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A New Approach to the Material, Design and Manufacture of the Oxide Cathode

By

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Abstract

In this project, two new oxide cathode designs, namely the \textit{integrated oxide cathode} and the \textit{two-layer/impregnated oxide cathode}, and their respective manufacture processes were designed and developed. The two oxide cathodes were both produced from \( \text{BaSr}(\text{CO}_3)_2 \), Ni filaments and polymer additives. The integrated oxide cathode is a one component mixture of \( \text{BaSrO}_2/\text{Ni} \) and the two-layer/impregnated oxide cathode consists of a porous Ni substrate with \( \text{BaSrO}_2 \) impregnated on and in it. Casting and heating are the two most important steps of manufacturing both cathodes. The effects of various processing parameters during these two main steps on the properties of the resultant cathodes were investigated by TGA, EDX and SEM.

The results revealed that the optimum compositions of the casting suspensions are 50wt\%BaSr(\text{CO}_3)_2/Ni, 50wt\%polymer, and a solid content of 13.3wt\% for the integrated oxide cathode and 15wt\%Ni, 85wt\%polymers, and a solid content of 13.3wt\% for the two-layer/impregnated oxide cathode. A two-steps heating process: a low temperature of 500\degree C in air and a high temperature of 1100\degree C in \( \text{N}_2/10\%\text{H}_2 \), was proven to be the proper heating conditions to obtain the appropriate microstructures for the oxide cathodes. The SEM microscopy showed that satisfactory porous microstructures with porosities of 50\% could be obtained in both two cathode materials through careful control of the processing conditions. Moreover, both the two manufacturing approaches showed much lower material wastage (55\% for the integrated oxide cathode and potentially 0\% for the two-layer/impregnated oxide cathode) compared with the conventional manufacture process, in which the material wastage was as high as 90\%.

The integrated oxide cathode showed a low mechanical strength, which prevented it from practical implication, while the two-layer/impregnated oxide cathode presented more promising properties for further investigation.
List of Acronyms

DHC    direct heated cathode
IHC    indirect heated cathode
CRT    cathode ray tube
LCD    liquid crystal display
SMFL   sub-miniature fluorescent lamp
CCFL   cold cathode fluorescent lamp
PVA    polyvinyl alcohol
PEO    polyethylene oxide
PEG    polyethylene glycol
XRD    X-ray diffraction
SEM    scanning electron microscopy
TGA    thermalgravimetric analysis
DTA    differential thermal analysis
THF    tetrahydrofuran
DMSO   dimethyl sulfoxide
PMAA   polymethacrylic acid
PAA    polyacrylic acid
EDX    energy dispersive X-ray microanalysis
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Part One
Introduction
Chapter 1

Introduction

1.1. **Background**

Cathodes are the devices that emit electrons under the influence of an activating energy, which may take the form of heat, light, voltage.\(^1\) They are very versatile components that are employed in many products, such as electronic displays, lighting, and fuel cells. There are many types of cathodes depending on the form of activation and/or the geometric shape, such as cold cathodes, hot cathodes, photo cathodes and secondary emission cathodes.

Of those, thermionic cathodes, which are a kind of hot cathodes in which the liberation of the free electrons is caused by the transfer of thermal energy from a heater, are the focus of this study.\(^2\) Broadly there are two main classes of such thermionic cathodes depending on the way of heating:\(^2\)

a) Direct Heated Cathode (in short DHC)—typically comprising a suitably coated heater filament which directly liberates electrons.

b) Indirect Heated Cathode (in short IHC)— typically comprising a separated emitter and heat source.

![Fig 1.1(a), Structure of IHC cathode (reproduced and modified from ref [2]).](image-url)
In addition, there are a wide range of subcategories of these cathodes such as impregnated, scandate, etc, of which the oxide cathode, which forms the focus of this study are one type.

Oxide cathodes can be used in both direct and indirect heating designs\cite{4} with the latter being the main emphasis of this investigation. A simplified structure of such a cathode is shown in Figure 1.1(a).\cite{2} In this case, the heating current does not flow through the cathode, but through a separate heated element that is known as filament. The heat energy from the filament is conducted into the emitting surface of the cathode between cathode and heater. The design of a typical commercial indirect heated oxide cathode is shown in Figure 1.1(b).\cite{3}

![Emitter material](image)

**Fig 1.1(b). Image of a commercial conventional oxide cathode for CRT display (reproduced from ref [3]).**

The basic design of this form of oxide cathode is made up of the emission material, which typically is a mixture of barium oxide (BaO) and strontium oxide (SrO) or a solid solution of these oxides in the form of a spray deposited coating on a metallic substrate, usually a nickel (Ni) alloy.\cite{4} Some designs of cathode also use a triple oxide formulation based on Ba, Sr and Ca oxides.\cite{4,19}

DHC oxide cathodes are in widespread use in low-pressure discharge lamps\cite{7} whilst the most important practical application of IHC oxide cathodes is in the
cathode ray tubes, such as television, computer monitors, automated teller machines, video game machines, oscilloscopes and radar displays.\textsuperscript{[1]} The continued rapid growths of television/computer applications and embedded computer controllers in a wide variety of products have led to increasing demand for such devices.\textsuperscript{[1]} Despite the advert of alternative display technologies, such as LCD, the cathode based on oxide cathode has still remained the most cost-effective means and the market for cathodes and CRT displays is envisaged to remain extremely large for at least the next decade.\textsuperscript{[6,31]}

More recently, oxide cathodes have been considered for potential applications in replacing the conventional sub-miniature or cold cathode fluorescent lamps (SMFL, CCFL) used as the backlights of liquid crystal displays (LCD's) and as light sources for optical scanners.\textsuperscript{[8]} Currently these employ cold cathode designs due to size and cost issues.\textsuperscript{[8]} However, the conventional oxide cathode based thermionic emission mechanism is intrinsically more efficient than the direct stimulation mechanism of the electrons in cold cathode operation in traditional SMFL/CCFL,\textsuperscript{[8]} which leads to a promising potential market opportunity for them.

The current manufacturing process for the IHC oxide cathode involves spraying the emission material onto a Ni alloy substrate, which provides both mechanical support and plays an active role in the "activator" and operation of the device.\textsuperscript{[4]} Established for more than 50 years, this process is effective, producing low cost manufacture with good microstructural control.\textsuperscript{[4]} However, there are also a number of significant drawbacks, in particular inherently extremely high waste of the material (>95%), low yield and potential for environmental damage due to the excessive use and release of harmful barium compounds.\textsuperscript{[11,12]}

There has been an active interest in developing and improving the performance of the cathode,\textsuperscript{[6,14]} especially in terms of increasing current densities (ideally at lower operating temperatures), and greater robustness, particularly in terms of ion bombardment.\textsuperscript{[31]} However, commercial and economic pressures have demanded that the improvements of the cathode are not associated with increase in raw materials or component costs,\textsuperscript{[22]} and there is an urgent need for new, more cost effective and
efficient materials and manufacturing processes to help achieve this. In the case of potential use of IHC oxide cathodes in lighting applications, the requirements to control cost are even more demanding than in CRT applications.
1.2. Aims

The main aim of this project is thus to develop new approaches to the materials processing and production process for the conventional oxide cathode emitter, in order to reduce the manufacturing costs by means of enhancing material usage and reduced manufacturing complexity. At the same time, it is hoped this will lead to a reduction in environmental impact. For practical implementation, this new system will be required to have high production yield, be relatively simple to implement, and also provide good quality and performance. Initially comparable emission performance of the new cathode is necessary whilst potentially improved emission performance would be desirable in the longer term.

To this end, two novel approaches have been developed, both of which have focused on the net shape fabrication of the emitting component of the cathode.

These comprise:

1. An integrated emitter in the form of a composite Ni/BaSrO$_2$ composite with the two components dispersed either homogeneously or in a functionally graded composition. The term “integrated oxide cathode” is used to describe this hereafter. A schematic picture showing this is shown in Figure 1.2(a).

2. A multilayer structure in which the emitting BaSrO$_2$ compound is incorporated into and onto a highly porous percolating conductive Ni framework denoted “two-layer/impregnated oxide cathode”. A schematic diagram of such a cathode is shown in Figure 1.2(b).

For comparison, the structure of conventional cathode is together shown in Figure 1.2(c).
Fig 1.2(a),(b). Schematic representation of new designs of oxide cathodes developed in this work, (a), integrated oxide cathode; (b), two-layer/impregnated oxide cathode.

Fig 1.2(c). Schematic representation of a conventional oxide cathode
1.3. Thesis

The work carried out during this research can be considered to comprise two discrete elements: (i) the development of the integrated oxide cathode, and (ii) the development of the two-layer/impregnated oxide cathode. Although the basic principles and methodology are broadly common and described jointly, the results and discussion for the two designs are separately reported in this thesis in Parts 4 and 5.
Part Two

Literature Review
Chapter 2

Oxide Cathode

2.1 The operation principle of oxide cathode

The remainder of this report will focus solely on the indirect heated oxide cathode, which was the subject of this investigation. This will be referred to as the "oxide cathode".

2.1.1 Emission principle – thermionic emission

The electron emission principle of the oxide cathode is based on "thermionic emission", which is the emission of electrons by substances that are highly heated with the charged particles being called thermions.$[^9]$

The thermal emission current of electrons from a thermionic cathode can be described by the Richardson-Dushman equation as below: $[^{15,16}]$

\[
J = A_o S T^2 \exp(-\Psi / kT)
\]

where $J$ is the thermionic emission current in A, $A_o$ is Dushman’s constant equal to $120 \text{A} \cdot \text{cm}^{-2} \cdot \text{deg}^{-2}$, $S$ the emission surface area in cm$^2$, $T$ the absolute temperature in K, $k$ Boltzman’s constant ($8.6 \times 10^{-5} \text{eV/K}$) and $\Psi$ the work function in eV, which is the energy required for an electron to be released from an emitter surface to the infinite vacuum.$[^{24}]$

From the Richardson-Dushman equation (2.1.1(a)), it can be seen that the thermionic emission is a function of the following parameters: the emission surface area, work function and the achievable operating temperature. In order to obtain a higher current ($J$), larger emitting surface area ($S$), higher operating temperature ($T$) and lower work function ($\Psi$) are desirable for the cathode.

The work function $\Psi$ varies approximately linearly with temperature, according to the following relationship: $[^{18,19}]$
2.1.1(ii)

\[ \Psi = \Psi_o + \alpha T \]

where \( \Psi_o \) is the work function at \( T = 0K \), \( \alpha \) is the temperature coefficient of the work function.

The work function (\( \Psi \)) is also a function of the composition of the emitting material. The (BaSr)O_2 composition used currently as the emitting coating in the oxide cathode exhibits exceptionally low values of \( \Psi \) compared to other coating material compositions. For example, the work function of a normal dispenser cathode is 2.1-2.2eV although special Os/Ru coatings can reduce this to 1.9eV.\(^{25}\) This compares to that of the oxide cathode, which is as low as 1.3-1.5eV.\(^{30}\) This low work function allows the oxide cathode to operate at relatively low temperatures, typically of the order of \( \approx 800^\circ C \),\(^{22,31}\) with this heat being generated both by the use of the heater filament and also internal resistive heating in the oxide material as the emission current is increased.\(^{37}\)

The second parameter, the surface area (\( S \)), depends on the oxide coating characteristics, such as particle size, shape and porosity in the coating.\(^{17}\) The high surface area, porous structure conventionally achieved by spray deposition of the oxide cathode emitter is thus crucial to the emission performance, with smaller particle size and high porosity in the coating being preferred. An example of the microstructure of such a coating in the oxide cathode is shown Figure 2.1.1(a).\(^{10}\)

Fig 2.1.1(a). Microstructure of the cathode material.(reproduced from ref [10])
In terms of the effect of the temperature \( T \), the number of electrons emitted increases rapidly as the temperature of the substance rises.\(^1\) However, in practice the maximum operational temperature is limited by the evaporation of the coating material (Ba and BaO), which is linked with the cathode life, in that the operation of an oxide cathode is based on the excess barium in the coating.\(^{20,21}\) The higher the operation temperature, the faster the evaporation of the Ba emitting material. Consequently, the operating temperature is a compromise, which can provide both satisfactory emission and good life.\(^{20}\)

All of these parameters of the cathode are determined by a combination of the materials used, process route, microstructure, chemical purity and device design, and in practice there is a complex relationship between these factors. For example, the emitting surface areas often change in service as a function of temperature and/or time due to coarsening process.

### 2.1.2 Conduction mechanism

Apart from the above parameters of the cathode, it has been found that the emission current is also influenced by the electronic conductivity in the oxide coating\(^{35,36}\) and the significance of this influence, in turn, depends on the operating temperature \( T \). There are altogether three conduction mechanisms for the electrons in the oxide coating, as depicted in Figure 2.1.2.\(^{35}\) The three conduction mechanisms as shown are surface conduction, pore conduction and solid-state conduction. The solid-state conductivity contains the effect of electron transfer from grain to grain.\(^{38}\)

Fig 2.1.2, Electron conduction mechanisms of in the oxide coating. 1, surface conduction. 2, pore conduction, 3, solid-state conduction (reproduced from ref [35]).
The electronic conductivity could also be written quantitatively\[^{38}\] as:

\[
\sigma_e = n_e q \mu_e
\]

where \(\sigma_e\) is the electronic conductivity, \(q\) is the charge of an electron, \(n_e\) is the electron density and \(\mu_e\) is the electron mobility in (BaSr)O\[^{38}\].

The accepted model by Loosjes and Vink\[^{27}\] proposed that emission at high current density at high temperatures (>700K) relies on the electron conduction through the pores in the coating, also called the pore plasma. Whilst at temperatures below 600K, conductivity is determined by the surface properties of oxide particles, that is mainly by surface conduction.\[^{26-29}\] These two processes operate in parallel for intermediate temperatures 600-700K.\[^{26-28}\] At normal operation temperatures (\(\approx\) 1100K), the pore plasma mechanism dominates, with the pore structure of the oxide emitter thus being critical to the effective operation of the cathode.
2.2 **Structure and material of oxide cathode:**

The basic structure of an IHC oxide cathode, as shown in Figure 2.2(a) and (b), typically consists of a nichrome tube about 1.5mm in diameter, with the top of the nichrome tube being covered with a metal cap. This metal cap serves as the substrate for the emitting coating and is normally made of a base metal such as nickel and essentially contains a small amount of important alloying additives such as Mg, Si, which function as the reducing element or activating elements (see Section 2.4.2).[40]

The electron emitting material is essentially a solid mixture of alkaline earth oxide (BaO+SrO)[4] in about equal molecular proportions, which is deposited as a thin (65±10μm) porous coating.[6]

The oxide coating of the cathode is a discontinuous structure with a porosity of more than 50%.[4] The emission performance of the cathode is primarily determined by the characteristics of this emitting material, for the reasons previously discussed, in terms of surface area for emission ad conduction mechanisms in the cathode. The metal cap is mounted on a coated nichrome tube, within which the heater s situated. The heater wire typically comprises a tungsten wire filament heated to achieve a sufficient cathode surface temperature, usually around 800°C,[22,31] for the efficient emission of electrons.

![Diagram of oxide cathode](image)

(a) (reproduced from ref [31])
Fig 2.2(a) and (b), Schematic diagram showing the structure of an IHC oxide cathode and a whole oxide cathode assembly made by Philips.

The cathode device is typically fixed in position within the electron gun assembly by a series of suspension bands, which are laser welded to the rigid metal support and sealed with a suitable glass materials through which the electrical connection are made via feed-through pins.\textsuperscript{[34]}
2.3. Conventional manufacturing process of oxide cathode

The present manufacturing process of the oxide cathode has been described by Herrmann and Wagener. Typically this involves compressed air spray deposition as indicated in the flow chart shown below (Figure 2.3).

Fig 2.3, Flow chart of the manufacturing process of commercial CRT cathode

The Ni substrate is made by nickel alloy containing reducing agents (as mentioned in Section 2.2) and the alloy is punched to form a cap-shape. Then, both degreasing and etching is applied to the Ni substrate, to ensure the good “wetting” between Ni and spraying solution, then washing in deionised water followed by an acetone rinse and air dry at room temperature.
Since the emitting material, BaSrO₂, is unstable in the presence of atmospheric moisture and CO₂, the cathode manufacturing process involves the use of the corresponding carbonate [BaSr(CO₃)₂] mixture or solid solutions as precursors. The coating is deposited by spraying a suspension of these barium/strontium carbonate [BaSr(CO₃)₂] particles in an organic carrier containing an organic binder, such as nitrocellulose, which is to provide adhesion between the carbonate particles and the nickel surface.

The spray deposition process involves mounting of the nickel cap and heater/filament on a jig and the application of a mask. The carbonate suspension is then sprayed onto the Ni substrate by a single spray nozzle using a robotic system. The as-sprayed carbonate coating has a thickness of 65±10μm, and planar surface area 0.0165cm². The Ni cap substrate has a thickness of 400μm and the same surface area. In general, the spraying technique is a mature, relative simple and effective technology, which has been employed for about 50 years. In industry, it allows production of the oxide cathode with required high surface area and high porosity, and to date, no viable suitable alternative has been identified.

The subsequent stages after the spraying deposition in the processing involve a "conversion" heat treatment to convert the carbonate precursor to oxide (BaSrO₂) under vacuum (10⁻⁷ mbar) in the tube assembly. The temperature of the conversion process differed from various investigations and manufacturers, normally being in the range of 800°C-1100°C. Finally a further heat treatment stage called "activation" is involved to make the oxide coating function as an electron emitter, which is carried out after thermal conversion. The activation process is carried out in situ inside the electron gun in the sealed tube assembly. Both conversion and activation will be discussed in more detail in Section 2.4.
2.4. Conversion and activation of oxide cathode

Following manufacture and assembly, the cathode must undergo two further stages before it can emit useful quantities of electrons in the gun tube for operation. These stages, shown in manufacturing process sequence (Figure 2.3), are known as: conversion (step 6) and activation (step 7).

2.4.1. Conversion of oxide cathode

As mentioned in Section 2.3, as the alkaline earth oxides are very sensitive to moisture and CO₂, the corresponding carbonates are used as precursors in the manufacturing process. These carbonates are subsequently decomposed to the oxides under vacuum in situ in the device according to the following reaction:

\[
\begin{align*}
BaCO_3 & \rightarrow BaO + CO_2 \\
SrCO_3 & \rightarrow SrO + CO_2 \\
or \quad BaSr(CO_3) & \rightarrow BaSrO_2 + 2CO_2
\end{align*}
\]

This initial decomposition stage in the cathode's operating life is known as "conversion" during which time both significant microstructural and electrical changes occur, most notably a change from insulating to semiconducting behaviour.

