chemistry occurring during the artificial poisoning process a cell was tested after impregnation of chromium nitrate solution but before sintering, a so-called ‘as-poisoned’ electrode. Data were obtained at room temperature and *in situ* at 670 °C and are displayed in Figure 8.13. A pre-edge feature similar to that seen for SrCrO$_4$ is evident in the *in situ* spectra. This indicates that even at the relatively low temperature of 670 °C chromium reactivity has occurred, with at least some of the initial Cr$^{3+}$ species oxidised. The consensus in the literature is that the Cr$^{6+}$ species SrCrO$_4$ is present on poisoned LSCF. These data are consistent with a mix of Cr$^{3+}$ and Cr$^{6+}$, however, without standard spectra for Cr$^{4+}$, Sr$_2$CrO$_4$ cannot be ruled out. What is unambiguous is that an oxidation has occurred; this should be taken into account for any further analyses on these artificially-poisoned cathodes.
Figure 8.13: Cr K-edge XANES data for 8% Cr-poisoned LSCF as-poisoned and in situ at 670 °C.

It was hoped that the chromium oxidation could be followed in situ during the heating process, enabling the kinetics of the reaction to be probed. This would have been similar to the tests done on L2N1 and L4N3 powders between room temperature and 650 °C (cf. Figure 7.4). Unfortunately equipment failure prevented this. Figure 8.14 compares the room temperature spectra for an as-poisoned electrode and an electrode poisoned then sintered at 900 °C for 2 hours, these are also compared to the spectra for Cr$_2$O$_3$ and SrCrO$_4$.

Figure 8.14: Room temperature Cr K-edge XANES data for 8% Cr-poisoned LSCF as-poisoned and after sintering at 900 °C for 2 hours, compared to Cr$_2$O$_3$ and SrCrO$_4$ spectra.
The overlap between the pre-edge peak for SrCrO₄ and the poisoned sintered electrode is clear, as is the shift to higher energy for the main absorption edge, indicating partial Cr³⁺ oxidation.

### 8.4.3.3 The effect of polarisation on artificially-poisoned LSCF

The custom *in situ* equipment has the ability to polarise the symmetrical cells during data collection. Electrode polarisation is known to be a factor in Cr-poisoning of LSM cathodes[44], however poisoning in LSCF is generally considered to be more chemically-driven[34, 45]. To explore this an 8% Cr-poisoned and sintered cell was polarised to ±1.5 V at 670 °C whilst *in situ* XANES data were collected. There was a slight reduction in the energy of the main absorption edge between room temperature and 670 °C, but the polarisation resulted in no change as evidenced in Figure 8.15. This implies that the mixed-valence chromium produced in the artificial poisoning process is insensitive to polarisation.

**Figure 8.15:** Normalised Cr K-edge XANES and first derivative for 8% Cr-poisoned and sintered LSCF electrode. Data obtained at room temperature and 670 °C under different polarisations.

### 8.4.3.4 Iron and cobalt chemistry in artificially-poisoned LSCF

The edge positions for iron and cobalt were probed as shown in Figure 8.16. It is clear that the cobalt K-edge is shifted towards lower energy for 8% Cr-poisoned LSCF compared to pure, whereas the iron edge is unchanged. The edge positions at maximum first derivative are shown in Table 8.2, and indicate a reduction in the oxidation state upon poisoning for cobalt, but no change for iron. This could reflect the role cobalt has in chromium poisoning. The formation of SrCrO₄ could form from reaction with a surface-segregated
layer of SrO, or direct reaction with the perovskite [33]. Both Itoh and Hagen have shown by XANES that cobalt is more readily-reduced than iron in bulk LSCF [2, 11]. The Co XANES found in this work shows a significant change in the pre-edge region between pure and poisoned LSCF. This could indicate the formation of a new cobalt-containing compound caused by the presence of the chromium contaminant. La(Co,Cr)O₃ and CoCr₂O₄ have been found on poisoned LSC electrodes [46] so these are potential candidates. These preliminary Fe and Co XANES data highlight an important area for further study.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Fe K-edge position / eV†</th>
<th>Co K-edge position / eV†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure LSCF</td>
<td>7127.7</td>
<td>7725.0</td>
</tr>
<tr>
<td>8% Cr poisoned-then-sintered</td>
<td>7127.7</td>
<td>7724.8</td>
</tr>
</tbody>
</table>

Table 8.2: Room temperature iron and cobalt K-edge positions for pure and 8% Cr poisoned-then-sintered LSCF. Edge positions obtained from maximum first derivative.

![Figure 8.16](image)

Figure 8.16: Room temperature iron and cobalt K-edge XANES data for pure and 8% Cr poisoned-then-sintered LSCF.

### 8.4.4 Discussion

This is the first time an in situ XANES study has been carried out on Cr-poisoned LSCF cathodes. The questions posed in the introduction have been answered to a greater or lesser degree. In answer to (a) it has clearly been shown that chromium poisoning can be probed in situ by XANES. The nearby edges from lanthanum and cerium do not interfere with the chromium absorbance; chromium can be observed even at concentrations as low as 1 wt.%; and can also been seen in situ at high temperature and under polarisation. This is proof-of-concept of the functionality of this technique.
For (b) the characteristic pre-edge peak from Cr\textsuperscript{6+} species has been identified as a means to gain insight into the chemical identity of the poisoning species. A linear combination fit was attempted for the data on poisoned electrodes. This is a mathematical procedure whereby XANES data from an unknown sample is compared to the spectra of a variety of standard compounds. The aim is to find a linear combination of the standard compounds that accurately matches the unknown sample. In the case of this research such a fit was attempted using the standard Cr\textsubscript{2}O\textsubscript{3} and SrCrO\textsubscript{4} spectra; however this did not give satisfactory results. The likely reason for this is that other chromium species are present beyond Cr\textsubscript{2}O\textsubscript{3} and SrCrO\textsubscript{4} and the standard spectra for these is required for an adequate fit. (La,Sr)CrO\textsubscript{3}, has been suggested as an intermediate species en route to SrCrO\textsubscript{4} formation so it would be useful to obtain XANES data on such perovskite materials \cite{37, 47}, also the Cr\textsuperscript{4+} phase Sr\textsubscript{2}CrO\textsubscript{4} would be informative. It is clear that further work needs to be done in this area to fully understand the chemical nature of the deposited chromium species. What this research shows is that this should be achievable \textit{in situ}. It is hoped that this could stimulate the community to move away from relying on post-mortem \textit{ex situ} analyses.

With regard to (c) it has been shown that the chromium species deposited by artificially poisoning LSCF with aqueous chromium (III) nitrate depend on the thermal history of the sample. Even at temperatures as low as 670 °C some oxidation of Cr\textsuperscript{3+} was observed. This means that future research using methods to simulate poisoning must consider the reactivity of the species they use.

Finally, the Fe and Co XANES data indicate that these \textit{in situ} techniques need not be confined to studies on chromium to further the understanding of chromium poisoning. Studying the cathode material itself as well as the deposited species could help guide research towards phases more tolerant chemically to chromium.

### 8.5 Summary

Novel equipment has been developed to enable simultaneous XANES and ACIS data to be collected \textit{in situ} on symmetrical cells at temperatures relevant to IT-SOFCs. This setup also allowed for the cells to be polarised during these measurements. The equipment was validated on the La-Ni R-P electrodes tested in Chapter 5. For the as-sintered nominally single-phase electrodes the nickel K-edge positions at room temperature were shifted from the edge positions of the relevant powders. These shifts were consistent with the phase changes seen in the XRD patterns which showed the presence of other R-P phases in the as-sintered electrodes. On heating to 670 °C, \textit{i.e.} to temperatures appropriate for IT-SOFC materials, the \textit{in situ} K-edge position for all electrodes moved to lower energy by 0.2-
0.3 eV. This agrees with the data on L2N1 and L4N3 powders in the previous chapter and correlates to a reduction in oxidation state of approximately 0.1. For L2N1 in the electrodes this will mean a decreased concentration of oxygen interstitials and for L4N3 an increased number of oxygen vacancies. ACIS data collected at open-circuit voltage using the in situ equipment were consistent with those of the dedicated in-house setup used in Chapter 5. Polarising the cells clearly affected the area specific resistance of the electrodes; however the XANES data were invariant. This result was discussed with respect to literature reports on the response of electrodes to polarisation. Particular attention was paid to the debate over the mechanisms behind this, with the contribution from this research being that the bulk nickel redox chemistry in La-Ni R-P materials is dominated by thermal effects. Hence it was concluded that any proposed involvement of nickel redox with the electrochemical performance of these electrodes under polarisation must occur at the surface.