Also, because nitrocellulose, organic binder, is added to the carbonate as a process aid for the spray deposition process, this binder is also required to be removed by pyrolysis during this heating stage. Thus large amounts of organic gases, such as CH₄, CO, CO₂ and NOₓ, are also released during the conversion. For this reason, the conversion process is carried out in the vacuum tube whilst continuously pumping to remove these by-products.
2.4.2. Activation of oxide cathode:

In practice, the emission characteristics of BaSrO₂ are rather poor, so a further stage is necessary to produce the cathode more suitable for thermionic emission, this is known as activation.\(^\text{[33]}\)

This activation process involves reactions of the converted BaSrO₂ with activators such as Al and Mg present in the Ni cap substrate as alloying additives. During this process the activators diffuse to the Ni cap surface and react with the oxide materials liberating free barium.\(^\text{[6,31]}\) In service, these free barium atoms migrate through the oxide lattice and pore structure toward the surface during the operating life of the cathode,\(^\text{[31,40]}\) and are then deposited on the porous oxide coating surface. Figure 2.4.2 shows schematically an oxide cathode after activation.\(^\text{[22]}\)

![Figure 2.4.2: A sketch map showing the oxide cathode after activation. (reproduced from ref (22))](image)

Two examples of the reduction of BaO with two of the activators, Al and Mg, are shown as following.\(^\text{[41]}\)

\[
3\text{BaO} + 2\text{Al} \rightarrow 3\text{Ba} + \text{Al}_2\text{O}_3 \hspace{1cm} 2.4.2(\text{i})
\]

\[
\text{BaO} + \text{Mg} \rightarrow \text{Ba} + \text{MgO} \hspace{1cm} 2.4.2(\text{ii})
\]
The reaction of the various reducing elements with barium oxide occurs at different rates, contributing to the emission of the cathode at different stages in its life.\textsuperscript{40} There are several theories proposed which can explain the importance of the activation process and the role of the free barium in promoting emission. In particular, it is believed that the barium (Ba) acts as donor in the oxide at coating, creating an n-type semiconductor there and thus enhancing conductivity.\textsuperscript{18} According to the electron conduction mechanism model proposed by Zalm,\textsuperscript{47} this free Ba is also responsible for the emission and conductivity. Similarly it has been supposed that the free Ba produced generates a coating on the BaO particles which creates an emissive surface with a low work function.\textsuperscript{45,47}
2.5. Properties and performances of oxide cathode

The reason for the continuing popularity of the oxide cathode based CRT display is that it offers a number of advantages such as large screen size, fast speed and full-colour.\textsuperscript{(1)} Most importantly, the costs of such systems remain substantially lower than competitive technologies, particularly for large displays as the complexity of the electronics does not increase with display size unlike flat panel display.\textsuperscript{(1)}

Another one of the principal advantages of the oxide cathode is the very low work function as discussed in Section 2.1.1. The lower work function of the oxide cathode ensures that they require less power in operation in comparison with alternative cathode technologies.\textsuperscript{(50)} In addition, they have a lower operation temperature and hence lower barium evaporation rate and longer operation life.\textsuperscript{(19)}

However, there are also a number of inherent drawbacks with the conventional cathode.\textsuperscript{(34)} One of the most serious problems is the extensive wastage of the raw materials during spraying process. The tiny surface area of the cathode metal cap (\(\approx 0.00165\text{cm}^2\)) leads to the wastage rates during spraying as high as \(>90\%\).\textsuperscript{(34)} In terms of economics, this is a significant problem in increasing the production cost. In addition, the large amount of over-spray cannot be viably recovered or reused and must be disposed of, causing potential environmental hazards associated with the toxic barium containing powder.\textsuperscript{(34)}

Moreover, the performance of the conventional oxide cathode based electronic display is limited in dc current due to their semiconductor nature and the emission density is usually limited to approximately 2 amps/cm\(^2\) due to resistive heating effects and dielectric charging.\textsuperscript{(49)} The life at these current densities is also limited to 10,000 to 20,000 hours.\textsuperscript{(49)}

Another important problem of the oxide cathode is the formation of an interface layer. As introduced in Section 2.4.2, free barium is formed at the interface by the reduction of barium oxide by the activators and then diffuses to the outer surface of the oxide providing a low work function electron-emitting surface.\textsuperscript{(45,47)} During
cathode life, an interfacial layer grows between the nickel alloy and oxide due to the build of the reaction products of the reduction reactions which occur there. The thickness of this interface layer gradually increases with operation of the cathode and normally the thickness becomes 1 μm. This can be schematically presented in Figure 2.5.

Fig 2.5. A sketch map showing the formation of an interfacial layer of the oxide cathode during operation (reproduced from ref[22]).

The formation of this interface layer deteriorates the cathode performance and reduce the useful operational lifetime of the oxide cathode by the occurrence of two major failures. The first one is a reduction, and even prevention, of the activator diffusion toward the coating, leading to the cathode “deactivation”. The second one, called “peeling”, is a complete loss of adherence between the emissive coating and the base metal, over a small or a wide cathode interface area.
2.6. Recent developments in oxide cathode research

The oxide cathode was invented by Wehnelt in 1903\textsuperscript{[50]} and since then, such a large majority of the scientific research has been devoted to this technology that it has been stated that little further improvement on its performance can be achieved with the currently used materials.\textsuperscript{[21]} However, the emerging customer requirements for better performance in displays, and the need to compete with new display technologies has led to renewed research activity to increase the performance of the oxide cathode in recent years. In particular, quite a lot of interest has been placed on two areas, namely the interface between the Ni substrate and the spray layer, and on the composition and modification of the spray material itself.\textsuperscript{[31]}

In terms of the interface, Mitsubishi have reported work in making a tungsten coating on the Ni substrate that can increase current density.\textsuperscript{[51]} Samsung also presented results describing the use of a fine-grained Ni top layer on the Ni substrate of around 1–2\textmu m thickness.\textsuperscript{[52]} This work was claimed to improve activator diffusion via grain boundaries and hence also increased the current density.\textsuperscript{[52]}

Other attempts have been concentrated on the addition or modification to the emission material coating itself.\textsuperscript{[31]} For example, Mitsubishi have reported the addition of \ce{Sc_2O_3} to \ce{Ba/Sr(Ca)} oxide,\textsuperscript{[53]} whilst other recent investigations by Matsushita Electronics Corporation centred on the doping effects of group IV and V oxides and have shown the beneficial influence of species such as \ce{ZrO} and \ce{EuO} on electrical conductivity.\textsuperscript{[54]}

In more recent years, studies of composite oxide cathodes modified with acicular Ni particles developed in collaboration between Hodgson and co-workers at Loughborough university and Philips display components have led to significant performance increases.\textsuperscript{[36]} The basic idea behind this technology is to overcome the conductivity limitation by addition of a percolating conductive phase and results in more steady conductivity in low temperature.\textsuperscript{[36,55]} This has led to a new generation of so-called “oxide-plus” cathodes. The work in this investigation has attempted to integrate these composite cathode materials with new manufacturing approaches.
Chapter 3

Properties of the Inorganic Materials in the Cathode

3.1 Properties of barium and strontium carbonates and derived oxides

3.1.1 General properties of barium (Ba), strontium (Sr) and their carbonates

Barium and strontium both belong to the alkaline earth metals.\textsuperscript{39} Some key properties of these elements are shown in Table 3.1.1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Strontium</th>
<th>Barium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>38</td>
<td>56</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>87.62</td>
<td>137.34</td>
</tr>
<tr>
<td>Atomic radius (Å)</td>
<td>1.92</td>
<td>1.98</td>
</tr>
<tr>
<td>Ionic radius (Å)</td>
<td>1.13</td>
<td>1.29</td>
</tr>
</tbody>
</table>

The chemical formula for barium carbonate is BaCO$_3$.\textsuperscript{56} This is a white crystalline solid of typically acicular morphology (as shown in Figure 3.1.1) at room temperature and has a molar mass of 197.37 g/mol.\textsuperscript{56,57} BaCO$_3$ is a relatively unreactive compound and nearly insoluble in water\textsuperscript{58,59,60} and only slightly soluble in carbonated water.\textsuperscript{57,61} Barium carbonate is an important raw material used in high temperature synthesis of electronic materials,\textsuperscript{62} in manufacturing magnetic materials, barium salts, and pigments.\textsuperscript{63,64}
3.1.2. Thermal decomposition behaviour of barium and strontium carbonate

In the standard procedure for manufacturing the oxide cathode, a porous BaSrO₂ film is obtained by thermal decomposition of the corresponding carbonates [BaSr(CO₃)₂], together with nitrocellulose binder. This so called "conversion process" was described in Section 2.4.1.

The conversion reactions described in equations 2.4.1(i)-(iii) are readily reversible under normal atmospheric conditions, and are best expressed as an equilibrium of the form shown in equation 3.1.2.

\[
MCO_3 \leftrightarrow MO + CO_2 (M=Ba, Sr)
\]  

Due to the equilibrium of this reaction, the actual onset decomposition temperatures depend on the partial pressure of the product gas surrounding the sample, i.e. by the partial pressure of CO₂, which is in turn controlled by the respective rates of reaction leading to an equilibrium \( P_{CO_2} \) in which the onset temperature is dependent on the supply or removal of CO₂. For example, the equilibrium pressure of CO₂ over BaCO₃ at 900°C is of the order of 0.3mbar. Figure 3.1.2(a) shows a relationship between the atmosphere and decomposition temperature of BaCO₃. When the evolved gas is removed by a sweep gas or a vacuum system, the
reaction will occur more readily, i.e., at a lower temperature.\textsuperscript{[65]} For this reason and to prevent the reconversion of the oxide product by reaction with the evolved gas, a vacuum atmosphere is normally employed during the cathode conversion step.

\begin{center}
\includegraphics[width=0.5\textwidth]{figure3.1.2a.png}
\end{center}

**Fig 3.1.2(a), Relationship between temperature and p(CO\textsubscript{2}) for the decomposition of BaCO\textsubscript{3} (reproduced from ref\textsuperscript{[66]}).**

The decomposition of these two carbonates has been investigated by different researchers and under different circumstances.

J.A.N. Goncalves et al have reported an investigation of the oxide cathode conversion in vacuum.\textsuperscript{[68]} Using the increases in vacuum chamber pressure to monitor the decomposition reactions, three discrete reactions were identified as shown in Figure 3.1.2(b).\textsuperscript{[68]} The first pressure peak was observed at 450K corresponding to the nitrocellulose (binder additive) degradation, as shown in Figure 3.1.2(b). A second peak was observed at 880K corresponding to the degradation of SrCO\textsubscript{3}, and at 1100K a third peak was related to the decomposition of BaCO\textsubscript{3}. Using a mass spectrometer, the released gases from the oxidation reaction could be identified. The gases identified from the decomposition process shown in the spectrogram of Figure 3.1.2(c) were CO\textsubscript{2}, which should come from equation A in Figure 3.1.2(b), N\textsubscript{2}+CO, and were attributed to the products of decomposition of the nitrocellulose binder, and H\textsubscript{2}O, which was attributed to the products of further reaction between the pyrolysate of carbonates and nitrocellulose.\textsuperscript{[68]}
Fig 3.1.2(b). Vacuum chamber pressure as function of cathode temperature during the carbonate conversion process (reproduced from ref[68]).

Fig 3.1.2(c). Spectrogram for carbonate degradation in conversion process (reproduced from ref[68]).

It has also been shown that other heating conditions have important influences on the decomposition behaviour of the carbonates. Table 3.1.2 provides a summary of the influence of various heating conditions on the decomposition of the carbonates under various atmospheres.
Table 3.1.2. Change of the decomposition temperature with the heating conditions

<table>
<thead>
<tr>
<th>Author</th>
<th>Heating rate</th>
<th>Atmosphere</th>
<th>Pressure</th>
<th>Decomposition temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suliman[69]</td>
<td>20K/min</td>
<td>Air</td>
<td>1 atm</td>
<td>1475K-1575K (≈1200°C)</td>
</tr>
<tr>
<td>Arvanitidis[71]</td>
<td>12K/min</td>
<td>Ar</td>
<td>1 atm</td>
<td>1300K-1580K (≈1000°C)</td>
</tr>
<tr>
<td>Suliman[69]</td>
<td>20K/min</td>
<td>Air</td>
<td>1 atm</td>
<td>1405K (=1132°C)</td>
</tr>
<tr>
<td>Arvanitidis[70]</td>
<td>10K/min</td>
<td>Ar</td>
<td>1 atm</td>
<td>1000K (=727°C)</td>
</tr>
</tbody>
</table>

In investigations[70,71] by Arvanitidis, both BaCO₃ and SrCO₃ were heated at different heating rates. The results showed that both the values of the onset temperature of the reaction and the time required for the complete decomposition decreased as the heating rates increased, as the sample would attain higher temperatures quickly at faster heating rates and consequently the reaction rate would be higher.

Other conditions affecting the thermal decomposition of the carbonates include characteristics of the carbonate coating, such as particle size, composition and crystallographic structure.[32] The effect of the carbonate particle size on the decomposition time was investigated by Benjamin et al.[72] with these experiments showing that the time required to complete the decomposition process tends to increase with carbonate particle size. Experiments into the effect of powder morphology and packing have also shown that the reaction rate of a pressed SrCO₃ flake is somewhat slower than that of a loose SrCO₃ powder, particularly at high conversion temperatures, presumably due to the ease of CO₂ diffusion.[70]
3.1.3 Phase transformation of the carbonates

The thermal decomposition reactions during the heating of these carbonates [BaSr(CO₃)₂] are accompanied by various phase transformations. The alkaline earth carbonates are polymorphic materials. The crystal structures of both barium carbonate (BaCO₃) and strontium carbonates (SrCO₃) at room temperature are of the aragonite type.

For BaCO₃, two phase transformations, one from orthorhombic to hexagonal at about 1079K (806°C) and another from hexagonal to cubic at 1237K (964°C) have been identified at a heating rate of 12°C/min. The phase transformation temperature from hexagonal to cubic was also investigated by Lander who identified this to take place at 1241K (968°C) at the same heating rate.

The phase transformation of SrCO₃ has also been investigated in the same study by Lander. This showed that a phase transformation in SrCO₃ from orthorhombic to hexagonal structure occurred at around 1204K (931°C). It was also revealed that this transformation temperature is affected by the experimental conditions. The effect of both heating rate and flow rate of the atmosphere on the transformation temperature are listed in Table 3.1.3 below.

Table 3.1.3. Change of phase transformation temperature of SrCO₃ with various heating rates.

<table>
<thead>
<tr>
<th>Heating rate (K/min)</th>
<th>Ar flow rate (ml/min)</th>
<th>Transformation peak (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>339</td>
<td>1204.6</td>
</tr>
<tr>
<td>10</td>
<td>49</td>
<td>1204.2</td>
</tr>
<tr>
<td>15</td>
<td>194</td>
<td>1204.1</td>
</tr>
<tr>
<td>20</td>
<td>194</td>
<td>1204.7</td>
</tr>
</tbody>
</table>

Other works by Charsley et al and Robbins et al have claimed that the orthorhombic to hexagonal phase transformation in SrCO₃ occurs after the onset of the decomposition reaction (equ 2.4.1(i)).
3.1.4. Eutectic reaction

Another phenomenon, which has been identified during the thermal decomposition of BaCO₃, is a eutectic reaction, leading to the formation of an intermediate compound BaO·BaCO₃. As early as 1937, Hackspill and Wolfe reported this eutectic reaction between BaCO₃ and BaO in the BaCO₃-BaO system. This was confirmed by research by Arvanitidis et al who also found that a BaO·BaCO₃ compound can be formed, with this compound having a relatively low melting point of 1333K.

As a result of the formation of the eutectic mixture described above, during the heating of BaCO₃, the melting of BaO·BaCO₃ forms a liquid layer. It has been reported that when the amount of the liquid is sufficient to cover the surface of the BaCO₃ particles, there will be a hindrance to the transport of CO₂ from the reaction region and further decomposition is retarded. For this reason, the thermal decomposition of pure BaCO₃ is slower than in the case of BaCO₃ with SrCO₃, with this being an important benefit in the use of multi-component system in the oxide cathode. In contrast to the BaO-BaCO₃ system, according to Baker, there is no melting reaction in the system SrO-SrCO₃ at temperatures below 1260K (987°C) at any CO₂ partial pressure below 1 atm.

3.1.5. Barium and strontium oxides

Following the carbonate conversion process, the cathode coating is changed to barium and strontium oxides (BaSrO₂). Some properties of barium oxide (BaO) and strontium oxide (SrO) relevant to this project are introduced in the section.

First, some key properties are shown in Table 3.1.5.

Table 3.1.5. Properties of the alkaline earth oxides

<table>
<thead>
<tr>
<th>Property</th>
<th>BaO</th>
<th>SrO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>153.36</td>
<td>103.63</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>6.05</td>
<td>5.05</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>2200</td>
<td>2700</td>
</tr>
</tbody>
</table>
The alkaline earth oxides (BaO and SrO) are very sensitive to \( \text{H}_2\text{O} \) and \( \text{CO}_2 \). They react rapidly with water and/or water vapour at room temperature to form the alkaline earth hydroxides, \( \text{BaSr(OH)}_2 \), according to reaction 3.1.5(i).\(^{39,71}\)

\[
\text{MO} + \text{H}_2\text{O} = M(\text{OH})_2 (M = \text{Ba}, \text{Sr}) \tag{3.1.5(i)}
\]

The alkaline earth hydroxide and/or oxide combines with \( \text{CO}_2 \) to form an alkaline earth carbonate according to the following reactions:\(^{39}\)

\[
\begin{align*}
M(\text{OH})_2 + \text{CO}_2 & = M\text{CO}_3 + \text{H}_2\text{O} (M = \text{Ba}, \text{Sr}) \tag{3.1.5(ii)} \\
\text{MO} + \text{CO}_2 & = M\text{CO}_3 (M = \text{Ba}, \text{Sr}) \tag{3.1.5(iii)}
\end{align*}
\]

In addition, the hydroxide can form the hydrate if sufficient water is available.\(^{39}\) It has been found that one molecule of strontium hydroxide or barium hydroxide can associate with up to eight molecules of water to form strontium hydroxide octahydrate \( \text{Sr(OH)}_2 \cdot 8\text{H}_2\text{O} \) or barium hydroxide octahydrate \( \text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} \), respectively.\(^{39}\) The physical changes associated with these chemical reactions were responsible for the abandonment of direct processing of the oxide cathode from oxide precursors, as used in the early oxide cathodes, with debonding and flaking of the oxide coating being attributed to the formation of the alkaline earth hydrate after the oxide coating is exposed to moisture.\(^{42,79}\)

### 3.1.6. Re-conversion of the oxide derived hydroxide

The reaction 3.1.5(i) is reversible and hence the oxide derived hydroxides can be re-converted to the oxides by heating.\(^{68}\)

Goncalves et al have studied the re-conversion of \( \text{(Ba,Sr)(OH)}_2 \) in the vacuum chamber.\(^{68}\) A first pressure peak corresponding to the decomposition of \( \text{Sr(OH)}_2 \) to \( \text{SrO} \) at 575K (302°C) by a similar process to that described in Section 3.1.1, followed by a second pressure peak at 675K (402°C), related to the decomposition of \( \text{Ba(OH)}_2 \) to \( \text{BaO} \), were detected, as shown in Figure 3.1.6(a). During the re-conversion process, water vapour is released as the main product of the reaction, the small amount of \( \text{N}_2, \text{CO}, \text{CO}_2 \) and \( \text{N}_2\text{O}_2 \) which were also detected\(^{68}\) are associated with small amount of carbonate and nitrocellulose binder in the system as shown as the spectrogram results.
in Figure 3.1.6(b).

Fig 3.1.6(a). Vacuum chamber pressure as function of cathode temperature during the oxide re-conversion process (reproduced from ref [68]).

Fig 3.1.6(b). Spectrogram of the products released in the oxide re-conversion process (reproduced from ref [68]).