Further to this, XANES has been demonstrated as a powerful technique for in situ studies on Cr-poisoned LSCF cathodes. It was found that chromium species used to simulate poisoning undergo oxidation on thermal treatment, and that polarisation does not lead to further changes. The cobalt oxidation state was observed to have changed during poisoning whereas iron remains constant. These findings were discussed and are considered to be proof-of-concept for further studies in this important area.
References

Chapter 9 - Surface chemistry of the La-Ni R-P series

9.1 Introduction

In a MIEC cathode the ORR occurs at TPBs and the gas/electrode interface. It seems highly unlikely that molecular oxygen can penetrate into the crystal structure; hence it is the outer surface layer where this reduction is believed to take place. This region is therefore of great importance to the electrochemical properties of the cathode material. In the previous chapter in situ XANES data obtained during polarisation indicated that any changes to the nickel redox chemistry in La-Ni R-P electrodes are confined to a surface region. This further emphasises the importance of the chemistry here. This chapter therefore explores the surface chemistry of the materials in question.

LEIS is a technique unique in that it can study the outermost layer of a material in isolation from those underneath (cf. Chapter 4.3.10). Other 'surface sensitive' methods in reality are sampling a near-surface region containing many atomic layers[1]. LEIS is therefore increasingly being used to examine the surfaces of SOFC materials. For the R-P series this has so far been confined to \( n = 1 \) members; \( \text{La}_2\text{Ni}_x\text{O}_{4+\delta} \) [2] and \( \text{La}_{2-x}\text{Sr}_x\text{Ni}_{4+\delta} \) [3], with AO termination found each time. In this chapter LEIS studies are extended across the whole range of the La-Ni R-P series, \( n = 1, 2, 3, \) and \( \infty \). This is the first time such a systematic study has been presented.

9.2 Materials selection

The materials tested were L1N1, L2N1, L3N2 and L4N3 as-described in Chapter 5. These were studied as-sintered, or as-received in the case of commercial L2N1 powder. Powders were loosely pressed into pellets for mounting in the LEIS analyser. These will therefore have a relatively rough surface, however in many previous cases such samples are known to give an adequate LEIS signal[4].

9.3 Results

9.3.1 Surface cleaning and characterisation

Under normal laboratory conditions the surfaces of materials are contaminated by a range of adsorbed species including water and organic molecules. These block the signal from the material surface and thus should be removed. A standard surface-cleaning method is to expose the samples to atomic oxygen[5]. The adsorbed species consist of light
elements; these are best resolved using a light primary ion therefore the cleaning process is followed using a 3keV \textsuperscript{4}He\textsuperscript{+} beam. A spectrum is taken of the as-received powder, this is then exposed to atomic oxygen for a period of time then re-analysed. This procedure is repeated until the exposure leads to no further changes in the LEIS spectra. The progression is displayed in Figure 9.1 for L4N3; this is representative for all samples. The spectra after 60 and 70 minutes of cleaning are identical hence the powder is considered clean after this period.

![LEIS spectra](image)

**Figure 9.1:** LEIS spectra for L4N3 powder sample cleaned by atomic oxygen for increasing exposures. Peaks identified in the shaded areas; expected energy for nickel indicated with no peak present. Primary ion beam: 3 keV \textsuperscript{4}He\textsuperscript{+}.

The region of increasing intensity at energies below 500 eV is a background signal due to secondary ions sputtered from the surface such as O\textsuperscript{+} [4]. There are three peaks evident on the cleaned surface of L4N3, the energy of each corresponds to a particular atom. These are identified in Figure 9.1 as belonging to lanthanum, oxygen, and sodium. The latter is a common contaminant which segregates to the surface during synthesis. The former two arise from the material itself. The expected energy region for nickel is identified and no peak is observed here leading to the conclusion that this material is A-site, \textit{i.e.} LaO, terminated. This was observed across the whole La-Ni R-P series.
9.3.2 Depth profiling

A light primary ion is required to follow the cleaning process, however this is not ideal for studying materials containing heavy elements such as lanthanum. Therefore for more detailed characterisation a primary 3keV $^{20}\text{Ne}^+$ beam was used. A negative consequence of switching to a heavier primary ion is that the secondary ion background will be greater. This is due to the higher energy of the primary beam leading to increased sputtering. Spectra were taken using $^{20}\text{Ne}^+$ for the cleaned surfaces of the materials and then depth profiles were obtained. This is achieved via an iterative process; LEIS data are collected using $^{20}\text{Ne}^+$, the analysis region is sputtered for 30 seconds using a 0.5 keV $^{40}\text{Ar}^+$ beam, then another LEIS spectrum of this area is taken. For L4N3 these data are shown in Figure 9.2, these are representative for the other phases. During the sputtering there will be some mixing of atomic layers, therefore beyond a certain level the bulk of the phase will have been reached and no further changes are seen in the spectra.

**Figure 9.2:** Depth profile for L4N3 obtained after successive 5 keV $^{20}\text{Ne}^+$ analysis and 0.5 keV $^{40}\text{Ar}^+$ sputtering. Peaks corresponding to Ni and La identified. Sputter dose is directly proportional to depth within the sample; initial, median, and final measurements are outlined as a guide for the eye. Data are representative for all La-Ni R-P phases.

At the surface only a lanthanum peak is evident. A contribution from nickel is seen after the first sputtering cycle indicating that it is present just under the surface of the materials. The intensity of this peak increases with the sputtering dose until a constant bulk value is reached. The contributions to the spectra are depicted in Figure 9.3. The secondary ion background signal is modelled as an exponential decay. The cations give a
surface peak and, under ideal conditions, a flat background at lower energies. This is due to scattering events from cations below the surface and is known as the ‘in-depth’ signal.

**Figure 9.3:** Contributions towards LEIS spectrum of L4N3 after sputtering to the bulk of the material. There is a background component due to sputtered secondary ions. For the cations the peaks are due to surface scattering, the flat profile at lower energy is the ‘in-depth’ contribution.

The intensity of a peak in the LEIS spectrum reflects the amount of the corresponding ion present at the surface probed by that scan. Once the sputtering has reached the material bulk it can be assumed that layer mixing results in a cation distribution equal to the stoichiometry, i.e. in the case of L4N3 the bulk spectra will reflect a 4La:3Ni ratio. This allows for an internal calibration process to quantify the intensity of the LEIS peaks. The peak intensity is averaged over the final 10 spectra and this taken to be the stoichiometric ratio. This is then applied to the intensity for all spectra to build up a depth profile. For a generic oxide with cations A\_a B\_b C\_c… this method is as follows;

\[
\text{cation signal (A)} = \frac{I_A}{I_{A,bulk}} \times \frac{a}{\sum \text{cations } a + b + c \ldots} \quad \text{Equation 9.1}
\]

\[
\text{normalised cation signal (A)} = \frac{\text{cation signal (A)}}{\sum \text{cations cation signal (A) + (B) + (C) \ldots}} \quad \text{Equation 9.2}
\]

where \(I_A\) is the peak intensity from cation A for that particular spectrum; \(I_{A,\text{bulk}}\) the peak intensity from cation A in the bulk region; and \(a, b, c\ldots\) the stoichiometries for cations A, B, C…

Due to this method the normalised cation signals will always sum to unity.
Depth profiles generated in this manner are shown in Figure 9.4 for the whole La-Ni R-P series. The non-zero signal shown for nickel at zero ion dose, i.e. at the cleaned surface, is due to the noise evident in the spectra (cf. Figure 9.2) being interpreted as peak intensity by the software. There is a swift increase in the nickel level over the initial sputtering steps, and a flat profile is reached after a similar ion dose for each material. This indicates that the lanthanum at the surface represents just a termination rather than a deeper segregation forming a lanthanum-rich region. The materials were tested as powders hence the depth sputtered to cannot be determined accurately. Similar experiments have been performed on epitaxial La$_{2-x}$Sr$_x$CoO$_{4+\delta}$ thin films and the depth found by white light interferometry[6]. La$_{2-x}$Sr$_x$CoO$_{4+\delta}$ is an R-P phase and can be expected to behave similarly to the materials tested in this research. The sputtering from a dense epitaxial film is anticipated to be different from that from a powder, but these values allow for a tentative depth estimate to be made.