The volume changes associated with this re-conversion would be expected to result in similar debonding problems to those described in Section 3.1.5 for the initial formation of the hydroxides, hence hydroxides are not normally used as precursor for cathode manufacture.
3.2. Properties of nickel (Ni)

As introduced in Section 1.2 and 2.6,[36,55] Ni filament is used as an important component in both the new designs of oxide cathode for both mechanical and performance purposes. The behaviour and reaction of Ni during the whole process is then crucial for the development of the desired structure and manufacturing process. For example, Ni filament is very likely to undergo chemical reactions (oxidation or reduction) during the heat treatment. Some properties which were thought to be helpful to understanding the behaviour of Ni in the oxide cathode are introduced in this section.

3.2.1. General properties of nickel (Ni)

Nickel (Ni) is a member of the transition group elements and it is a malleable and ductile metal.[180,181] Some key properties of nickel are listed in Table 3.2.1.[180,181]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>28</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>58.71</td>
</tr>
<tr>
<td>Atomic radius</td>
<td>1.24 Å</td>
</tr>
<tr>
<td>Density</td>
<td>8.9 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1453°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2730°C</td>
</tr>
</tbody>
</table>

At ordinary temperatures, nickel is not affected by either water[181] and not oxidised by dry or moist air.[181]

3.2.2. Oxidation of nickel (Ni)

The most common oxidation state of nickel is +2, though 0, +1, +3 and +4 Ni complexes are also observed.[183] The normal oxidation reaction is as follows:[183]

\[ \text{Ni} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NiO} \] 3.2.2(i)

Nickel is theoretically capable of reacting with oxygen over a wide range of temperatures[183] as evidenced by the Ellingham diagram as shown in Figure 3.2.2.[192] This indicates that the oxidation of Ni to NiO (reaction 3.2.2(i)) has negative free energy over the whole temperature range (0–1600°C).
Although it is reported by many studies that the oxidation reaction of nickel is normally exothermic,\textsuperscript{195-197} there is other investigations implied that another reaction may happen. During the preparation of many Ni materials, a stabilisation process is always involved which containing the chemisorption of CO\textsubscript{2} in order to make the Ni materials safe to handle under normal conditions.\textsuperscript{195} So, in application an endothermic reaction may happen to these Ni as follows:

\[ \text{Ni} : \text{CO}_2 \rightarrow \text{Ni} + \text{CO}_2 \]  
\[ 3.2.2(ii) \]

\subsection*{3.2.3. Reduction of nickel oxide (NiO) by hydrogen (H\textsubscript{2})}

In addition to the oxidation of Ni, the reduction of NiO previously formed is of interest during the manufacturing process of the newly designed cathode. The reduction of nickel oxide(NiO) by hydrogen(H\textsubscript{2}) can be written as equation 3.2.3\textsuperscript{184} which is suggested to be irreversible and slightly exothermic.\textsuperscript{184}
As indicated by the relative positions of the lines on the Ellingham diagram,[192] this reaction is thermodynamically anticipated at all temperatures because at any given temperature (0~1600°C), with the reaction of oxygen to form H₂O being more preferable (lower free energy) than NiO.

This reaction has been the object of numerous studies,[184,191] because NiO is a component commonly used in many oxidation catalysts[186,191] and electromagnetic devices.[187,188,191] However, many different experimental findings and results about this reaction have been obtained[184,191] due to the variations in the experimental conditions used, such as the pressure of hydrogen, and/or the properties of the oxide samples, such as the presence of defects in the outer surface of NiO grains.[189,190]

Despite the differences in these experimental results, there are some conclusions regarding the reduction that are accepted generally. For example, the mechanism of the reduction include the dissociation of hydrogen initially by NiO then by Ni metal and surface diffusion of hydrogen atoms to a reactive centre.[188]

Another very important and commonly observed phenomenon is that despite the fact that the reduction of NiO by H₂ is anticipated at all temperatures, in practice this reaction does not happen until after an induction-or delay-period.[185,191] It is found that during this period, oxygen vacancies are created within the crystal of NiO. These vacancies then favour the adsorption of hydrogen to the oxide and substantially lower the energy barrier associated with the cleavage of hydrogen bonds. At the same time, adsorbed hydrogen can induce the migration of oxygen vacancies from inside the NiO crystal to the surface. By inducing more oxygen vacancies on the surface, the hydrogen atoms thus “autocatalyse” the oxide reduction process, which becomes more and more efficient over time.[185,191]

Despite the range of result of various investigations into NiO reduction by H₂ obtained by different researchers, some broad conclusions can be drawn.

Rodriguez et al[191] have studied the reduction of NiO by H₂ under temperature ranging from 25°C to 400°C in which they found that NiO was directly reduced to Ni
at atmospheric pressures and elevated temperatures (250°C-350°C). The induction period can be shown by Figure 3.2.3(a), which is an X-ray diffraction pattern showing the reaction of hydrogen with a NiO powder at 280°C. During the first 50 minutes, the intensity of the diffraction lines for NiO remains constant (red). Then, these lines begin to disappear while lines for metallic Ni appear (blue). The authors also found that the magnitude of the induction time decreased when the temperature of the sample increased.\(^{[191]}\) For example, no induction time was found for experiments done at temperatures higher than 310°C. The study indicated that oxygen vacancies play a key role in the reduction of NiO, by generating the necessary sites for the dissociation of H\(_2\) and the subsequent auto-activation of the oxide.\(^{[191]}\)

![Fig 3.2.3(a). Time-resolved x-ray diffraction results for the reaction of a NiO powder with hydrogen at 280°C (red lines: NiO; blue lines: Ni) (reproduced from ref[191]).](image)

In contrast to the 50 minutes induction time found in the investigation found by Rodriguez et al.,\(^{[191]}\) other studies such as James et al.\(^{[184]}\) have found much shorter induction time as shown in Figure 3.2.3(b) which is a plot of the disappearance of NiO and appearance of Ni versus time at 175°C in an atmosphere of N\(_2\)/20%H\(_2\) and heating rate of 10°C/min.\(^{[184]}\) The results indicated an much shorted induction period followed by a steady decrease in NiO concentration and a corresponding increase in Ni concentration. This shortened induction time at a lower reducing temperature is thought to be due to the increased H\(_2\) concentration used in these experiments.
In the same study, James et al also studied the NiO reduction by H₂ under continuously increasing temperature as shown in Figure 3.2.3(c), which is the thermal analysis results of reduction of NiO in 20%H₂/N₂ at a flow rate of 243cm³/min and heating rate of 10°C/min. The thermal results indicated a slow reduction until 275°C, at which point an accelerated loss of weight occurred until complete reduction was achieved at 350°C.

![Graph of NiO disappearance and Ni appearance at 175°C](image)

Fig 3.2.3(b). NiO disappearance and Ni appearance at 175°C (reproduced from ref[184]).

![Graph of thermal analysis data for NiO reduction at 10°C/min](image)

Fig 3.2.3(c). Thermal analysis data for NiO reduction at 10°C/min (reproduced from ref[184]).
Chapter 4

Powder Processing Techniques

The new production processes being developed for the materials and structures designed in the project closely parallel some commercial powder processing routes used in ceramic fabrication. This section of the thesis briefly introduces these analogous processes as a basis for understanding the findings of this study.

4.1 Shape Forming Process

Shape forming is the general term given to processes used to transform particulate starting materials into a consolidated form having a particular geometry and microstructure. For the creation of a ceramic green body, several shaping methods can be used depending on the initial state of the ceramic material. These include slip casting, dip coating, and tape casting for ceramic suspensions; extrusion and injection moulding for ceramic pastes; dry pressing and isostatic pressing for dry ceramic powders. Many of these techniques require the addition of suitable (normally organic) additives.

4.1.1 Die-pressing process

Die pressing, also called dry compaction, is one of the most popular shape forming processes, since it involves a relatively simple technology while allowing high production rates. Two categories of pressing are commonly used (1), uniaxial and (2), isostatic. In isostatic compaction, a powder is poured into a rubber bag and stress is applied by means of a liquid which acts as a pressure transmitter. In uniaxial compaction, the stress is applied by a punch in a mould whose sidewalls cannot move. Since no rubber is involved, the control of green dimensions is better than in the isostatic case.

Although die compaction is a widely used technique for the processing of various ceramic powders and composites, it has not been widely reported for the materials used in oxide cathode manufacture. However the process has been
developed for other types of cathode. Sugimura et al.\textsuperscript{[84]} reported in 1999 a so-called “HIP cathode” made by pressing Ni, carbonate and Sc\textsubscript{2}O\textsubscript{3} powder by a hot isostatic pressing, followed by the slicing and polishing of the green body to form the cathode pellets. The emission properties of this cathode were estimated as providing 3A/cm\textsuperscript{2} for 22,000 hours at 880\textdegree{}C. More recently a new Ni-pressed cathode has been developed\textsuperscript{[85]} in which a mixture of Ni, Sc\textsubscript{2}O\textsubscript{3} and W with the conventional triple alkaline earth carbonate (Ba, Sr and Ca carbonates, as introduced in Section 1.1) for application in high resolution and/or wide screen CRTs) was fabricated by cold isostatic pressing to form a green disk of 0.4mm thick which was subsequently cut into pellets of 1mm in diameter followed by the subsequent necessary post-forming process. The resultant cathode was reported to have emission current density of 6.6–9.6 A/cm\textsuperscript{2} for the cathode Ni- (Ba, Sr, Ca)O-W- Sc\textsubscript{2}O\textsubscript{3} composition and 5A/cm\textsuperscript{2} for Ni-(Ba,Sr,Ca)O-W composition at 850\textdegree{}C (brightness).

\subsection*{4.1.2 Suspension Casting}

The family of casting process essentially involves the deposition of the powder from a suitable liquid suspension by the removal of the liquid component in a suitable mould.\textsuperscript{[83,86]} The forming technique developed for the new cathode designs in this work can be considered to be a variant on suspension casting technology.

The advantages of suspension casting processes are a more complete powder dispersion than other techniques in a relatively low-viscosity liquid, leading to more homogeneous packing of the powders, the complexity of product shape permissible, and the relatively low capital cost.\textsuperscript{[80]} The disadvantages of casting are the lower production rates and lower dimensional precision commonly obtained.\textsuperscript{[80]}

The two most common casting processes are referred to as tape casting and slip casting. Slip casting, as shown in Figure 4.1.2(a),\textsuperscript{[87]} is the conventional casting of a slip or slurry in a porous gypsum mould, during which capillary suction of water into the mould concentrates and coagulates the particles in the slip near the mould surface, forming the cast.\textsuperscript{[80]}

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In tape casting, by comparison, a concentrated slurry flows beneath a blade, and then forms a film on a moving carrier substrate which is then dried in air or other suitable atmosphere.[80] As schematically shown in Figure 4.1.2(b), paper-thin and flexible sheets can be produced in a continuous process.[88]

The manufacturing process used in the project is slightly different from either of the process discussed above, and can be considered to be a combination of the two processes. In this case, the slip/slurry is poured into a suitable mould (as with slip casting) but with the liquid removal achieved by evaporation in air instead of being drawn into the mould.

### 4.1.3. Suspension processing additives

When processing ceramics, several different additives must be introduced into the system to produce the particle dispersion and flow behaviour necessary for forming.[80]

These additives may be categorised as follows:[80]

- Liquid/Solvent,
- Surfactant (wetting agent),
- Deflocculant (dispersant),
These additives are essential from a processing perspective although they are eliminated during subsequent processing and do not appear in the final product.\textsuperscript{80} Most processing additives are organic chemicals, as when compared to most inorganic chemicals, the organics have the advantage of being combustible, so they can be completely removed during the early stages of firing.\textsuperscript{89} Therefore, less concern is necessary for the possible effect of residues that might degrade the final products.\textsuperscript{81}

\textbf{4.1.3.1. Liquid media in suspension process}

The liquid media is used in suspension processing to temporarily disperse the powder particles to create a fluid and as a solvent to dissolve and incorporate the processing additives.\textsuperscript{89} The ceramic powder itself is not normally dissolved, but rather is present in the form of an suspension allowing easy flow.\textsuperscript{89} At a later stage in the process, the liquid is evaporated out of the system.

Generally, two categories of liquid media, organic (non-aqueous) and inorganic (aqueous) are used.\textsuperscript{81} Although non-aqueous slurries are used more dominantly in traditional processing because of the greater ease of powder dispersion and slurry drying, aqueous tape casting, i.e. water-based casting, is increasingly employed in new processes due to safety and environmental reasons.\textsuperscript{175}

Water is a polar liquid and thus is a good solvent for polar and ionic compounds.\textsuperscript{80} The main advantage of water is that it is cheap and safe.\textsuperscript{89} However, the slow evaporation and agglomeration due to hydrogen bonding of water mean that water does not evaporate as quickly as some organic solvents and therefore drying is much slower and requires more heating.\textsuperscript{89} Moreover, compared with non-aqueous liquid media, the variety of suitable (water-soluble) binder and plasticiser systems is restricted.\textsuperscript{175} These characteristics make the water-based system less widely used. Nevertheless, water-based systems are preferred in terms of toxicity, environmental impact and price, and the use of water-based systems represents an increasingly important alternative to the traditional non-aqueous tape casting.\textsuperscript{175}
4.1.3.2. Other processing additives

Binders:

Binders are the most important and common additive used in ceramic processing. Whilst the capillary forces in wet processed ceramics provide some bonding effect during initial processing, this effect is lost as the liquid is removed during drying and it is generally necessary to add an additional component to provide continued strength to the green body at this stage.\textsuperscript{[81]}

| Table 4.1.3.2. Molecular type binder materials\textsuperscript{[80]} |
|---------------------------------|--------------------------------------------------|
| **Organic**                     | **Examples**                                    |
| Natural gums                    | Xanthan gum, gum Arabic                        |
| Polysaccharides                 | Refined starch, dextrine                        |
| Cellulose ethers                | Methyl cellulose, hydroxyethyl cellulose, sodium carboxymethyl cellulose |
| Polymerised alcohol             | Polyvinyl alcohol                              |
| Polymerised butyral             | Polyvinyl butyral                              |
| Acrylic resins                  | Polymethyl methacrylate                        |
| Glycols                         | Polyethylene glycol                            |
| Waxes                           | Paraffin, wax emulsions, microcrystalline wax  |

There are in general two categories of binders: colloidal particle type binder and molecular binder.\textsuperscript{[81]} Colloidal binders include inorganic materials such as colloidal silica, used to form mainly low density parts such as insulation materials.\textsuperscript{[81]} Molecular binders are low- to high- molecular weight polymer molecules, which range widely in composition.\textsuperscript{[80]} Both natural and synthetic substances are used. The inorganic colloidal molecular binders are used when the inorganic component is compatible with the particles composition and the service behaviour of the product, since these binders are essentially retained even after sintering.\textsuperscript{[81]} By comparison, the organic molecular binders introduce relatively little residual impurities.\textsuperscript{[81]} These binders can differ significantly in composition and molecular size. Some typical binders are listed in Table 4.1.3.2.\textsuperscript{[80]}
Dispersant:

These materials, sometimes called deflocculants,\textsuperscript{[89]} are very important additive in ceramic processing. The function of a deflocculant is to prevent “agglomeration” (due to interparticle attractive forces) by an additive adsorbed on the particles which increase the repulsive forces by electrical charging and/or by sterically hindering the close approach of particles which can aid and maintain dispersion.\textsuperscript{[81,83]}

Plasticiser:

Plasticiser is a low molecular weight materials that can be added to the binder composition which lowers the glass transition temperature of the polymeric binder and prevents brittleness of the binder.\textsuperscript{[81,89]} It is believed that these small “plasticising” molecules soften the binder and the dried body by distributing among the larger polymer molecules and cause the polymer to pack less densely and reduce the Van der Waals forces binding the larger molecules together.\textsuperscript{[81]} The presence of plasticiser can also cause the polymers to migrate or flow in a way similar to the flow of solvent during the drying of the ceramic green body.\textsuperscript{[81]}

The details of the polymer additives (including binder, dispersant and plasticiser) used in the process routes developed in this project will be introduced in detail in Chapter 5.

4.1.3.3. Deagglomeration

In many ceramic processes, especially the casting process, dispersion or deagglomeration is carried out to the casting suspension to break down soft agglomerates into individual particles and to ensure a regular packing in the compact formed.\textsuperscript{[90]} Dispersion can be promoted by mechanical action and/or chemical additives.\textsuperscript{[90]} The chemical additives is called the dispersant as just introduced. Possible mechanical actions are ultrasonic treatment, ball milling and attrition milling.\textsuperscript{[90]} Ultrasonic treatment will be used in the preparation of BaSr(CO$_3$)$_2$ containing suspension in this project and its principle is introduced.

Ultrasonics are most often used for powder deagglomeration in the laboratory.\textsuperscript{[80]} This technique is frequently used with submicron-sized powders which are hard to disperse by other methods. When a liquid is exposed to progressively higher ultrasonic power, small vapour bubbles start to appear above a certain
threshold energy.\textsuperscript{[91]} Beyond the threshold, the number of cavities increase rapidly with increased ultrasonic power.\textsuperscript{[80]} Cavities form everywhere within the ultrasonic field and collapse violently after a short lifetime, of the order of 2\mu sec.\textsuperscript{[80]} When these cavities collapse, they produce locally very high velocity jets in the neighbourhood of 100m/sec and pressure gradients of 20GPa/cm.\textsuperscript{[92]} The resulting mechanical forces on the aggregated particles are extremely strong and continue as long as the ultrasonic power is above the threshold value for cavitation. These hydrodynamic forces are strong enough to break apart weakly bonded particles, such as those joined by Van der Waals forces.\textsuperscript{[93]}
4.2 Drying process

Drying is the removal of the liquid used to suspend the ceramic powder.\[81\] It is necessary that after drying, the product possess desirable properties, such as flatness, appropriate microstructure, and mechanical strength.

During this process the suspension system is either heated or placed in an atmosphere where the solvent evaporates.\[81\] Drying is achieved by the transportation of energy into the suspension system and by the transportation and evaporation of liquid into the surrounding atmosphere.\[82,94\] The rate and energy requirement for this process are often important parameters, with these being dependent on the heat of vaporisation of the liquid present. Heats of vaporisation for several processing liquids are listed in Table 4.2.\[81\] Generally less energy is required for the evaporation of organic solvents and thus they evaporate more readily and easily than water. This can be important in achieving rapid production rates in commercial systems. However as already mentioned there are significant drawbacks to the use of organic liquids such as cost, flammability and environmental impact.

| Table 4.2. Latent Heat of Vaporisation of Several Processing Liquids\[81\] |
|------------------|------|------|------|
| Temperature (°C) | H₂O  | CH₃OH| C₂H₅OH|
| 20               | 2.45 | 1.17 | 0.91 |
| 40               | 2.40 | 1.14 | 0.90 |
| 60               | 2.36 | 1.11 | 0.88 |
| 80               | 2.31 | 1.06 | 0.85 |
| 100              | 2.26 | 1.01 | 0.81 |

4.2.1 Water Evaporation and Shrinkage

Drying is often regarded as occurring in three stages corresponding to the ranges of liquid content for which the drying rate is increasing, constant and decreasing.\[80,94,95\] Correspondingly, there are described as increasing rate, constant rate and decreasing rate stages of drying.