**Figure 9.4:** Internally-calibrated depth profiles taken from LEIS spectra obtained after successive sputtering steps. Closed circles: lanthanum; open circles: nickel. Depth estimated from data on epitaxial La$_{2-x}$Sr$_x$CoO$_{4+\delta}$ thin films.

### 9.4 Discussion

The surfaces of the whole La-Ni R-P series were found to be lanthanum-terminated. No nickel was observed until the surface had been removed by sputtering. Considering the generic R-P structure, (ABO$_3$)$_n$AO, this corresponds to AO termination, and agrees with that found previously for L2N1 and other $n = 1$ R-P phases[2]. For strontium-doped L2N1
the surface contains both lanthanum and strontium, consistent with their shared occupancy of the A site in the structure [3]. LEIS studies on materials with structures related to R-Ps also show exclusively AO termination; on the perovskites LSM[7], LSCF[8] and Sm1−xSrxCoxO3−δ [9], and for the double perovskite GdBaCo2O5+δ [2]. These experiments have been carried out on samples of a range of different morphologies – single crystals, dense ceramics, and powders – and after various different heat treatments. Throughout these AO termination persists. This is an important result with respect to the properties of these materials as SOFC cathodes. The ORR is thought to occur via the redox chemistry of transition metal ions in the structure[10], yet these are found on the B site hence are not at the surface. In order for ORR to take place there must therefore be a means by which oxygen can come into contact with these ions. Entropy dictates that the surface of a material will not be perfect and must contain some defects. Two such defects that would allow for transition metal ions to be visible at the surface are cation antisite disorder;

\[
A^x_{\text{A, surface}} + B^x_B \leftrightarrow B^x_{\text{A, surface}} + A^x_B
\]  

Equation 9.3

and A-site Schottky defects at the surface revealing B-site cations underneath. These are depicted in Figure 9.5.

![Figure 9.5: Schematic of Schottky and antisite surface defects. Adapted from [4].](image)

The detection limit of LEIS is of the order of 10 ppm under ideal conditions[1], however sensitivity will decrease when looking at powder samples. Antisite defects will not be seen in a LEIS experiment if at low enough concentration. Further to this, B-site ions revealed by surface Schottky defects will not give a strong signal due to the blocking of scattered ions. Therefore it is highly likely that such defects are present but not observable by LEIS and are what allow for B-site cation catalysis of oxygen reduction. The AO termination of these R-P materials is not ideal for their electrochemical properties. This may be reflected in the high activation energies found for surface exchange compared to self-diffusion in
L2N1 [11-13]. These ionic transport properties are yet to be determined for L3N2 and L4N3, but these may show similarly high values for surface exchange.

An alternative means for considering the surfaces of materials is by computational modelling. This has been applied to R-P phases, however BO or mixed AO/BO termination is the consistent prediction [14-17]. This opposes the wealth of experimental data and indicates that care must be taken over the interpretation of such computational studies. It is clear that further work is required in this area if simulations are to accurately reflect material properties.

9.5 Summary

LEIS measurements have probed the surface chemistry for the L1N1, L2N1, L3N2 and L4N3, i.e. spanning the whole La-Ni R-P series. This is the first time such a systematic study across a whole series has been presented. The surfaces for all materials were found to be LaO terminated. This was discussed with respect to published reports on the surfaces of other SOFC materials; these are also AO terminated. The implications of this with regard to the ORR were considered, and surface Schottky and cation antisite defects proposed allowing for B-site cations to come into contact with oxygen. It was noted that computational studies on \( n = 1 \) R-P phases predict BO or mixed AO/BO termination, opposing these experimental data.
References

Chapter 10 - Conclusions and further work

This research was undertaken with two broad aims – to develop SOFC cathodes working within the Ruddlesden-Popper family of phases, and to apply novel in situ characterisation techniques to SOFC cathodes.