The evaporation of liquid always starts from the wet external surface of the suspension system.\[80\] During both the increasing and constant rate stages, the surface of the suspension body remains wet, due to the transport of liquid from the interior of the solid to the evaporation surface occurring at a sufficient rate to keep
the surface wet.\textsuperscript{[94]} This flow comes from the re-arrangement of the particles and/or agglomerates in the system, which is caused by the compressive capillary pressure at the surface of the green body and causes the total volume of the body to decrease.\textsuperscript{[81,80]} During the constant rate period, the rate is only dependent on the external conditions, such as air temperature, air moisture, and air velocity.\textsuperscript{[80,81]} As long as these conditions are constant, the evaporation rate is constant.\textsuperscript{[94]}

As the process progresses, eventually as the water between the particles cannot reach the surface at a sufficient rate to keep the surface completely wet leading in turn to a reduction in the total wet surface exposed to the ambient air and thus, causing the evaporation rate to change from constant to a decreasing rate.\textsuperscript{[94]} The end of the constant rate is called the critical point, at which the vapour/liquid interface moves into the pores of the drying body.\textsuperscript{[95]} During this decreasing rate stage, there is still shrinkage of the body.\textsuperscript{[81]} This residual shrinkage comes from the elimination of the water films either on the surface of the body particles or between neighbouring particles, i.e. the final adjustment of the particles inside the body to establish a mutual contact.\textsuperscript{[94]}

4.2.2 Drying stress

The evolution of stress during drying and its impact on important parameters such as mechanical strength, surface flatness and structural integrity is an important consideration in all “wet” powder processing routes such as those being developed in this investigation.\textsuperscript{[81]} Typically the processes of structural evolution during drying give rise to several types of defects in the dried product, such as cracks, distortion/warping, or phase segregation.\textsuperscript{[96]} Of these both cracking and warping are the result of stresses generated during drying whilst phase segregation can result in the generation of such stresses. The avoidance as far as possible of these defects is one of the goals of the process development in this study. Here the theoretical bases of these phenomena are discussed as the basis for subsequent discussion of the experimental findings and process route development.

It is proposed that a stress-free state in dried materials is possible only for constant distributions of moisture content and temperature.\textsuperscript{[82,97]} However, many processes take place simultaneously during drying including removal of liquid and vapour from the drying material and the phase transition of liquid into vapour. Each
of these processes give rise to changes of the moisture content and temperature within the drying system and result in drying induced stress.\cite{82,97}

The development of stress during drying of cast materials has been investigated by various researchers. For a casting suspension without any organic additive, this takes place initially as a period of increasing stress followed by a maximum stress (i in Figure 4.2.2(a)) and a subsequent decline to a stress-free state as represented in Figure 4.2.2(a).\cite{98} It shows the drying stress evolution during drying of a calcium carbonate suspension. Experiments showed that the stress is originated from the capillary induced pressure which reaches maximum value at the critical point.\cite{97-99} Beyond this point, liquid menisci form and begin to recede into the particle network and open pores appear.\cite{100} The maximum capillary force is expressed as following:\cite{95}

\[ P_r = \frac{(\gamma_{SV} - \gamma_{SL})S_p}{V_p} \quad \text{4.2.2(i)} \]

where \( P_r \) = maximum capillary pressure, \( \gamma_{SV} \) = surface tension of solid/vapour, \( \gamma_{SL} \) = surface tension of solid/liquid, and \( \frac{S_p}{V_p} \) = surface-to-volume ratio of pore space.\cite{95} The amount of solid material in the suspension (the initial volume fraction) also plays an important role with the stress developed increasing with larger initial solid volume fraction as shown in Figure 4.2.2(a) (i and i').\cite{98}

Fig 4.2.2(a): The drying stress as function of the drying time for pure calcium carbonate films with two different initial solid volume fractions, \( \phi = 0.21 \) and \( \phi = 0.44 \). (reproduced from ref [98])
Significantly different behaviour has been reported for the development of drying stress in the presence of organic binders indicating the important role that organic species play in stress development. In this case, the development of drying stress with time typically follows the pattern shown in Figure 4.2.2(b), which is the drying stress evolution as a function of time for a calcium carbonate PVA film.\textsuperscript{[100]}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4.2.2b.png}
\caption{The drying stress evolution as a function of time for calcium carbonate PVA film. (reproduced from ref[100])}
\end{figure}

As shown in the figure, during the drying of a material containing an organic binder, very little stress relaxation occurs after the first stress peak (I in Figure 4.2.2(b)), with this being then followed by a second stage of increasing stress (I'). After the final stage of drying, a large amount of residual stress is left in the dried product.\textsuperscript{[98,100]} The first stage of the stress development is also caused by the capillary force generated, with this process occurring similarly both with or without presence of organic binders.\textsuperscript{[97-99,101]}

The residual stress in the binder containing material is believed to be related to the shrinkage of the binder.\textsuperscript{[98,102,100]} To understand the behaviour of organic binder during drying, Croll\textsuperscript{[102]} has studied the development of internal stress in solvent-cast thermoplastic coatings and showed that the residual internal stress (\(\sigma\)) is a function of the Young’s modulus (\(E\)) of the film and the volume fraction of solvent in the film at the solidification point (\(\phi_s\)) and in the dry state (\(\phi_r\)), according to expression 4.2.2(ii):\textsuperscript{[98,100,102]}
\[ \sigma = \frac{E}{1-u} \frac{\phi_s - \phi_r}{3(1-\phi_r)} \] 4.2.2(ii)

where \( u \) is Poisson's ratio.

The volume fraction at the point of solidification (\( \phi_s \)) is usually identified as the solvent concentration at which the glass transition temperature (\( T_g \)) of the polymer-solvent system is equal to the ambient temperature.\(^{[100]}\) This \( \phi_s \) was related by many researchers to the glass transition temperature (\( T_g \)) of the polymer binder in the material system.\(^{[103-105]}\) They suggested that it is the glass transition temperature of the binder that has a decisive influence on the stress development during drying because \( T_g \) controls the shrinkage of the polymer film beyond the solidification point.\(^{[100]}\) A polymer with a high \( T_g \) will contain more solvent at the solidification point than a polymer with a low \( T_g \) and thus shrink more.\(^{[100]}\)

The plasticising effect of additives to the glass transition of a polymer system has been considered by many researchers\(^{[103-107]}\) and can be expressed by the Gordon-Taylor equation\(^{[103]}\)

\[ T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \] 4.2.2(iii)

with

\[ k = \frac{\rho_1 T_{g1}}{\rho_2 T_{g2}} \] 4.2.2(iv)

Where \( w, T_g, \) and \( \rho \) are the weight fraction, glass transition temperature, and the density for the pure components 1 and 2, respectively.\(^{[103]}\)

Apart from the effects of the polymers, large amount of stresses are also likely to be produced by the inhomogeneity of the drying system, such as the increased pressure or moisture gradient brought by the higher evaporation rate, the inhomogeneous distribution or different particles inside the solid material, and the asymmetrical surface-drying of the green body as shown in Figure 4.2.2(c).\(^{[80,81,95]}\)
Fig 4.2.2(c). Schematic map of inhomogeneous surface drying: (a), wet green body; (b), dried and warped green body. (reproduced from ref [82])

It has been generally accepted that cracking takes place when the stress generated is higher than the critical stress intensity of the material. Moreover, according to the common observation, cracking is more likely if the body is thick or the drying rate is high, and that cracks generally appear at the critical point during drying.

It has been proposed by many researchers that it is mainly the capillary pressure that is responsible for the creation of cracking in the cast ceramic materials with and without binder. This is based on the observation that cracks generally appear at the critical point. The maximum value of the capillary stress is introduced in equation 4.2.2(i), although the limitation of this equation is that it does not explain the importance of drying rate and body thickness.

It has been suggested by Scherer that the stress responsible for the cracking is:

\[
\sigma_x = \left( \frac{L\eta_L V_e}{2D} \right) \left( \frac{z}{L} \right)^2 \left( \frac{1}{3} - \frac{1}{L^2} \right) \ ...
\]

where \( \eta_L \) is the liquid viscosity, \( V_e \) is the evaporation rate, \( D \) is the permeability, \( \frac{z}{L} \) is the half-thickness of the drying body, and \( \sigma_x \) is the maximum stress which is always \( \leq \) the capillary force \( (P_R) \). In this expression the stress increases in proportion to the thickness of the plate and the rate of evaporation.

All these investigations into the stresses responsible for cracking phenomena didn’t take the effect of the polymeric additives into account, although it is generally considered that the addition of polymer binder is helpful to depress cracking. Nevertheless, cracking can still occur in the presence of organic binders. Annika has reported that cracking observed in a system containing latex binder occurred
because the latex did not act as a binder until it had coalesced fully upon drying, whilst the onset of cracking occurs before this stage.

However, there is another explanation suggesting that cracking is caused by the disappearance of the capillary force between the particles during drying.\cite{81} As mentioned in Section 4.1.3.2, when the green body is wet by the liquid, it has a compressive capillary force, which holds it together.\cite{81} During drying, this capillary force disappears along with the removal liquid.\cite{81} In some materials with a polymeric binder present, the compressive capillary force is replaced by the cohesive force of the binder. However, the cohesive force of the binder is normally smaller than the original compressive capillary force arising from the liquid. Due to its weakened state, cracking appears if undue stress is generated during drying.\cite{81}

A number of approaches have been reported to reduce the possibility of cracking. For example, surfactants can be added to the pore liquid to reduce the interfacial energy and thereby decrease the capillary force.\cite{95} Supercritical drying and freeze-drying are two other processes which are often used to avoid cracking.\cite{95}

4.2.3. Polymer surface segregation

It was found during the experiments in this study that polymer segregation could normally be observed on the surface of the as cast materials, but no literature has been found for the same phenomenon. However, this polymer accumulation was found to be quite similar to the polymer surface segregation reported during the spray drying of polymer-water-ceramic slurry.\cite{107,108}

Zhang et al.\cite{107,108} has investigated the spray drying process of PVA-Water-Al\textsubscript{2}O\textsubscript{3} slurry during which PVA surface segregation happened and suggested that this surface segregation resulted from two mass transfers: the migration of polymer to the surface caused by liquid and the back-diffusion driven by the concentration gradient of polymer.

As introduced in Section 4.2.1, during the increasing and constant rate stages of drying, water has to transport from the interior of the suspension to the evaporation surface to keep the surface wet\cite{81,80,94} and the water-soluble polymer molecules are subsequently carried by water migration from the interior to the surface leading to polymer segregation on the surface of the resultant material. The amount of polymer carried by this process is mainly decided by the concentration of polymer in the liquid.
and the total content of the liquid.\textsuperscript{109} With higher concentration of polymer in the liquid, more polymer is transported with it. The higher the amount of water, the longer the constant period of drying during which transport occurs, which also results in more polymer accumulation.

On the other hand, with more polymers moved to the surface, their concentration in the surface region is increased as water evaporated, with this being higher than interior concentration.\textsuperscript{107} The binder molecules then diffuse through the liquid back to the interior because of this concentration gradient. The extent of this process was thought to be related to the diffusion coefficient of the polymers and the thickness of the polymer surface layer formed before.\textsuperscript{107,109}

Although polymer segregation is governed by the two competing processes described above, both experiments and mathematical models have shown that the total amount of polymers on the surface is still related to the water content of the slurry and the concentration of polymers.\textsuperscript{107-109}
4.3 Thermal Treatment

The final set of process operations which are commonly applied to all powder processed materials is heat treatment to develop the desired microstructure and properties.\(^8^0\) This heating process during which high temperatures are applied is commonly called "sintering".\(^8^1,^1^0\) In practice the process normally involves the following three stages: \(^8^0\) 1). Reactions preliminary to sintering, 2). Sintering, and 3). Cooling.

The reactions preliminary to sintering are largely chemical changes, such as the decomposition of the organic additives, the vaporisation of chemically combined water.\(^8^0\) The removal of organic processing additives is discussed in more detail in Section 4.3.1 below. Sintering does not commonly begin until these chemical reactions complete,\(^8^0\) and is discussed in more detail in Section 4.3.2.

4.3.1 Removal of processing additives

4.3.1.1 Polymer burnout

As introduced in Section 4.1.3.2, it is common in many powder-forming processes to incorporate organic additives such as binders and dispersants as process aids, which remain in the dried product. The removal of these polymer additives by thermal decomposition during the initial low temperature stage of the heat treatment process is an important step in determining the final characteristics, properties and reliability of the final parts.\(^8^1^1\) Generally it is necessary to achieve complete removal of organics without creating substantial porosity and other damage in the resultant body.\(^8^0\) Conversely, in the cathode product developed in this project, the goal has been to exploit these processes to deliberately engineer substantial porosity in the resultant material. The rate and extent of these reactions is very dependent on the composition of the polymer material and the composition and flow of the gas surrounding the product and in the pores of the product.\(^8^0\)

It is found that a single polymer with a narrow range of molecular weight will burn out too suddenly, exerting excessive pressure from inside the product and thus causing cracking.\(^8^9\) For this reason, processing additives comprising a wide range of molecular weights, or even a mixture of different molecular species, are often used to make the out-gassing occur over a wider temperature range.\(^8^9\)
During decomposition, the polymers can degrade along many possible degradation pathways, which include: 1). Scission of the main chain. 2). Reaction with side chains and substituents, and 3). Cross-linking and cyclisation ending in carbon formation. Of these, polymers that undergo chain scission (or depolymerisation, "unzipping") are desirable for ceramic binders because they are likely to burnout cleanly with little carbon residue.

For proper additive removal, the heating parameters, such as time, temperature, and atmosphere, of sintering must be carefully controlled. Proper polymer removal is normally achieved by slowly raising the temperature to a level at which the binder can volatise, and holding at this temperature until the binder is gone. The temperature can then be increased to the sintering temperature.

The atmosphere in which the polymer decomposition carried out is another very important parameter. In air or pure oxygen, the polymer removal is completed by combustion. Whereas, in other non-oxidising atmosphere, such as nitrogen or argon, all of the binder removal has to be accomplished by evaporation. Moreover, in a reducing atmosphere, carbon is stable to 3652°C, where it sublimes, making carbon very difficult to remove before sintering materials. This leads to carbon impurities in the final material. In an oxidising atmosphere, carbon will readily react with oxygen at temperatures < 800°C. For this reason, oxidising atmospheres are normally used for polymer removal.

Another very important factor in affecting polymer removal is the amount of these polymer additives present in the product. If large percentages of additives are present, such as in injection-moulded ceramics, the binder may have to be removed very slowly as a gas or liquid by thermal decomposition. Too-rapid removal results in formation of cracks in the component.

4.3.1.2. Effect of metals and ceramics on the polymer decomposition

Although no specific publications were found in the literature about the decomposition of the three polymers (PVA, PEO and PEG) in the presence of Ni or BaSr(CO₃)₂ as used in this project, the presence of metal (including metal oxide, metallic salts, etc) and ceramics are commonly reported to affect the decomposition behaviour of many polymers. Considering polymer decomposition will be carried out in the presence of both metal (Ni) and ceramics (BaSr(CO₃)₂) in the new cathode
material during manufacturing, some examples of these polymer decompositions with catalyst are outlined.

For example, it is reported that rhodium can be used as catalyst which largely lowered the decomposition temperature of polyethylene from about 300°C to 180°C.\textsuperscript{[112]}

Maksimova et al\textsuperscript{[113]} have studies the thermal decomposition of polyvinyl alcohol in the presence of $\alpha$-FeO(OH) as the catalyst. The investigation showed that the decomposition of PVA products changed in the presence of Fe containing catalyst from which they have concluded that $\alpha$-FeO(OH) acts as a catalyst for PVA decomposition.\textsuperscript{[113]} However, there is no report on the decreasing of decomposition temperature of PVA. It is supposed that it is the unsteady-state of $\alpha$-FeO(OH), which underwent a number of phase transfers over the temperature range of polymer decomposition, responsible for the catalyst function.\textsuperscript{[113]}

It has also been shown that powdered polypropylene is oxidised in the presence of metallic salts in the following order of catalytic reactivity,\textsuperscript{[80]}

\[
\text{Co} > \text{Mn} > \text{Cu} > \text{Fe} > \text{V} > \text{Ni} > \text{Ti} > \text{Al} > \text{Mg} > \text{Ba}
\]

The effects of ceramic oxides on the binder burnout of poly(vinyl butyral) (PVB) has been studied\textsuperscript{[114]} and the results showed that the reaction rates in air was shown to be a strong function of the ceramic oxide present.\textsuperscript{[114]} In all cases, the oxide decreased the temperature necessary for thermal decomposition compared to PVB alone.\textsuperscript{[114]}
4.3.2 Sintering process.

Sintering of the alkaline earth oxides and Ni composite materials used in this investigation has received very little specific investigation—however in view of its importance to the formation of the desired microstructure, and the interpretation of the results obtained in this investigation, a brief overview of the principles of sintering is given here.

4.3.2.1 Coarsening and densification

Sintering is the term used to describe the consolidation of a powder-derived product at elevated temperature, implying that within the product, particles have joined together into an aggregate that has strength.\(^{[82]}\) Almost all density variations in the green compacts tend to amplified during sintering.\(^{[81]}\)

For the majority of applications, the requirement of sintering is to increase the density of the product by the removal of the pores to produce strong products.\(^{[83]}\) This is called *densification* and is normally accompanied by grain growth and other microstructural changes, and by macroscopic shrinkage.\(^{[83,110]}\)

In some special applications like filters and highly porous refractory insulation products, and the emitter materials in this investigation, it is necessary to increase the strength without increasing the density extensively.\(^{[81]}\) This requires bonding of the particles to take place during sintering while suppressing the densification. Such processes are called *coarsening*, in which the average size of the particles increases but with little or no shrinkage.\(^{[110]}\)

In practise, these two mechanisms are usually in competition during sintering.\(^{[110]}\) The governing of the mechanism during sintering of any specific material system is difficult to predict and depends on many variables, such as particle size and packing, sintering atmosphere, degree of agglomeration, temperature, and presence of impurities.\(^{[110]}\) For the desirable porous microstructure of the emitter material in this investigation (as described in Section 2), the goal of the sintering process is to encourage coarsening mechanism and associated formulation of interparticle contacts as described in the following section, while, suppressing densification.
4.3.2.2. Sintering mechanism

For all sintering mechanisms, the driving force for sintering has its origin in the reduction in the total free energy $\Delta G_T$ of the system:\[81\]

$$\Delta G_T = \Delta G_v + \Delta G_b + \Delta G_s,$$

4.3.2.2

where $\Delta G_v$, $\Delta G_b$, and $\Delta G_s$ represent the change in free energy associated with the volume ($\Delta G_v$), boundaries ($\Delta G_b$) and surfaces ($\Delta G_s$) of the grains, respectively.\[81\]

The microstructure changes significantly, either by densification or by coarsening, during sintering to minimize the energy of the material.\[110\]

The development of microstructure with increasing temperature is a direct consequence of mass transport through several possible paths. Various mechanisms for material transport can occur during sintering as shown in Table 4.3.2.2.\[82,83\] and Figure 4.3.2.2.\[110\]

<table>
<thead>
<tr>
<th>Material transport mechanism</th>
<th>Source</th>
<th>Driving energy</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation-condensation</td>
<td>Surface</td>
<td>Vapour pressure difference</td>
<td>Coarsening</td>
</tr>
<tr>
<td>Surface diffusion</td>
<td></td>
<td>Difference</td>
<td></td>
</tr>
<tr>
<td>Volume diffusion</td>
<td></td>
<td>Difference in free energy or chemical potential</td>
<td></td>
</tr>
<tr>
<td>Lattice diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td>Grain boundary</td>
<td>Capillary pressure, surface tension</td>
<td>Densification</td>
</tr>
<tr>
<td>Viscous flow, diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is generally accepted that evaporation (path 1 in Figure 4.3.2.2), surface diffusion (path 2 in Figure 4.3.2.2) and volume diffusion (path 3 in Figure 4.3.2.2) from the surface to the neck area will lead to coarsening, because such a mechanism does not allow the particle centres to move closer together.\[82,110\] These mechanisms
instead result only in changes in the shape of the pores, a growth in the neck size, and a concomitant increase in strength.

Fig 4.3.2.2. Basic atomic mechanisms that lead to (a), coarsening and change in pore shape; and (b), densification (reproduced from ref[110]).

For densification to occur, the source of material has to be the grain boundary or region between powder particles, and the sink has to be the neck or pore region.[110] Consequently, the mechanisms that can lead to densification are grain boundary diffusion (path 4 in Figure 4.3.2.2) and lattice diffusion (path 5 in Figure 4.3.2.2) from the grain boundary area to the neck area.[110]

In terms of the materials system for sintering, there are two broad categories of sintering: solid-state sintering and liquid-state sintering.[110]

4.3.2.3. Solid-state sintering

Sintering of a powder compact in which little (<2 vol%) or no liquid phase is formed at the sintering temperature is defined as solid state sintering.[81] Such sintering is normally described as occurring in three stages according to the sequence of the physical changes occurring within the product.[81,90,110] These three stages can be described as: an initial stage, an intermediate stage and a final stage. The microstructure changes occurring during each of these three stages are listed in Table 4.3.2.3. The mechanisms and microstructural changes during these three stages are also outlined in the following sections.
### Table 4.3.2.3, Microstructural changes observed in the initial, intermediate, and final stages of solid-state sintering (powder compact)\(^{[81, 110]}\)

<table>
<thead>
<tr>
<th>Stage</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>Neck growth</td>
</tr>
<tr>
<td></td>
<td>Surface smoothing of particles</td>
</tr>
<tr>
<td></td>
<td>Grain boundaries form</td>
</tr>
<tr>
<td></td>
<td>Rounding of interconnected, open pores</td>
</tr>
<tr>
<td>Intermediate</td>
<td>Decrease of open pore size (result in volume shrinkage)</td>
</tr>
<tr>
<td></td>
<td>Intersecting grain boundaries</td>
</tr>
<tr>
<td></td>
<td>Mean porosity decreases significantly</td>
</tr>
<tr>
<td></td>
<td>Slow grain growth</td>
</tr>
<tr>
<td>Final</td>
<td>Closed pores intersect grain boundaries</td>
</tr>
<tr>
<td></td>
<td>Pores shrink to a limited size or disappear</td>
</tr>
<tr>
<td></td>
<td>Pores larger than grains shrink relatively slowly</td>
</tr>
</tbody>
</table>

**4.3.2.3.1 Initial stage**

The initial stage of sintering is frequently referred to as the neck formation stage.\(^{[81]}\) The neck size is an important factor in determining the strength of the ceramic.\(^{[86]}\)

In the context of this investigation, initial stage sintering is highly desirable. For the Ni porous base (for the two-layer/impregnated cathode as described in Section 1.2), it promotes mechanical strength in the base to produce the necessary robustness to withstand stresses generated during drying and/or sintering and thermal stresses generated during mounting operation. It also provides support to the whole emitter for the subsequent application in vacuum tube. Neck formation in the initial stage is also important to provide good electrical contact in the cathode material to facilitate conduction.

The driving force for this material transportation is the difference in curvature difference between the neck and particles surface.\(^{[81]}\) The negative curvature of the
neck, compared to the positive curvature of the particle surface, results in a lower partial pressure, free energy or chemical potential, and this difference in energy causes the transport of material by the fastest means available.\textsuperscript{[81,80,110]} So, any mechanism listed in Table 4.3.2.2 can predominate during sintering depending on conditions.

In the following sections, some of the mass transfer mechanisms are outlined which can give us a general idea of how the microstructure will change with the variables, such as the sintering temperature and particle size.

4.3.2.3.1.1. Vapour-transport

In this mechanism, the excess pressure introduced by the surface curvatures difference of particles and neck causes the material from the surface of the particle flow to the intersection of the two particles and produce the neck.\textsuperscript{[81,82,110]}

The following expression expresses the relationship for the growth rate of the neck diameter, \( \chi \), with time:\textsuperscript{[110]}

\[
\frac{\chi}{a} = \left[ \frac{6\gamma_{sv}\Omega_{MX}P_{\text{flat}}m_{MX}A}{\sqrt{2\pi k}} \right]^{\frac{1}{2}} a^{-\frac{1}{2}} \gamma_{sv} T^{\frac{1}{2}} T^{-\frac{1}{2}}
\]

where

\( \chi \) -- neck radius

\( a \) -- particle radius;

\( \gamma_{sv} \) -- solid-vapour surface energy

\( \Omega_{MX} \) -- volume of a formula unit (for simplicity, in the following, it will be assumed that one is dealing with an MX compound)

\( P_{\text{flat}} \) -- partial pressure above the flat surface

\( m_{MX} \) -- mass of the evaporating gas molecule

\( A \) -- evaporation coefficient of the evaporating gas molecule

\( T \) -- sintering temperature;

\( t \) -- time

\( k \) -- Boltzmann's constant

58
It shows that the rate of growth of the neck region is (1), a function of particle size \(a\), (2), the time being sintered \(t\), and (3) the sintering temperature \(T\). Moreover, the term \(\left[ \frac{6\gamma_{sv}\Omega_{MX}P_{\text{sat}}m_{MX}A}{\sqrt{2\pi}k} \right]^{1/3} \) can be regarded as a constant which includes the interfacial energy of the solid/vapour \(\gamma_{sv}\), the Boltzmann constant \(k\), the vapour pressure \(P\), etc.

### 4.3.2.3.1.2. Surface diffusion

However, vapour-phase sintering is normally important in few material systems.\(^{[83]}\) If the vapour pressure is low, then the materials transfer is more likely to occur according to the other solid state mechanisms, such as surface diffusion and bulk diffusion.\(^{[83]}\) In this model, the atoms are assumed to diffuse along the surface from an area that is near the neck region toward the neck area.\(^{[83,110]}\) The appropriate expression for the growth of the neck with time is\(^{[115]}\)

\[
\frac{\chi}{a} = \left[ \frac{225\delta_{s}D_{s}\gamma_{sv}\Omega}{k} \right]^{1/3} \quad \text{4.3.2.3.1.2}
\]

where \(D_{s}\) and \(\delta_{s}\) are, respectively the surface diffusivity and surface thickness,\(^{[115]}\) and all the other parameters were defined in Section 4.3.2.3.1.1.

### 4.3.2.3.1.3. Bulk diffusion:

The driving force for bulk diffusion is the higher concentration of vacancies beneath a concave surface than beneath a flat or convex surface.\(^{[83,86]}\) This will cause the transport of vacancies from the concave surface which can occur by the lattice and boundary diffusion, with a concomitant flow of atoms in the opposite direction.\(^{[83,110]}\)

Different researchers have determined different expressions of the change of the neck radius \(\chi\), via these two mechanisms.
For lattice diffusion mode, Johnson\cite{116} has given the equation as:

\[ \frac{\kappa}{a} = \left[ \frac{64D_{amb} \gamma_{SV} \Omega}{k} \right]^{1/4} a^{-\gamma_4} T^{-\gamma_2} \]  \hspace{1cm} 4.3.2.3.1.3(i)

For grain boundary diffusion, Coblenz\cite{115} et al expressed it as:

\[ \frac{\kappa}{a} = \left[ \frac{192\delta_{gb} \gamma_{SV} \Omega^2}{k} \right]^{1/4} a^{-\gamma_4} T^{-\gamma_2} \]  \hspace{1cm} 4.3.2.3.1.3(ii)

where \( D_{amb} \) is the ambipolar diffusivity and \( \delta_{gb} \) is the width of grain boundary\cite{110} and all the other parameters were defined in Section 4.3.2.3.1.1.

Alternatively Ring\cite{80} proposed just one equation for both cases, which has been observed experimentally in a number of metal and ceramic systems\cite{81}, as:

\[ \frac{\kappa}{a} = \left( \frac{40\gamma_{SV} \Omega D^*}{k} \right)^{1/4} a^{-\gamma_4} t^{1/2} T^{1/5} \]  \hspace{1cm} 4.3.2.3.1.3(iii)

where \( D^* \) -- the self-diffusion coefficient for vacancies and all the other parameters were defined in Section 4.3.2.3.1.1.

4.3.2.3.1.4 Summary

Although there are various expressions of various mass transfer mechanisms, it can be concluded from the above equations that for a given materials green body, the main parameters influencing the sintering behaviour is the particle size \((a)\), the sintering time \((t)\) and the sintering temperature \((T)\). However, it is also suggested that control of temperature \((T)\) and particle size \((a)\) is extremely important, but that control of time \((t)\) is less important.\cite{82}

Usually the activation energies for surface, grain boundary, and lattice diffusivity increase in that order.\cite{110} Thus surface diffusion is favoured at lower temperatures and lattice diffusion at higher temperatures.\cite{110} Lattice diffusion is favoured at long sintering times, high sintering temperatures, and larger particles.\cite{110}
4.3.2.3.2 Intermediate stage

The two subsequent stages, intermediate and final stages of sintering, are undesirable in the context of the cathode emitter materials in this work, since they normally lead to densification.

The intermediate stage begins after grain and pore shape changes during which the pore approximates a continuous cylindrical channel situated between three grain edges, with these cylindrical pores simply shrinking.\[81,110\] Moreover, the sizes of the necks continuous to increase and the centres-to-centre distance of the particles decreases.\[81,82\] Most of the densification and shrinkage of a powder compact occurs during it.\[110\]

Modelling of the shrinkage in this stage is complicated by grain growth and a change in the pore geometry, and can depend strongly on the particle packing.\[81,110\] More than one mass transport mechanism may contribute significantly to the changes in microstructure.\[81\] However, a simplified equation to express the linearly decrease of fractional porosity $P_c$ with time is derived by Barsoum\[110\] according to:

\[
P_c = (\text{const}) \left[\frac{D_{gb} \delta_{gb}}{a_v^4} \left(\frac{\gamma_{sv} \Omega}{k b T}\right) (t_f - t)\right]^{2/3}
\]

where $D_{gb}$ is the grain boundary diffusivity, $\delta_{gb}$ is the width of grain boundary and $t_f$ is the time at which the cylindrical channels vanish and $a_v$ is the average diameter of the sintering particles.\[110\] All the other parameters are as previously defined.

Eventually the cylindrical pores break up into a string of spherical and closed pores when the length to radius ratio exceeds a critical ratio.\[81\] Intermediate sintering continues as long as pore channels are interconnected and ends when pores become isolated.

Whilst some intermediate stage sintering may be acceptable, it is crucial in the oxide cathode that the surface area for emission is not reduced too much, and also that the interconnected pore structure is maintained as a pathway for conduction in the oxide material as described in Section 2.
4.3.2.3 Final stage

During the final stage, the strings of the closed pores produced in the intermediate stage will migrate to the point of lowest energy of the grain boundary.\textsuperscript{[81,94]} The pores are then be eliminated via the boundary diffusion and lattice diffusion from sources on the boundary.\textsuperscript{[81]} In addition to the elimination of pores, a general coarsening of the microstructure by grain growth also occurs.\textsuperscript{[110]} During this process, the average grain size increases with time as the smaller grains are consumed by larger grains.\textsuperscript{[110]}

4.3.2.3.4 Other parameters affecting the sintering process

Apart from the particle size and the sintering temperature, there are other variables that are also highly important to the final properties of the sintered produces, these being uniformity of particle packing, the particle shape, and the particle size distribution.\textsuperscript{[117,118]} If particle packing is not uniform in the greenware, it will be very difficult to eliminate all the porosity during sintering and agglomerates are a common source of nonuniformity.\textsuperscript{[82]} Particle shape can also be important.\textsuperscript{[82]} Too high a concentration of elongated or flattened particles can result in bridging during forming, producing a large or irregularly shaped pore that is difficult to remove during sintering.\textsuperscript{[82]} Particle size distribution is also critical.\textsuperscript{[82]} Particles that are all of one size are difficult to pack efficiently; they form compacts with large pores and a high volume percentage of porosity.\textsuperscript{[82]}

In the context of producing the porous cathode material, the microstructure of the cathode material before sintering is thus aimed at encouraging those features that can result in pores that are retained after heating.
4.3.2.4. Liquid-phase sintering

As the eutectic reaction $\text{BaO} \cdot \text{BaCO}_3$ sometimes takes place in $\text{BaCO}_3$ containing system (as described in Section 3.5), which may cause a liquid-phase sintering in the material, so a brief introduction of the liquid-phase is presented below.

During liquid phase sintering, the composition of the power and the sintering temperature are chosen such that a small amount of liquid forms between the grains.\cite{86} The essential requirement for the liquid-phase sintering occurring is when the liquid thoroughly wets the solid particles.\cite{83,110}

Liquid phase sintering is much more rapid than the solid-state sintering and it normally results in uniform densification.\cite{110} This is because that the presence of the liquid reduces the friction between particles and introduced capillary forces that result in the dissolution of sharp edges and the rapid rearrangement of the solid particles.\cite{110}

There are three overlapping stages with each stage is dominated by one mechanism during the sintering process according to the sequence: these mechanisms being particle rearrangement, solution reprecipitation, and solid-state sintering.\cite{86,110}

As the temperature of the material is raised, liquid will form at some point.\cite{86} Particle rearrangement and liquid redistribution happened under the influence of capillary forces and filling of pores by liquid phase.\cite{110,86} This process is very rapid, and normally occur at the early stage of the sintering.\cite{110} If the liquid volume is large enough, full densification can be achieved by rearrangement alone.\cite{86}

The solution reprecipitation process normally occurs after the rearrangement and during which, liquid phase still present. The solid dissolves at the solid-liquid interface with a higher chemical potential, diffuses through the liquid, and precipitates on the particles at other sites with a lower chemical potential.\cite{110,86}

Both coarsening and densification happen in the final stage of the liquid-phase sintering.\cite{86} Coarsening is obtained by grain growth and densification is achieved by the further flowing of the liquid into the isolated pores.\cite{86}
The rate of liquid-phase sintering is also strongly affected by temperature. For most compositions a small increase in temperature results in a substantial increase in the amount of liquid present.

In the context of this investigation, liquid phase sintering, and the associated loss of porosity and emitting surface area can be considered an undesirable phenomenon.
4.4. **Diffusion**

Considering the high temperatures used during processing of the two-layer/impregnated oxide cathode, it is envisaged that diffusion of the Ba and Sr may occur, so some basic introductions of diffusion are given in this section.

Diffusion is the movement of particles from higher chemical potential to lower chemical potential.\(^{[193]}\) Fick's First Law is used in steady state diffusion, i.e., when the concentration within the diffusion volume does not change with respect to time.\(^{[193]}\) It can be expressed as:\(^{[77,194]}\)

\[ J = -D \frac{\partial \phi}{\partial x} \]  
4.4(i)

where \( J \) is the diffusion flux, \( D \) is the diffusion coefficient or diffusivity, \( \phi \) is the concentration, \( x \) is the position.\(^{[77,194]}\)

The diffusion coefficient at different temperatures is often found to be well predicted by:\(^{[194]}\)

\[ D = D_o e^{-\frac{E_A}{RT}} \]  
4.4(ii)

where \( D_o \) is the maximum diffusion coefficient (at infinite temperature); \( E_A \) is the activation energy for diffusion, \( T \) is the temperature in units of absolute temperature and \( R \) is the gas constant.\(^{[77,194]}\)

Although there is no information found for the diffusion of Ba and Sr in conventional cathodes, the diffusion of these two elements have been investigated as trace elements in studies of magma melts\(^{[171]}\), which showed that Sr was found to have a higher diffusivity than Ba in most cases.\(^{[171,172,174]}\) However, the opposing trend as identified in these investigations has been reported for alkaline earth elements in other studies, for example in research into haplogranitic melts by Mungall.\(^{[173]}\)
Chapter 5

Polymer Additives Used in Project

Four types of organic materials were investigated as processing and microstructure modifying additives within this project, these being polyvinyl alcohol (PVA), polyethylene oxide (PEO), polyethylene glycol (PEG) and a commercial organic additive supplied by R.T.Vanderbilt with the trade name being Darvan821A. The polymers were chosen to impart particular properties, with PVA being used as binder in the material, PEO being used as macro- and microstructure modifying additive, whilst PEG is mainly used as a plasticiser. Darvan821A is used as a dispersion aid for the formulation of suspensions of the BaSr(CO3)2 particles.

As mentioned in Chapter 4, polymer additives play an important role in the processing and formation of the desired microstructure of the material. Also, because these additives need to be thermally removed, the thermal decomposition behaviour of these polymers also plays a critical role in the final purity, properties and anticipated emission behaviour of the cathode material produced.

5.1 Polyvinyl Alcohol (PVA)

5.1.1 Structure, preparation and application of PVA

Polyvinyl alcohol is widely used as a binder in ceramic processing due to its high binding strength, water solubility and low cost.\textsuperscript{67}

The basic structure of the PVA polymer comprises a carbon chain backbone with hydrogen atoms and hydroxyl (-OH),\textsuperscript{[119]} with the basic structure shown in Figure 5.1.1.\textsuperscript{[120]} However, the majority of commercial PVA is prepared by alkaline or acid hydrolysis of poly (vinyl acetate),\textsuperscript{[119,120]} which results in a polymer in which a small fraction of un-hydrolysed acetate side groups are present as pendent side groups. The structure of the PVA produced from poly (vinyl acetate) is shown in Fig 5.1.1(b).\textsuperscript{[80]} The amount of these un-hydrolysed acetate side groups is denoted as “the percentage hydrolysis of PVA”. According to the percentage hydrolysis, PVAs are
generally divided into two groups, which are: (i) fully hydrolysed PVA with degree of hydrolysis above 98% (i.e. <2 mol% unhydrolysed acetate group), and (ii) partly hydrolysed PVA with up to 87 to 89% hydrolysis (up to 13 mol% un-hydrolysed acetate group). The basic properties of polyvinyl alcohol depend on its degree of polymerisation and hydrolysis as shown in the diagram in Fig 5.1.1(d).