L2N1 was identified as an R-P phase with attractive ionic conductivity at SOFC temperatures. This phase has been widely studied by the community however its performance as a cathode material is limited by its poor electronic conductivity. This material was taken to be a starting point identifying the promise of R-P phases as SOFC cathode materials; improvements were sought whilst remaining in this family. The higher order phase L4N3 is known to have better electronic conductivity than L2N1 and to date has received little attention in this field. This phase was synthesised by a sol-gel method and tested for its potential as an SOFC cathode material. Its chemical compatibility with the common electrolyte LSGM was confirmed by reactivity studies; however the phase itself undergoes spontaneous decomposition at the high temperatures required for it to adhere adequately to a dense LSGM pellet. The maintenance of high electronic conductivity despite this slight decomposition was confirmed. The performance of L4N3 as an SOFC cathode material was found to be inferior to that of L2N1. For example, symmetrical cells had an ASR of 9.77 Ωcm$^2$ at ≈ 600 °C compared to 3.79 Ωcm$^2$ for L2N1 cells. The properties of L2N1 and L4N3 were considered together and it became apparent that they are good candidates for forming a composite cathode; the former with good ionic and the latter with good electronic conductivity. Chemical compatibility between the two was confirmed at the expected temperature range and symmetrical cells with composite electrodes covering a range of L2N1:L4N3 ratios were tested. A 50:50 wt.% mix was found to give the best performance and this surpassed both single phase L2N1 and L4N3 electrodes with an ASR of 2.82 Ωcm$^2$ at ≈ 600 °C. SEM micrographs of fracture surfaces of these cells revealed a non-ideal microstructure, particularly in terms of the electrolyte/electrode connectivity. It was therefore reasoned that the performance of these electrodes could be improved upon whilst still remaining within the R-P family. With this in mind, functionally graded electrodes were fabricated consisting of a thin compact L2N1 interlayer adjacent to the electrolyte, then a thicker porous L2N1+L4N3 composite layer, topped by a thin porous L4N3 current-collinating layer. The performance of these graded electrodes was an improvement over the ungraded composites. The lowest ASRs found in this research were 15.59, 2.29, and 0.53 Ωcm$^2$ at 500, 600, and 700 °C respectively for an electrode with thin compact L2N1|50:50 L2N1+L4N3 composite|thin porous L4N3 layers. These results are amongst the best-in-class for this family of material.
The electrochemical performance of each layer in the graded electrodes could be further examined using improved current collection, such as a thin layer of platinum or silver. This would help to ascertain the origins of the improved performance seen in the complete graded electrode; whether this is simply an effect of improved current collection via the outer L4N3 layer, or if there is significant a contribution from the microstructural enhancement.

Similar functional grading research carried out over a parallel timeframe has shown that using PLD to deposit the L2N1 interlayer is an improved method over the screen printing used in this research [1]. It would be of interest to modify the functionally graded L2N1+L4N3 electrodes to utilise this technique as this is expected to lower the ASR. Further efforts could also be made to optimise the graded electrodes microstructurally by careful variation and control over parameters such as particle size, ink composition, sintering temperature, and electrode thickness. These experiments would be essentially iterative and should in general be applied to any system thought to show enough promise.

For unusual materials such as R-P phases attempts should also be made to understand their fundamental properties. For L2N1 these are well established with a variety of studies published concerning its crystal structure and ionic-electronic conductivity. Experiments probing the latter are facilitated by the ease of formation of dense specimens of this phase. L4N3 is much less understood and this is partly due to the current inability to form said dense specimens. This difficulty can be overcome in a variety of ways. Computational modelling can be an invaluable tool for predicting the behaviour of a material. L4N3 has yet to be considered in this manner therefore such work could be of great interest. However care must be taken over the interpretation of such studies as discrepancies between available experimental and computational data can occur. For \( n = 1 \) R-P phases, the excellent agreement between the diffusion pathway predicted by molecular dynamics simulations and that found experimentally by MEM analysis on neutron diffraction data is highlighted as an example of successful modelling (cf. Figure 2.5); however the prediction of Ni-terminated surfaces in L2N1 contradicts consistent experimental observations of La-termination, providing a counter-example (cf. Chapter 9.4). Computational studies on L4N3 should be carried out but attempts also made to verify any findings experimentally. Methods do exist for gaining insight into oxygen reduction kinetics of porous or powdered samples. These include conductivity relaxation, where the electrical conductivity of a sample is monitored over time with an abrupt change in \( pO_2 \) [2]; and pulse isotopic exchange, where a brief ‘pulse’ of \(^{18}\text{O}\)-enriched oxygen is passed over a sample and the resultant \(^{18}\text{O}_2/^{16}\text{O}^{18}\text{O}/^{16}\text{O}_2\) ratio probed [3]. These techniques could be applied to L4N3 to
explore its catalytic activity towards oxygen reduction and would be the first time such
data have been presented.