![Diagram](https://example.com/fig5.1.1a.png)

**Fig 5.1.1(a). Basic structure of PVA (reproduced from ref [120]).**

![Diagram](https://example.com/fig5.1.1b.png)

**Fig 5.1.1(b). Structure of polyvinyl alcohol (PVA) (reproduced from ref [111]).**

![Diagram](https://example.com/fig5.1.1d.png)

**Fig 5.1.1(d). Changes occurring in the properties of polyvinyl alcohol as the degree of hydrolysis and molecular weight change (reproduced from ref [67]).**

The glass transition temperature of PVA is determined to be largely depend on many aspects of the sample, including the degree of residue acetate and adsorbed water, and the range of the glass transition temperature of PVA is 60°C–80°C.
5.1.2. Solubility and Crystallinity

Polyvinyl alcohol is a hydrophilic polymer that dissolves in water and is used mainly when dissolved in water.\textsuperscript{[121,120]} A critical temperature above about 70°C is usually required to bring about rapid solution.\textsuperscript{[121]} The solubility of PVA in water depends largely on its hydrolysis.\textsuperscript{[120]} Its many hydroxyl groups cause it to have high affinity to water, whilst the strong hydrogen bonding between the intra- and intermolecular hydroxyl groups, greatly impeding its solubility in water.\textsuperscript{[120]} The residual acetate groups in partly hydrolysed polyvinyl alcohol are essentially hydrophobic, and weaken the intra- and intermolecular hydrogen bonding of adjoining hydroxyl groups.\textsuperscript{[120]}

PVA is a semi-crystalline polymer and the melting temperature of it vary with the distribution of the residual acetyl groups, with the temperature being normally in the range of 210°C- 250°C.\textsuperscript{[120]} The crystallinity can be indicated by the broad and shallow diffraction peak around the 2θ value of 18° in XRD as shown in Figure 5.1.2(a), which is the XRD of an aqueous solution cast PVA film.\textsuperscript{[119]}

![Figure 5.1.2(a). X-ray diffraction of aqueous solution cast PVA film (reproduced from ref[119]).](image)

However, SEM investigation of the same PVA film has shown no obvious features attributable to any crystalline morphology, as illustrated in Figure 5.1.2(b).\textsuperscript{[119]} This absence of observable crystalline structure in SEM is likely to be due to the limitations of the SEM used, with the sizes of these structures being submicron in dimensions.\textsuperscript{[119]}
Fig 5.1.2(b). Scanning electron micrograph of aqueous solution cast PVA film (reproduced from ref [119]).

5.1.3. Thermal decomposition

The thermal stability of polyvinyl alcohol has been investigated by many workers on various PVA samples under various conditions. These investigations revealed that the stability of polyvinyl alcohol on heating varies significantly with both molecular structure, particularly with molecular weight, and degree of hydrolysis, with the decomposition conditions also having an important effect. Consequently, most of the data published by different investigators cannot be compared directly, due to the different experimental conditions used.

5.1.3.1. TGA analysis

In Table 5.1.3.1 are the TGA results obtained from a number of different investigations of PVA decomposition under N₂ atmosphere with various PVA structures, fabrication routes and heating rates.¹¹⁹,¹²²,¹²³,¹²⁴ It is evident that the various PVA samples exhibit substantially different properties, such as the start temperature of decomposition and the temperature range of each decomposition process depending on the experimental conditions. Examination of the data in Table 5.1.3.1 suggests that range of temperatures over which decomposition occurs and the number of discrete stages of decomposition appears to increase with increasing
molecular weight and degree of hydrolysis, although some care is needed in interpreting these data due to the different experimental conditions of the various published results.

Table 5.1.3.1. Different TGA decomposition results of different PVA samples.

<table>
<thead>
<tr>
<th>Property</th>
<th>A* Heating conditions</th>
<th>TGA results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>Hydrolysis</td>
<td>Heating rate</td>
</tr>
<tr>
<td>$M_w = 2,000$</td>
<td>Aqueous solution cast</td>
<td>10°C/min</td>
</tr>
<tr>
<td>[124]</td>
<td>film</td>
<td></td>
</tr>
<tr>
<td>$M_w = 78,000$</td>
<td>Aqueous solution cast</td>
<td>20°C/min</td>
</tr>
<tr>
<td>[123]</td>
<td>film, 88% hydrolysis</td>
<td>N2</td>
</tr>
<tr>
<td>$M_w = 137,770$</td>
<td>Aqueous solution cast</td>
<td>5°C/min</td>
</tr>
<tr>
<td>[119]</td>
<td>film, 82% hydrolysis</td>
<td></td>
</tr>
<tr>
<td>$M_w = 178,000$</td>
<td>99.7% hydrolysis</td>
<td>5°C/min</td>
</tr>
<tr>
<td>[122]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A*: Atmosphere

Different atmospheres are also shown to have significant effect on the thermal decomposition of PVA. For example, when PVA is decomposed in vacuum, it is reported that the decomposition proceeds in two stages.\textsuperscript{120} The first stage, which begins at 200°C, mainly involves dehydration accompanied by the formation of some volatile products.\textsuperscript{120} The residues are predominantly polymers with conjugated
unsaturated structures.[120] In the second stage, the polyene residues are further degraded at 450°C to yield carbon and hydrocarbons.[125]

For the thermal decomposition of PVA in the presence of oxygen, the first stage degradation reactions are fairly similar to those obtained in vacuum.[126] With increasing temperature, oxidation of the unsaturated polymeric residue from the dehydration reaction introduced ketone groups into the polymer chain.[127] These groups then promote the dehydration of neighbouring vinyl alcohol units producing conjugated unsaturated ketone structure.[127]

The effect of heating rate on the thermal-stability of PVA has also been investigated. Shie et al[128] have studied the thermal decomposition of a PVA powder under nitrogen atmosphere. The result of the TGA investigation is shown in Fig 5.1.3.1(a) and reveals that the higher the heating rate, the earlier the decomposition starts, and the less complete the combustion.

![Thermogravimetric curve of polyvinyl alcohol with different heating rate](image)

Fig 5.1.3.1(a). Thermogravimetric curve of polyvinyl alcohol with different heating rate 1, 2, 3=5, 10, 25°C/min (reproduced from ref[128]).

Despite all the various reported decomposition processes of PVA, there still can be found some similarity. As shown in Figure 5.1.3.1(b), which is a typical thermal decomposition process of PVA under N₂,[122] the decomposition of PVA always consists of an initial stage which is attributed to dehydration reaction and is then followed by multistage decompositions at higher temperatures due to different decomposition mechanisms of PVA molecules depending on the heating conditions.
5.1.3.2. DTA analysis

The DTA analyses of PVA by various investigators generally showed the same effects, that the decomposition of PVA is significantly effected by the various sample properties and heating conditions, with later having especially significant influence. Two atmospheres were normally used, being nitrogen (N₂) and air.

The DTA curve of a PVA sample with $M_w = 178,000$ during thermal decomposition in N₂ is shown in Figure 5.2.3.2(a), \cite{122} in which three endothermic peaks at about 270°C, 370°C and 440°C are detected, corresponding to the three stages of weight loss shown by TGA in Fig 5.1.3.1(a).\cite{122}
PVA decomposition in air has also been studied. However, not many investigations have been reported for pure PVA samples and most of them were PVA composites. There are two DTA curves illustrated in Figures 5.1.3.2(b) and (c) showing the decomposition of two different PVA containing composites.\textsuperscript{129,130}

Fig. 5.1.3.2(b). DTA curve of precursor fibres of PVA/zinc acetate composite (reproduced from ref[130]).

Figure 5.1.3.2(b) is a DTA curve of PVA/zinc acetate which was produced by electrospinning.\textsuperscript{130} The PVA used has a molecular weight of 80,000 and DTA on this composite material was performed in air at the heating rate of 4°C/min.\textsuperscript{130} As observed in the DTA curve, there were two endothermic peaks below 300°C (around 80°C and 263°C) corresponding to the loss of absorbed water,\textsuperscript{130} decomposition of zinc acetate, and the pyrolysis of PVA by a dehydration on the polymer side chain.\textsuperscript{130} The exothermic peak at about 333°C, 419°C and 463°C in the DTA curves was attributed by the author to be the continued decomposition of zinc acetate and the main chain of PVA.\textsuperscript{130}
Figure 5.1.3.2(c) is a DTA curve of a PVA based micro-porous polymer electrolyte prepared by soaking the porous PVA film in LiClO$_4$.\textsuperscript{[129]} The PVA used has a molecular weight of 146,000 and DTA on this composite material was performed in air at the heating rate of 10\textdegree C/min.\textsuperscript{[129]} Two large exothermic peaks are observed at 289.1\textdegree C and 443.9\textdegree C which were both thought to be caused by the decomposition of PVA.\textsuperscript{[129]}

Both the DTA curves showed that when PVA decomposes in air, exothermic peaks were normally present in DTA instead of endothermic peaks under N$_2$ indicating again the different decomposition mechanism of PVA in these two atmospheres. Although no detailed investigations have been made to explain the differences, it is generally considered that pyrolysis happens during PVA decomposition in nitrogen and combustion happens in air.\textsuperscript{[122, 131]}
5.2 Polyethylene oxide (PEO)

5.2.1 Structure, preparation and applications of PEO

Poly (ethylene oxide) (PEO) is a polymer that is used in agricultural engineering, food, dental and pharmaceutical fields because of its aqueous solubility, high gelation and low toxicity.[132-134] It is also widely used as a binder for ceramics, where it also improves the lubricity of the ceramic material for easier mould release and easier compaction.[135]

PEO is a thermoplastic linear homopolymer with etheric linkages and a formula of \((\text{CH}_2\text{-CH}_2\text{-O})_n\).[119,136,137] The structure of PEO is shown in Fig 5.2.1(a).

\[
\text{(CH}_2\text{-CH}_2\text{O})_n
\]

Fig 5.2.1(a). Structure of polyethylene oxide (reproduced from ref [133]).

PEO is normally synthesised by the heterogeneous catalytic polymerisation of ethylene oxide monomer, which comprising a ring structure with the formula \(\text{CH}_2\text{-CH}_2\text{-O}\).[137] The general synthesis process is shown in Fig 5.2.1(b).

**Synthesis of polyethylene oxide**

![Synthesis process of polyethylene oxide](image)

Fig 5.2.1(b). Synthesis process of polyethylene oxide (reproduced from ref [138])

As PVA, the glass transition temperature of PEO differs from different individual materials even if they were with the same molecular weight. But they are all far below the room temperature. For example, Lin[176] Kuo[177] and Zheng[178] all reported the glass transition temperature between -62°C and -67°C for the PEO material with a molecular weight of 20,000.
5.2.2 Solubility and Crystallinity

Polyethylene oxide has a high solubility in water due to hydration of the ether oxygen.\cite{137,139}

Polyethylene oxide is a semi-crystalline polymer with melting temperature normally in the range of 57-73°C.\cite{137} The crystallinity can be determined by the presence in a typical XRD pattern of two well-defined reflection peaks at $2\theta = 19.1^\circ, 23.3^\circ$ as shown in Fig 5.2.2(a).\cite{119} Other investigations also showed the crystallinity in PEO.\cite{140-142} However, as with PVA cast films (Section 5.1.1), no evidence of crystallinity is apparent from SEM images of aqueous solution cast PEO,\cite{119} with the reason probably being a very small crystalline size. By contrast, when PEO films are cast from DMSO (Dimethyl sulfoxide) solution, the presence of PEO crystallites can be determined as shown in Fig 5.2.2(b).\cite{119}

![Fig 5.2.2(a). X-Ray diffraction of aqueous solution cast PEO film (reproduced from ref [119]).](image)

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5.2.3 Thermal decomposition of PEO

As with PVA, the thermal decomposition of PEO with various properties has been investigated under various heating conditions leading to different results. Compared to PVA, the incorporation of oxygen into the backbone of an aliphatic chain polymer results in thermal instability of PEO since the C-O bond is less stable than a C-C bond\cite{159}. It has also been reported that when exposed to air or oxygen, PEO has been reported to oxidatively degrade in both\cite{136} bulk and in solution\cite{137}.

Because PEO is frequently used as processing additives, the thermal analyses of this material were normally carried out only over a limited temperature range which could not show the complete process of PEO decomposition. This lack of the information of PEO decomposition is especially obvious in DTA analysis results as introduced in Section 5.2.3.2.

5.2.3.1. TGA analysis

Figures 5.2.3.1(a) and (b) are TGAs of the thermal decomposition processes of PEO film cast from two different solutions, aqueous ammonia solution and aqueous solution respectively.\cite{143,144} The decompositions of PEO reported in these investigations both exhibited a single major weight loss event indicating a one step
decomposition. It can be seen from these two figures that little residue of PEO is left after 500°C.

Fig 5.2.3.1(a). TGA thermogram of aqueous ammonia solution cast PEO under nitrogen atmosphere and at a heating rate of 10°C/min (reproduced from ref [143]).

Fig 5.2.3.1(b). TGA thermogram of aqueous solution cast PEO under nitrogen atmosphere and at a heating rate of 5°C/min. (reproduced from ref [144]).

The thermal decomposition of PEO ($M_w = 5 \times 10^6$) under different atmosphere has also been reported.\textsuperscript{[145]} Figure 5.2.3.1(c) is a TGA of a PEO under low temperature heating in two different atmospheres, air and Ar respectively. The weight decreased rapidly in air but more gradually under Ar whilst the weight loss in air was larger than that in Ar at 300°C. These results indicated that the oxygen in the air
lowers the decomposition temperature of PEO, and accelerates its decomposition rate.\textsuperscript{[145]}

Fig 5.2.3.1(c). TGA thermogram of PEO in air and Ar at a heating rates of 10°C/min (reproduced from ref\textsuperscript{[145]}).

The effect of heating rate on the thermal-decomposition under a nitrogen atmosphere has been reported for a THF solution cast PEO ($M_w = 20,000$), with the results shown in Figure 5.2.3.1(d).\textsuperscript{[146]} As with PVA, both the onset temperature of decomposition of PEO and the quantity of final residue increased with increasing heating rate.

Fig 5.2.3.1(d). Thermogravimetric curves of PEO at different heating rate. (a). 5°C/min; (b).10°C/min; (c).20°C/min; (d).40°C/min (reproduced from ref [146]).
5.2.3.2. Differential thermal analysis (DTA)

Figure 5.2.3.2(a) shows two DTA curves of the same PEO \((M_w = 5 \times 10^6)\) material, decomposed under air and Ar atmospheres.\(^{[145]}\) The two endothermic peaks identified by DTA both at 75\(^\circ\)C (P and P') were attributed to melting of PEO and the melting temperature of PEO was shown to be independent of the atmosphere. However, the effect of the atmosphere can be seen in the exothermic peaks over about 170\(^\circ\)C.\(^{[145]}\) The reaction with exothermic peaks started at about 170\(^\circ\)C in air, but did not start until over 185\(^\circ\)C in Ar gas.\(^{[145]}\) These results indicate that the oxygen in the air lowers the decomposition temperature of PEO, and accelerates its decomposition rate.

Fig 5.2.3.2(a). DTA of the PEO in air and Ar atmosphere at a heating rate of 10\(^\circ\)C/min (reproduced from ref[145]).

Figure 5.2.3.2(b) is a DTA curve of decomposition of a PEO sample in air with a molecular weight 6\(\times\)10\(^4\) being heated in air at a heating rate of 10\(^\circ\)C/min from room temperature to 400\(^\circ\)C.\(^{[147]}\) This experiment showed a single, large exothermic peak over the temperature range under investigation which resulted from the decomposition of PEO.
Fig 5.2.3.2(b). DTA curve of PEO in air (reproduced from ref[147]).
5.3 Polyethylene glycol (PEG):

5.3.1 Structure, preparation and application of PEG

Polyethylene glycol (PEG) has a formula of HO-(CH₂-CH₂-O)ₙ-H,[148] as shown in Figure 5.3.1. As shown in Figure 5.2.1(a), PEG has an identical monomer structure as that of PEO[149] with PEO and PEG both being polyethers.[149]

![Fig 5.3.1. Formula of polyethylene glycol (reproduced from ref [77]).](image)

The major difference in functionality between them is the terminal end-groups.[149] As shown from these two figures, PEG has one hydroxyl end-group while PEO is not terminated by hydroxyl groups.[148,139]

Another difference between PEO and PEG is the chain length of these two kinds of polymers.[149] Compared with the long molecular chain and high molecular weight of PEO, PEG comprises oligomers or polymers with low molecular weight.[149,139]

Normally PEG is commercially available with molecular weight between 200 and 20,000g/mol.[148] If the molecular weight is at the lower end of this range, the material is a liquid, with this form of the polymer being used as a dispersant or plasticiser in ceramics.[139] However, if the molecular weight is several thousand, the material is wax-like.[149] These higher molecular weight PEG polymers are often used as binders. The glass transition temperature of dry PEG polymers are in the range of -67°C to -27°C.[151] Like PEO, PEG is also produced by polymerisation of ethylene oxide.[149]

PEG has good stability, adhesional wetting, low toxicity and also burns out completely, resulting in wide application in the casting of ceramic.[152] For example, it is used in fabrication of electrically insulative substrates for integrated circuit electronic devices[153] and in manufacturing BaTiO₃.[154]
5.3.2 Solubility and Crystallinity

Because both vinyl (--C--C--) and ether (--C--O--C--) groups are present, PEG is soluble in water and a variety of organic solvents such as alcohols.\textsuperscript{148}

PEG is a semi-crystalline polymer irrespective of the molecular weight. Crystallinity can be detected\textsuperscript{155} by the DSC for example as shown in Fig 5.3.2 for PEG with a number-average molecular weight 1,600. The peak detected at 49.9°C is the melting temperature of the crystallites in this PEG sample.

![Fig 5.3.2. Differential Scanning Calorimeter thermograms of PEG (reproduced from ref[155]).](image)

5.3.3 Thermal decomposition of PEG

As with the studies of PVA and PEO, the DTA of PEG also changed with different heating conditions.

It is suggested that because PEG contains oxygen in its backbone structure, it is subjected to exothermic oxidative degradation at about 180°C.\textsuperscript{180} For the thermolysis of polyethylene glycol in air, decomposition occurs by the mechanisms of chain scission and oxidative degradation.\textsuperscript{180} Whilst when PEG is decomposed in nitrogen atmosphere, the thermolysis proceeds differently.\textsuperscript{180} Some initial oxidation of PEG may occur from the oxygen in the molecules.\textsuperscript{180} Vaporisation is more predominant and in general the thermolysis is endothermic and is shifted to a higher temperature.\textsuperscript{180}
5.3.3.1. Thermal gravimetric analysis (TGA)

The decomposition of PEG has been shown to be relatively rapid and simple due to the lower stability of the C—O bond compared to the C—C bond.\textsuperscript{[168]}

The results of a thermogravimetric (TGA) study\textsuperscript{[156]} showing the thermal decomposition of polyethylene glycol under different atmospheres are shown in the following two figures. Fig 5.3.3.1(a) shows a TGA thermogram of a PEG with molecular weight 2000 under nitrogen atmosphere and Fig 5.3.3.1(b) shows the same material but under air. The decomposition of PEG takes place as a single step process as shown in Fig 5.3.3.1(a) under nitrogen atmosphere, whereas two degradation steps are detected under air as shown in Fig 5.3.3.1(b).\textsuperscript{[156]} Compared to the corresponding TGA analysis under nitrogen, another degradative process takes place at lower temperature ($T_2 \approx 290^\circ C$ and $\Delta W=20\%$) so that the overall stability of PEG is decreased in air in addition to the decomposition stage at $T_1 \approx 390^\circ C$ ($\Delta W=75\%$).\textsuperscript{[156]} These two different TGA curves indicated the different decomposition mechanisms of PEG in N\textsubscript{2} and air.

![TGA Thermogram](image)

Fig 5.3.3.1(a): Thermogrametric analysis of decomposition of Polyethylene glycol with $M_w = 2000$ under nitrogen atmosphere (reproduced from ref [156]).
Fig 5.3.3.1(b): Thermogrammetric analysis of decomposition of Polyethylene glycol with $M_w = 2000$ under air atmosphere (reproduced from ref [156]).

5.3.3.2. Differential thermal analysis (DTA)

Figure 5.3.3.2(a) shows the result of a DTA investigation of PEG being heated in air at a heating rate of $10^\circ$C/min.\textsuperscript{[157]} An endothermic peak was found at about $50^\circ$C, which was attributed to the melting temperature of PEG.\textsuperscript{[157]} With increasing temperature, a broad exothermal peak appeared from $160^\circ$C to $300^\circ$C, which involves a highest peak at $260^\circ$C and another two small peaks at about $200^\circ$C and $275^\circ$C respectively.\textsuperscript{[157]}

Fig. 5.3.3.2(a). DTA analysis of PEG in air at a heating rate of $10^\circ$C/min (reproduced from ref[157]).
A DTA curve of a nanosized TiO₂ stabilised by PEG is shown in Figure 5.3.3.2(b).\textsuperscript{[158]} Thermal analysis was carried out in both air and oxygen at a heating rates of 10°C/min. The two exothermic peaks, 360°C in oxygen and 495°C in air, were both due to oxidation of the PEG phase.\textsuperscript{[158]} The shift of the peaks in these two atmospheres was thought to because of the easier oxidation reaction of PEG in oxygen atmosphere.\textsuperscript{[158]}

The investigations were both in agreement with the findings previously mentioned\textsuperscript{[80]} that exothermic reaction occur during PEG decomposition in the presence of oxygen. However, no reports were found about the DTA of PEG decomposing in nitrogen, in the literature.
5.4. **Combinations of the polymers**

The properties of the three polymers, PVA, PEO and PEG, were introduced in Section 5.1 to 5.3 respectively. In this project, these polymers are used as a combination in the cathode material. The use of combinations of these polymers has been previously reported for the combination of PVA/PEO, PVA/PEG and PEO/PEG, these findings being introduced in the following sections. There was no literature found in which these three polymers were used together.

5.4.1. Combination of PVA and PEO

Rachna et al\[119\] investigated PVA/PEO material with various compositions. One of the distinctive features of the PVA/PEO combination is the occurrence of phase separation. Rachna’s study found that mutual miscibility of PEO and PVA was likely to exist over only a small range of compositions (PEO:PVA=80:20).\[119\] The mixtures otherwise formed only microscopically immiscible blends which did not possess a tendency for extensive mutual solubility.\[119\] The phase separation could be shown by SEM micrograph.

The SEM images of the microstructure of three PVA/PEO blend cast films with different proportions of PVA and PEO are shown in Figures 5.4.1(a) to (c) with increasing PVA content.\[119\] It showed that for the PVA/PEO of 60/40, phase separation exhibited with droplet like features as shown in Figures (b).\[119\] These droplets were likely to be amorphous PVA while the other portions which appear like lamellae are PEO.\[119\] But in the case of 50/50 blend (Figure(a)) there was evidence of only the formation of lamellae which are also sparse and distributed in an amorphous matrix.\[119\] It is difficult to identify features in this SEM attributable to induced crystallisation of PVA.\[119\] Figure 5.4.1(c) shows the microstructure of PVA rich composition, which were essentially featureless with only occasional feature attributed to the formation of fibroids.\[119\] The investigation also revealed that both in PEO rich and PVA rich blends neither the droplet nor the lamellaer morphology were as prevalent as in those intermediate compositions.\[119\]
Macroscopically coherent films were found to be formed by PVA and PEO no matter what is the composition between them.\cite{119}

Fig 5.4.1(a), SEM of polymer film with 50\%PEO and 50\%PVA (reproduced from ref\cite{119}).

Fig. 5.4.1(b). SEM of polymer film with 40\%PEO and 60\%PVA (reproduced from ref\cite{119}).
Fig 5.4.1(c). SEM of a PVA rich PEO/PVA blend cast film (reproduced from ref[119]).

PEO-PVA combinations have also been reported for use in polymer electrolyte.[159] Scanning electron micrographs of the PEO-PVA-KOH film are shown in Figures 5.4.1(d) and (e).[159] The compositions of each component in the film was PEO:PVA:KOH:H₂O =19.5:19.5:38:23. Similarly as observed in pure polymer film with 50PVA/50PEO[119] (Figure 5.5.1(b)), the polymer forms a three-dimensional network structure with its surface also containing many small pores of different sizes.

(d)low magnification
Fig 5.4.1(d),(e). SEM of alkaline PEO based polymer electrolyte with PEO:PVA=5:5 and PEO:PVA:KOH:H2O=19.5:19.5:38:23 of lower (d) and higher (e) magnification (reported from ref[159]).

Different results have been reported regarding the crystallinity of the PVA/PEO blends by different workers.

Rao et al[119] showed that crystallites exists in PVA/PEO blends with all compositions by both X-ray diffraction and DTA studies as shown in Figures 5.4.1(f) and (g), which are the X-ray diffraction and DTA of pure PVA, PEO cast films and PVA/PEO blend cast film with 50wt%PVA/50wt%PEO. The appearance of the peaks in XRD and DTA both indicated the existence of the crystallinity.

However, Yang suggested that when PEO was mixed with PVA, the whole material changed gradually from a semi-crystalline to an amorphous phase by the shift of the melting temperature of PEO towards a lower temperature in DSC curve as shown in Figure 5.4.1(h).[159] Moreover, when PVA ratio is 50%, the material changed completely to an amorphous state.[159]
Fig 5.4.1(f),(g). X-ray diffraction (f) and DTA analysis (g) of PVA and PEO pure polymer and 50PVA/50PEO blend cast films (reported from ref[119]).
Fig 5.4.1(h). DSC thermograph for PEO-PVA-KOH electrolyte at various compositions of PEO:PVA (reproduced from ref[159]).

5.4.2. Combination of PEO and PEG

Studies of the compatibility between PEO and PEG were carried out by Abdel-Azim and co-workers\textsuperscript{[160]} in benzene at 293.15K and 303.15K by viscometric technique. Three molecular weights of PEO were used, which were $1\times10^5$(PEO1), $3\times10^5$(PEO3) and $6\times10^5$(PEO6) respectively with the molecular weight of the PEG investigated being $1\times10^5$.\textsuperscript{[160]} The study showed that only compatible blends were achieved when the molecular weight of PEG and PEO nearly equal, while for the polymer blends with PEG and higher molecular weight PEO, no compatibility was found for all the compositions.\textsuperscript{[160]} Even for the PEO/PEG blends with nearly equal molecular weight, the compatibility is detected only in case of the blends PEG(75%)/PEO1(25%) and PEG(10%)/PEO1(90%).\textsuperscript{[160]}

5.4.3. Combination of PVA and PEG

PVA and PEG are used together mainly for two purposes. When used in ceramic casting process, PVA and PEG are popular candidates for binder and plasticizer, respectively. More recently, PVA/PEG hydrogels have been widely explored as water-soluble polymers for numerous biomedical and pharmaceutical applications due
to the advantages of non-toxic, non-carcinogenic and bio-adhesive properties.\textsuperscript{161} The hydroxyl groups in PVA and PEG allow them to be crosslinked with several reagents.\textsuperscript{161} However, the PVA/PEG used in this project is not crosslinked but only mechanically blended in aqueous solvent.

Abd et al\textsuperscript{162} investigated the PVA/PEG aqueous cast films with various compositions of PVA and PEG and suggested that although individual PVA and PEG could form homogeneous and clear films, transparent PVA/PEG aqueous cast films were only formed by solution casting of containing low ratios of PEG up to 30\% indicating the miscibility between these two polymers. When the contents of PEG in the polymer blends were increased beyond 40\%, phase separation was observed and the transparency no longer occurred.

Halabalova et al have investigated PVA and PEG blends in dilute solution of water and dimethyl sulfoxide (DMSO).\textsuperscript{163} In this case, the composition of PEG in all materials were equal or bugger than that of PVA. The results provided evidence of the compatibility of these polymers in both solvents.\textsuperscript{163}
5.5. Darvan821A

As introduced in Section 4.1.3.2, dispersants are very important processing additives for suspension processing, where they are used to reduce agglomeration and flocculation of particles.\cite{90} Dispersants based in carboxylic acid units, such as ammonium salts of polymethacrylic acid (PMAA) and polyacrylic acid (PAA) are examples of very common dispersants of this type which have been used by researchers, often in combination with other processing additives, such as binder.\cite{153} They are known to be effective in stabilising concentrated suspensions of different ceramic oxides, as well as Al₂O₃ and BaTiO₃ aqueous suspension.\cite{164}

The ammonium salt of polyacrylic acid (PAA-NH₄) was used in this project, this material being sold commercially under the trade name Darvan821A. Darvan821A comprises 40wt% ammonium polyacrylate in solution and has a molecular weight of approximately 3500.\cite{165} It is an anionic dispersant used especially in water.\cite{81,153} The active agent in it is polyacrylic acid.\cite{153}

In polar media, such as water, there are three basic mechanisms of suspension stabilization, which are electrostatic stabilization, steric stabilization and electrosteric stabilization.\cite{166} In electrostatic stabilization, repulsive electrostatic forces between particles caused by excess electric charges are used to prevent agglomerations, the charges being present on the particle surface, which can be caused by the selective adsorption of charged species from the dispersant.\cite{90} In steric stabilization, adsorbed organic molecules are employed to induce steric repulsion, preventing the close approach of particles. In comparison to the electrostatic effect, steric stabilization is a short-range force.\cite{90}

It is proposed\cite{90} that Darvan dispersant stabilises the dispersions by electrosteric stabilization, which is a combination of the above two mechanisms. These dispersants contain at least one type of ionized group within a molecule structure.

However, the effectiveness of the electrosteric dispersant on stabilising the suspension depends on the pH of the suspension.\cite{90,167} For Darvan821A used it is
suggested that at pH values ≤2, the functional groups remain as COOH and the polyelectrolyte behaves as a neutral polymer.\textsuperscript{165} As the pH is increased, H\textsuperscript{+} ions dissociate from the polymer, leaving charged COO\textsuperscript{-} groups along the chain to help provide dispersion,\textsuperscript{165} with the dissociation process expressed in equation 5.5.\textsuperscript{90} At this stage, the polyacrylic acid anions adsorb on the positively charged ceramic surface and the ceramics can be stabilised due to the presence of repulsive forces.\textsuperscript{90} Further increasing the pH promotes H\textsuperscript{+} dissociation until pH≥7 where the polyelectrolyte is nearly fully dissociation.\textsuperscript{165}

\[ R-COOH + H_2O \rightleftharpoons R-COO^- + H_3O^+ \]  

5.5

Darvan\textsuperscript{821A} is reported to have a low ash content and work well when prolonged ball milling or shear mixing are necessary.\textsuperscript{153} In comparison to the other types of dispersant such as the sodium silicate system, this polyelectrolyte is claimed to produce suspensions with longer casting range, higher solids content, improved viscosity and stability.\textsuperscript{153}
Part Three
Experimental Methods
Chapter 6

Materials Processing Methods

6.1. Chemicals used

**Barium Strontium Carbonate (BaSrCO\textsubscript{3})**

The Barium Strontium Carbonate [BaSr(CO\textsubscript{3})\textsubscript{2}] used in this project is a white solid powder mixture of barium carbonate (BaCO\textsubscript{3}) and strontium carbonate (SrCO\textsubscript{3}) and is provided by LG-Philips Displays. The ratio of BaCO\textsubscript{3} to SrCO\textsubscript{3} in the mixture is 57±2.5\% to 43±2.5\% by weight and the density at 20°C is 4g/cm\textsuperscript{3}.\textsuperscript{[169]} The particles have specific area of 2.6±0.3m\textsuperscript{2}/g. 84\% of the particles are in the size range of 2.7±0.4\,\mu m and 50\% of them are in the range of 1.5±0.3\,\mu m, with the remaining 16\% being in the size range of 0.8±0.2\,\mu m.\textsuperscript{[169]}

**Filamentary Ni:**

INCO Nickel Powder 210 was selected as the conductive metallic phase addition in these experiments. This is a grey odourless powder with the atomic weight 58.71. The average particle size is between 0.5-1.0\,\mu m and bulk density < 0.8g/cm\textsuperscript{3}. The purity of the Ni filament is 99.0\%.\textsuperscript{[169]}

**Polymer additives**

**Polyvinyl Alcohol (PVA):** The PVA used in these studies was 98\% hydrolysed and with a Mw≈ 22,000 and viscosity of 4\% aqueous solution at 20°C about 6cPs. The material was obtained from BDH Laboratory Supplies (Catalogue No305735B).

**Polyethylene Oxide (PEO):** The PEO used in these investigations comprised a white, free-flowing powder supplied by Amerchol Corporation (POLYOX WSR N-10); the approximate molecular weight is 100,000 and the viscosity of this powder in 5\% aqueous solution is 30-50 cPs.
**Polyethylene Glycol (PEG)**: the PEG used in these investigations had an average molecular weight of 1,000 and was in the form of a wax like solid. The material was supplied by Sigma-Aldrich (Catalogue No20,242-8).

**Darvan 821A**: Darvan 821A is a pale yellow liquid which comprises ammonium polyacrylate and water.\textsuperscript{[170]} Chemical name is 2-propenoic acid, homopolymer, ammonium salt. It has a solid content of 39.5-40.5\% and has a pH value of 7.0-7.5.\textsuperscript{[170]} The specific gravity is 1.16-1.19\text{mg/m}^3 at 25\textdegree C and is purchased from R.T.Vanderbilt Company, Inc.

* No data is available on the purity of these materials.
6.2 **Manufacture of new oxide cathode designs**

Two different structures have been designed for the new oxide cathode, the *integrated oxide cathode* and *two-layer/impregnated oxide cathode*, as introduced in Figures 1.2(a) and (b). In this chapter, the two new designs of cathodes and the manufacturing processes developed to produce them during this work are described.

The integrated oxide cathode (Figure 1.2(a)) is essentially in the form of a porous pellet with the material being a mixture of barium strontium oxide and Ni filament (BaSrO$_2$/Ni). The other cathode structure designed, the two-layer/impregnated cathode (Figure 1.2(b)), comprises of a porous Ni pellet as the base, with barium strontium oxide (BaSrO$_2$) distributed in and on it.

As in conventional oxide cathode processing (introduced in Section 2.3), BaSr(CO$_3$)$_2$ is used as the precursor material in the manufacture of both these new cathode designs, with this being thermally converted to BaSrO$_2$ in a subsequent heating step. The material produced in the initial stage of the manufacturing process containing barium strontium carbonates [BaSr(CO$_3$)$_2$] is called the cathode precursor in the following sections.

The manufacturing process of the BaSr(CO$_3$)$_2$ containing cathode precursor is based on variant of a very common ceramic forming technique — casting. The essential process consists of casting the materials containing appropriate compositions of constituents in the form of a film with suitable macro and micro-structures and mechanical properties, followed by stamping out the cathode emitter component (precursor) directly from this film. The manufacturing processes of these BaSr(CO$_3$)$_2$ containing cathode precursors are described in Section 6.2.1 for the integrated oxide cathode and Section 6.2.2 for the two-layer/impregnated cathode respectively.

After a cathode precursor is produced with appropriate macro and micro properties, it is then thermally converted to BaSrO$_2$ in a subsequent step. This heat treatment step will be introduced and described in Section 6.3 for both the new designs of cathode. Although for practical reasons, heat treatments were not performed under vacuum in these experiments. In the final form of this process, it is
envisaged that this process will be carried out in situ within the sealed CRT tube in order to ensure that the resultant oxide material is not degraded by atmospheric reactions.

**6.2.1. Manufacture of integrated oxide cathode precursor**

The production of the precursor of this new cathode structure \([\text{BaSr(CO}_3]_2/\text{Ni}\) as a form of pellet will be introduced in this section. The complete manufacturing process developed is illustrated diagrammatically in the flowchart shown in Figure 6.2.1.

As shown above, the production process involves the following main steps:

1. The formation of a suitable casting suspension (Section 6.2.1.1);
2. Casting to form a solid film (Section 6.2.1.2);
3. Stamping the cathode component precursor from the cast film as a form of pellet (Section 6.2.1.2).

The resultant cathode precursor is then subjected to a final heat treatment for thermal conversion to remove organic process additives, and to obtain a suitable microstructure. This heat treatment is described in Section 6.3.1.

![Flowchart of the manufacturing process of the integrated oxide cathode](image)

Fig 6.2.1. Flowchart of the manufacturing process of the integrated oxide cathode
6.2.1.1. Formation of the casting suspension

The casting suspension comprises three basic components: (a), the active components of the cathode (BaSr(CO₃)₂ powder and Ni filament); (b), a number of organic based processing additives (binders and plasticiser); and (c), solvent (water). An aqueous system was developed for the process, in which the water played a dual role as a suspension media for the insoluble compounds and a solvent for the hydrophilic polymer additives. As introduced in Chapter 5, three polymers, PVA, PEO and PEG, were used in this material as the processing additives.

A typical formulation used would comprise equal additions of active components and polymer additives by mass. The amount of each individual material component used will be expressed as:

\[ m_i \% = \frac{m_i}{m_{carbonate} + m_{Ni} + m_{polymer}} \% \]  
6.2.1.1(i)

where \( m_i \) — the mass of the relevant component added.

The concentrations of the casting suspensions are measured as the solid content of the suspension which is expressed as:

\[ \text{Solid content}\% = \frac{m_{carbonate} + m_{polymer}}{m_{carbonate} + m_{polymer} + m_{water}} \text{ wt}\% \]  
6.2.1.1(ii)

The preparation of the casting suspension comprises several steps as shown in Fig 6.2.1.1.

1.1. Mixing of BaSr(CO₃)₂, Ni with solvent by magnetic stirring at room temperature for 1 hour

1.2. Adding polymer additives to the suspension and magnetic stirring at 90°C for 1 hour

1.3. Leave at room temperature whilst stirring for another 1 hour

Fig 6.2.1.1. Flowchart showing preparation of casting suspension
In the initial mixing step, BaSr(CO\textsubscript{3})\textsubscript{2} and Ni are mixed with water to produce a suspension which is stirred for one hour using a magnetic stirrer under ambient conditions to obtain homogenous mixing. As shown in Fig 6.2.1.1, the polymer additives are then added to the suspension and the system is heated to 90°C and stirred for 1 hour to achieve polymer dissolution. Finally, the suspension is cooled to room temperature and kept stirring for 1 hour for further mixing of all the components to give a well-distributed suspension.

Experiments showed that macrostructures of the as cast films were decided largely by the proportions of each component in the casting suspension. An initial series of experiments were performed in which the proportions of the individual components in the casting suspensions were changed separately to investigate their effects on the resultant materials. The effect of three variables were investigated, these being (a), the compositions of the polymer additives (PVA, PEO and PEG); (b), the solid content (amount of liquid); and (c), the ratios of BaSr(CO\textsubscript{3})\textsubscript{2} to Ni in the cathode material.