One of the reasons for considering La-Ni R-P phases in the first place is the absence of
strontium; this element has been linked with various deleterious phenomena in traditional
perovskite cathodes. It has been suggested that strontium-free cathodes may show better
long term stability under operating conditions however this has yet to be fully established.
Electrodes developed in this research have only been tested for up to 120 hours at
operating temperatures. Viable devices are expected to operate for periods in excess of
10,000 hours so it is clear that further work in this area could be carried out. These
experiments should be extended to probe the influence of humidity and chromium
poisoning. Reactivity with platinum was noted at high temperatures so this should be exclud-

The in situ study of SOFC cathodes was identified as an area with great scope for further
work. XANES was chosen as a powerful non-destructive technique that can investigate the
redox chemistry of elements within materials. Importantly this capability is available at
ambient pressures; a clear advantage over other methods. Preliminary experiments were
performed on powder samples of L2N1 and L4N3 dispersed in h-BN at SOFC-relevant
temperatures. These demonstrated proof-of-concept that the transition metal oxidation
state can be probed and changes observed between room temperature and elevated
temperature. From these the changing concentration of ionic change carriers in the two
materials was inferred. For L2N1 there will be a reduction in the number of interstitial
oxygen ions whereas for L4N3 there will be a greater number of oxygen vacancies.

Building on this work, bespoke equipment was developed to enable the simultaneous
acquisition of in situ XANES and ACIS data on symmetrical cells at operating temperature
and under electrical polarisation. This represents a significant advance as these conditions
are close to those typical for an SOFC in operando. This equipment was tested on the L2N1,
L4N3, and composite L2N1+L4N3 electrodes developed during this research. Electrical
polarisation was found to have a strong effect on the ACIS data causing a contraction in the
Nyquist plot arcs indicating a reduction in the ASR. Interestingly polarisation led to no
observable changes in the XANES data; this was confirmed up to ±2.4 V and for electrodes
thin enough to be fully penetrated by the X-ray beam. This shows that the bulk nickel
redox chemistry in these materials is dominated by thermal effects. These findings were
discussed with respect to published work on the polarisation response of La-Ni R-P
cathodes as well as traditional perovskite cathodes. A variety of mechanisms were
considered and it was suggested that the role of transition metal redox chemistry in this
process must be confined to a near-surface region of the electrode that is beyond the detection limit of the XANES technique.

In order to verify the capabilities of the bespoke in situ equipment on an alternative system attention was turned to the problem of chromium poisoning of LSCF cathodes. This area was identified as a significant barrier to commercialisation of SOFCs that remains not fully understood. Given that this phenomenon occurs primarily during operation it is surprising that little in situ work has been presented in this area. Artificially-poisoned LSCF symmetrical cells were tested in the bespoke in situ equipment to gain insight into the chemical identity of the chromium deposits. This could be achieved at concentrations as low as 1 wt.% Cr. A strong pre-edge feature was noted as indicative of a chromium oxidation state of +4 or +6. For electrodes poisoned with a Cr 3+ species this pre-edge rapidly became apparent on heating to operating temperatures. This demonstrates that Cr oxidation occurs readily under SOFC cathode conditions and that further reactivity of artificial contaminants must be taken into account in such experiments. The iron and cobalt redox chemistries in LSCF were also explored. Poisoned cathodes had a lower cobalt oxidation state than virgin cathodes, with the iron oxidation state being unchanged.

This thesis has demonstrated that in situ XANES and ACIS data can be obtained for porous symmetrical cell electrodes at operating temperatures under polarisation. The logical next step would be to extend this capability to porous electrodes of prototype anode|electrolyte|cathode single cells. This will clearly require some equipment modification, or perhaps the manufacture of a second bespoke system. Gas handling will be necessary to provide fuel to the anode. Given the combustible nature of this fuel, the high temperatures required for in situ study, and the stringent health and safety requirements at synchrotron light sources, this equipment will require careful design and extensive in-house testing before final use. In the current setup symmetrical cells simply ‘slot in’ to a re-usable sample holder, an arrangement that allows for quick and easy sample changing at the beamline. Due to the requirement of gas-tight seals around each single cell this is unlikely to be feasible in a new system. A potential approach could be to fabricate a series of identical sample holders and seal a single cell into each. The integrity of these could then be confirmed in-house. These holders would be designed in parallel with a furnace that allows for them to slot in and out at the synchrotron facility with relative ease.

The work done on chromium poisoning opens up a large area for further work. An advantage of in situ studies in this area is the high performance and ubiquity of LSCF – it is
a material of interest for a range of fields and industries. Successes in this area would therefore be widely read in the community, highlighting the value of advances in *in situ* characterisation. Improvements could be made in a number of ways. Spectra from a greater variety of chromium compounds should be obtained for comparison to the data from poisoned cathodes. The use of a third generation synchrotron such as the Diamond Light Source would enable data acquisition with much greater speed and resolution. It is possible to foresee an experiment simulating the *in operando* poisoning of LSCF: a chromium source could be placed close to a porous LSCF electrode in a furnace and Cr K-edge XANES data collected as a function of time via sequential measurements. The pre-edge feature would be expected to 'grow in' to the spectra, and the changing intensity of this peak could be used to extract kinetic data on the poisoning process. This would be a significant improvement over current testing methods which often involve *ex situ* post-mortem analysis.

The surface monolayer of SOFC cathode materials is believed to play a key role in performance as it is here where oxygen reduction and incorporation will take place. Therefore a systematic study of the surfaces of the \(\text{(LaNiO}_3)_n\text{LaO} \)\(R-P\) series was carried out using the LEIS technique. Each phase \( n = 1,2,3 \) and \( \infty \) was found to be lanthanum-terminated. This is the first time an entire family of phases has been considered in such a manner. The implications of this surface chemistry were discussed. Lanthanum is considered to be less catalytically-active than nickel towards oxygen, therefore defects revealing nickel at the surface were proposed as allowing for reduction and incorporation of the gaseous species. These LEIS studies could be extended to explore the influence of temperature and electrical polarisation on the surface chemistry. The latter experiment would provide insight into the mechanisms behind the large influence polarisation has been shown to have on the ASR of electrodes made from these materials. A satisfactory explanation for this has yet to be put forward and remains an area for further investigation.
References

List of Publications

Journal publications from this research

"In situ determination of the nickel oxidation state in La$_2$NiO$_{4+\delta}$ and La$_4$Ni$_3$O$_{10-\delta}$ using X-ray absorption near-edge structure"

"Materials development for intermediate-temperature solid oxide electrochemical devices"

"Novel La$_2$NiO$_{4+\delta}$ and La$_4$Ni$_3$O$_{10-\delta}$ composites for solid oxide fuel cell cathodes"

"Functionally graded composite La$_2$NiO$_{4+\delta}$ and La$_4$Ni$_3$O$_{10-\delta}$ solid oxide fuel cell cathodes"
R.J. Woolley, S.J. Skinner, *Solid State Ionics, manuscript submitted for review*

"In Situ Measurements on Solid Oxide Fuel Cell Cathodes – Simultaneous X-ray Absorption and AC Impedance Spectroscopy on Symmetrical Cells"
R.J. Woolley, M.P. Ryan, S.J. Skinner, *Fuel Cells, manuscript submitted for review*

Conference contributions from this research

"In situ studies of cathodes for solid oxide fuel cells"
Poster presentation, 31st RSC Solid State Group Christmas Meeting, University of Liverpool, 19th-20th December 2011

"Synthesis and in situ studies of cathodes for solid oxide fuel cells"
Oral presentation, Zing Solid State Chemistry Conference, Lanzarote, 24th-27th February 2012

"Improved in situ studies on SOFC cathodes: simultaneous X-ray absorption and AC impedance spectroscopy on layered Ruddlesden-Popper phases"
Poster presentation, 10th European SOFC Forum, Lucerne, 26th-29th June 2012

"Synthesis and in situ studies of cathodes for solid oxide fuel cells"

"Improved in situ studies on SOFC cathodes: simultaneous X-ray absorption and AC impedance spectroscopy on layered Ruddlesden-Popper phases"
Oral presentation, MRS Fall Meeting & Exhibit, Boston, 25th-30th November 2012

"High performance functionally graded Ruddlesden-Popper cathodes for IT-SOFCs"
Oral presentation, 19th International Conference on Solid State Ionics, Kyoto, 2nd-7th June 2013

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