6.2.1.1. Effect of polymer compositions in the casting suspension

As cast BaSr(CO\textsubscript{3})\textsubscript{2}/Ni/polymer composite films with various compositions of three polymer additives were produced for investigation and determining the suitable polymer composition for producing a cast film with suitable macrostructure. The proportions of the other components, including BaSr(CO\textsubscript{3})\textsubscript{2}, Ni and solvent were kept standardized in this series of experiments with a solid content of 13.3 wt% being used throughout these investigations. The percentages of the various components in the casting suspension were determined as described in equations 6.2.1.1(i) and 6.2.1.1(ii).
6.2.1.1.1. As cast materials with individual polymers

Initially, the three polymers were separately added into the casting suspension in order to ascertain their effects. The compositions of the resultant casting suspensions are listed in Table 6.2.1.1.1.

Table 6.2.1.1.1: Compositions of each component in casting suspensions with different type and amount of polymer.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>BaSr(CO₃)₂</th>
<th>Ni</th>
<th>PVA</th>
<th>PEO</th>
<th>PEG</th>
<th>Solid content</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSr(CO₃)₂</td>
<td>48 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>2 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>50 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO</td>
<td>50 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50 wt%</td>
<td></td>
</tr>
<tr>
<td>Solid content</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.3 wt%</td>
</tr>
</tbody>
</table>

6.2.1.1.2. As cast films with PVA and PEG

A series of experiments were then carried out in which PVA and PEG were used in combination as processing additives in the suspension. In this case, PVA is used as main binder and PEG is used as plasticiser. The compositions investigated are listed in Table 6.2.1.1.2.

Table 6.2.1.1.2: Compositions of each component in casting suspensions with different proportions of PVA and PEG.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>BaSr(CO₃)₂</th>
<th>Ni</th>
<th>PVA</th>
<th>PEO</th>
<th>PEG</th>
<th>Solid content</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSr(CO₃)₂</td>
<td>48 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>2 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>45 wt%</td>
<td>35 wt%</td>
<td>25 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG</td>
<td>5 wt%</td>
<td>15 wt%</td>
<td>25 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid content</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.3 wt%</td>
</tr>
</tbody>
</table>
6.2.1.1.3. As cast films with PVA and PEO

In the next set of experiments, the effects of combinations of PVA and PEO as organic additives were investigated, where both act as binders. Both the amount of BaSr(CO$_3$)$_2$, Ni and the solid content of the suspension were kept constant. The range of formulations investigated is shown in Table 6.2.1.1.3.

Table 6.2.1.1.3: Compositions of each component in casting suspensions with different proportions of PVA and PEO.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>BaSr(CO$_3$)$_2$</th>
<th>48 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2 wt%</td>
<td></td>
</tr>
<tr>
<td>Polymer additives</td>
<td>PVA</td>
<td>45 wt%</td>
</tr>
<tr>
<td></td>
<td>35 wt%</td>
<td>25 wt%</td>
</tr>
<tr>
<td>PEO</td>
<td>5 wt%</td>
<td>15 wt%</td>
</tr>
<tr>
<td></td>
<td>25 wt%</td>
<td></td>
</tr>
<tr>
<td>PEG</td>
<td>10 wt%</td>
<td>20 wt%</td>
</tr>
<tr>
<td></td>
<td>20 wt%</td>
<td></td>
</tr>
<tr>
<td>Solid content</td>
<td></td>
<td>13.3 wt%</td>
</tr>
</tbody>
</table>

6.2.1.1.4. As cast films with PVA, PEO and PEG

Finally, the effect of combinations of PVA, PEO and PEG as processing additives in the casting suspension were investigated. In these experiments, three different compositions between PVA, PEO and PEG were employed as described in Table 6.2.1.1.4. The PVA and PEO comprised the organic binders whilst PEG was added as a plasticiser in these experiments.

Table 6.2.1.1.4: Compositions of each component in casting suspensions with different proportions of PVA, PEO and PEG.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>BaSr(CO$_3$)$_2$</th>
<th>48 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2 wt%</td>
<td></td>
</tr>
<tr>
<td>Polymer additives</td>
<td>PVA</td>
<td>40 wt%</td>
</tr>
<tr>
<td></td>
<td>30 wt%</td>
<td>20 wt%</td>
</tr>
<tr>
<td>PEO</td>
<td>5 wt%</td>
<td>10 wt%</td>
</tr>
<tr>
<td></td>
<td>20 wt%</td>
<td></td>
</tr>
<tr>
<td>PEG</td>
<td>5 wt%</td>
<td>10 wt%</td>
</tr>
<tr>
<td></td>
<td>10 wt%</td>
<td></td>
</tr>
<tr>
<td>Solid content</td>
<td></td>
<td>13.3 wt%</td>
</tr>
</tbody>
</table>
6.2.1.1.5. Preparation of cast polymer films

As a control, and to better understand the role of the organic components, a series of polymer films were also produced in the same way as the BaSr(CO$_2$)$_2$/Ni/polymer composite films but without the carbonate and Ni components. The range of formulations produced and tested is listed in Table 6.2.1.1.5.

Table 6.2.1.1.5. Compositions of the suspension used to produce the polymer cast films.

<table>
<thead>
<tr>
<th>Film Compositions</th>
<th>PVA</th>
<th>PEO</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Individual</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>polymer films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA film</td>
<td>100wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO film</td>
<td></td>
<td>100wt%</td>
<td></td>
</tr>
<tr>
<td>PEG film</td>
<td></td>
<td></td>
<td>100wt%</td>
</tr>
<tr>
<td><strong>Bi-polymer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA-PEG film</td>
<td>90wt% ~</td>
<td></td>
<td>10wt% ~</td>
</tr>
<tr>
<td></td>
<td>50wt%</td>
<td></td>
<td>50wt%</td>
</tr>
<tr>
<td>PVA-PEO film</td>
<td>90wt% ~</td>
<td>10wt% ~</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50wt%</td>
<td>50wt%</td>
<td></td>
</tr>
<tr>
<td>PEO-PEG film</td>
<td></td>
<td></td>
<td>90wt% ~</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10wt% ~</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50wt%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50wt%</td>
</tr>
<tr>
<td><strong>Tri-polymer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA-PEO-PEG film</td>
<td>60wt%</td>
<td>20wt%</td>
<td>20wt%</td>
</tr>
<tr>
<td>film</td>
<td>40wt%</td>
<td>40wt%</td>
<td>20wt%</td>
</tr>
</tbody>
</table>
6.2.1.1.2. Effect of the solid content in the casting suspension

In this series of experiments, the effect of variations in the casting suspension was investigated by changing the amounts of water used to prepare the suspensions with the weights and proportions of the other constituents were kept constant. The amount and proportions of the constituents were calculated as outlined in equations 6.2.1.1(i) and 6.2.1.1(ii) with the following formulations being investigated.

Table 6.2.1.1.2: Different solid contents in casting suspensions.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>Polymer additives</th>
<th>Solid content</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSr(CO₃)₂</td>
<td>Ni</td>
<td></td>
</tr>
<tr>
<td>48 wt%</td>
<td>2 wt%</td>
<td>9.8 wt%</td>
</tr>
<tr>
<td></td>
<td>20 wt%</td>
<td>10.5 wt%</td>
</tr>
<tr>
<td></td>
<td>20 wt%</td>
<td>11.0 wt%</td>
</tr>
<tr>
<td></td>
<td>10 wt%</td>
<td>13.3 wt%</td>
</tr>
<tr>
<td></td>
<td>10 wt%</td>
<td>13.9 wt%</td>
</tr>
<tr>
<td></td>
<td>10 wt%</td>
<td>17.5 wt%</td>
</tr>
</tbody>
</table>
6.2.1.1.3. Effect of Ni/carbonate ratios in the cathode material

The proportions between the active components of the cathode, BaSr(CO$_3$)$_2$ and Ni, have also been studied for their effects on the macrostructures of the cast composite film. These different proportions of BaSr(CO$_3$)$_2$ and Ni are expressed as the ratios of BaSr(CO$_3$)$_2$ to Ni as BaSr(CO$_3$)$_2$/Ni. Two ratios were used for initial investigation as shown in Table 6.2.1.1.3 with the combined total amount of these two constituents being kept constant, at 50 wt% of the total solid materials. For each ratio investigated, three different solid contents were trialled as shown in Table 6.2.1.1.3.

Table 6.2.1.1.3. Compositions of casting suspension with different ratio of BaSr(CO$_3$)$_2$ and Ni.

<table>
<thead>
<tr>
<th>Cathode material BaSr(CO$_3$)$_2$ : Ni</th>
<th>Polymer additives</th>
<th>Solid content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PEO</td>
<td>PVA</td>
</tr>
<tr>
<td>48 wt% : 2 wt%</td>
<td>20 wt%</td>
<td>20 wt%</td>
</tr>
<tr>
<td>40 wt% : 10 wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.8 wt%</td>
<td>9.8 wt%</td>
</tr>
<tr>
<td></td>
<td>13.3 wt%</td>
<td>13.3 wt%</td>
</tr>
<tr>
<td></td>
<td>17.5 wt%</td>
<td>17.5 wt%</td>
</tr>
</tbody>
</table>
6.2.1.2. Casting and stamping

Following the formation of the casting suspensions with various formulations described in Section 6.2.1.1, the suspensions were then poured into a mould and left under ambient conditions for further drying for a period of about 5 days depending on the environmental conditions, after which thin, semi-flexible composite films were obtained. In these experiments a square plastic tray, with a surface area of 34 cm$^2$ was used as the mould.

The next process is stamping. The as-cast film was cut to the pre-calculated dimensions about 2.95-3mm in diameter to allow for subsequent shrinkage during thermal conversion. In these initial experiments the stamping was performed using a thin walled (0.31mm) hollow steel tube, which was simply pressed into the cast film to cut out the cathode pellet. Inside the steel tube a steel plunger with a diameter of 0.78mm was used to push the resultant stamped cathode pellet out of the tube. In Fig 6.2.1.2 is a schematic map showing the basic design of the cutting tool. The so-stamped cathode precursor was then ready for thermal conversion which is introduced in Section 6.3.1.

![Schematic map showing the structure of the steel tube and steel stick for stamping out the cathode pellet.](image)

Fig 6.2.1.2. Schematic map showing the structure of the steel tube and steel stick for stamping out the cathode pellet.
6.2.2. Manufacture of two-layer/impregnated oxide cathode

The two-layer/impregnated oxide cathode is designed as a two component system consisting of a porous Ni substrate with BaSrO₂ particles distributed either as a thin layer on its surface, and/or with these particles penetrating the porous structure to form a BaSrO₂ impregnated Ni matrix after conversion heat treatment to form a so-called two-layer or impregnated oxide cathode respectively. The type of structure obtained is dependent on the respective sizes of the pore structure in the nickel substrate and the particle agglomerate sizes in the carbonate suspension. The main processes are shown as a flowchart in Fig 6.2.2.

![Flowchart of the manufacturing process of the two-layered/impregnated oxide cathode.](image)

**Fig 6.2.2. Flowchart of the manufacturing process of the two-layered/impregnated oxide cathode.**
As shown above, the manufacturing process for this two-layer/impregnated cathode entailed three main steps:

(1). Fabrication of porous Ni substrate (Section 6.2.2.1 and Section 6.3.2.1);
(2). Preparation of BaSr(CO₃)₂ containing suspension (Section 6.2.2.2)
(3). Application of BaSr(CO₃)₂ particles onto the Ni substrate (Section 6.2.2.3);

As with the integrated oxide cathode, the resultant cathode precursor is then subjected to a final heat treatment for thermal conversion and to obtain a suitable satisfactory microstructure. This heat treatment is described in Section 6.3.2.2.

6.2.2.1. **Fabrication of porous Ni substrate**

As shown in Figure 6.2.2, the fabrication of the porous Ni substrate used in the two-layer/impregnated oxide cathode was produced in a similar way to the integrated oxide cathode and was also based on a casting technique. The detailed fabrication process is introduced in the following sections.

6.2.2.1.1. **Preparation of Ni/polymer composite suspension**

The Ni casting suspension comprised three components: (a), Ni filaments; (b), a number of processing additives (polymers); and (c), solvent (water). The stages involved in the preparation of the Ni suspension used for casting in this process (step 1.1 in Fig 6.2.2) are shown below in Figure 6.2.2.1.1:

1.1.1. Mixing and magnetic stirring of Ni and water at room temperature for 1 hour

1.1.2. Adding polymer processing additives to the suspension and magnetic stirring at 90°C for 1 hour

1.1.3. Leave at room temperature with stirring for 1 hour

Fig 6.2.2.1.1. Flowchart of preparation of Ni/polymer casting suspension.
The Ni containing casting suspension is also produced by mixing Ni, polymer and solvent. Experiments were carried out to investigate the proper amount of Ni and polymer additives in the suspension which produced the Ni substrate with optimum macrostructure and microstructure. Ni containing suspensions with four different proportions of Ni and polymer additives were prepared with the solid contents and the polymers additive were kept constant. The formulations of each component in the suspensions are listed in Table 6.2.2.1.1. The proportions of these components being determined as previously described in equations 6.2.1.1(i) and 6.2.1.1(ii).

Table 6.2.2.1.1: Different proportions of Ni filament and polymer additives used in Ni/polymer casting suspensions.

<table>
<thead>
<tr>
<th>Ni</th>
<th>Polymer content</th>
<th>Polymer compositions</th>
<th>Solid content</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt% (0.2g)</td>
<td>90 wt% (1.8g)</td>
<td>PVA:PEO:PEG 20wt%:20wt%:10wt%</td>
<td>13.3 wt%</td>
</tr>
<tr>
<td>15 wt% (0.3g)</td>
<td>85 wt% (1.7g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 wt% (0.4g)</td>
<td>80 wt% (1.6g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 wt% (0.5g)</td>
<td>75 wt% (1.5g)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.2.2.1.2. Casting and mechanical stamping

The method used for casting and stamping of the Ni substrate was the same as described in Section 6.2.1.2. After the formation of these Ni/polymer casting suspensions, these were poured into the mould and dried under ambient conditions. After casting and drying, the resultant Ni/polymer composite films were stamped into pellets with diameter of 2.95-3mm using the same cutting tool.

6.2.2.1.3. Heat treatment to make a porous Ni substrate

Following the stamping step, the stamped Ni/polymer pellet was subsequently heated to remove the polymers and generate the required porous structure, and also to provide some mechanical strength by partially sintering. This heat treatment of the Ni
substrate is different from the final heat treatment (for BaSr(CO$_3$)$_2$ conversion) and is denoted the initial heat treatment (step 1.4 in Figure 6.2.2). This heating step is described in Section 6.3.2.1.

### 6.2.2.2. Preparation of BaSr(CO$_3$)$_2$ suspension

In order to obtain the designed two-layer/impregnated cathode structure, the BaSrO$_2$ emitting material was embedded into Ni substrate by applying the BaSr(CO$_3$)$_2$ precursor powder in the form of an aqueous suspension onto the porous Ni substrate. The preparation of BaSr(CO$_3$)$_2$ suspension is described in this section.

A flowchart showing the basic stages in the preparation process is shown in Figure 6.2.2.2.

![Flowchart of the preparation of BaSr(CO$_3$)$_2$ suspension](image)

**Fig 6.2.2.2. Flowchart of the preparation of BaSr(CO$_3$)$_2$ suspension**

As shown above, various conditions (dispersant and ultrasonic treatment) for preparing the BaSr(CO$_3$)$_2$ suspension were used to investigate their effects on the morphology and sizes of BaSr(CO$_3$)$_2$ powder and the subsequent effects on the structure and microstructure of the resultant cathode. Four different BaSr(CO$_3$)$_2$ suspensions were thus prepared which were:
(a). BaSr(CO$_3$)$_2$ + water;
(b). BaSr(CO$_3$)$_2$ + water + dispersant;
(c). BaSr(CO$_3$)$_2$ + water + 15 minutes ultrasonic treatment;
(d). BaSr(CO$_3$)$_2$ + water + dispersant + 15 minutes ultrasonic treatment;

In the suspension containing only BaSr(CO$_3$)$_2$ and water, a solid content of 13.04 wt% was used (refer to equation 6.2.1.1(ii)). When Darvan 821A is added, normally a 1 wt% of the weight of the BaSr(CO$_3$)$_2$ was used.

SEM was used to investigate these conditions and additives on the morphology and size of the BaSr(CO$_3$)$_2$ particles as described in Section 6.4.1. The BaSr(CO$_3$)$_2$ suspension was then ready for the next cathode preparation step (Section 6.2.2.3).

6.2.2.3. Manufacturing of two-layer/impregnated oxide cathode precursor-Impregnation

After formation of a well dispersed BaSr(CO$_3$)$_2$ suspension as described in Section 6.2.2.2, appropriate additions of the suspension were applied to the Ni substrate in the experiments this was carried out using a hypodermic syringe with 1.28mm in diameter needle in a two stage process.

Initially, one drop of suspension (≈0.02ml, which contains about 0.003g of BaSr(CO$_3$)$_2$) was applied to each Ni substrate. The “coated” cathode was then left at room temperature for 1 hour to remove the liquid by evaporation, after which the same amount of suspension was again applied to the Ni substrate and left under ambient conditions for a further 2 hours to allow the cathode to dry completely.

The dried cathode component was the cathode precursor and ready for the final heat treatment (step 4 in Figure 6.2.2) in a tube furnace. This heat treatment is described in Section 6.3.2.2.
6.3 Heat treatment to the newly designed cathodes

As introduced in Section 2.4, heat treatment is the final step in producing the oxide cathode. Practically in the final application, this heat treatment of the cathode should be carried out after the cathode has been mounted into the vacuum electron gun. However, to facilitate the development of the process in these experiments, the heating process was carried out under a suitable atmosphere in a laboratory furnace in order to broadly investigate how the properties, especially the development of the desired microstructure, of the new cathode material and the removal of the organic process aids could be accomplished.

All the heat treatments of these two cathodes were two-stages processes, a low temperature heating step (L) and a high temperature sintering stage (H), as shown schematically in Figure 6.3 with the conditions decided by the materials processed. All heat treatments were carried out in a tube furnace. The heat treatment of the integrated oxide cathode is described in Section 6.3.1 with that of the two-layer/impregnated oxide cathode being described in section 6.3.2.

![Fig 6.3. Schematic map showing the two stages heat treatments.](image-url)
6.3.1. Heat treatment of integrated oxide cathode

The purpose of the low temperature heating of the integrated oxide cathode is to burnout the processing additives (polymers) to create the pores in the material. The conditions of this heating stage, including the temperature \((T_L)\) and time \((t_J)\), were decided from the thermal decomposition analysis of the three polymers used in the cathode material (PVA, PEO and PEG). This heat treatment was carried out in air to facilitate decomposition of the polymers.

The high temperature stage has two main purposes, these being the is for BaSr\((\text{CO}_3)_2\) conversion and also for providing satisfactory microstructural and mechanical properties to the cathode by sintering. Following completion of the low temperature heating stage, the furnace atmosphere was switched to a protective atmosphere \((A_H)\) and the temperature increased to the higher sintering temperature \((T_H)\) and held at this temperature for 30 minutes followed by cooling also under the atmosphere \((A_H)\) to room temperature. Again, the sintering conditions, including the atmosphere, temperature were decided by both the thermal analysis of the cathode material and the resultant properties of the cathode. A gas mixture of N\(_2\)/5%H\(_2\) was used for the high temperature heat treatment step, with heating and cooling rate being 5°C/min.

6.3.2. Heat treatment of two-layer/impregnated oxide cathode

In order to produce the two-layer/impregnated oxide cathode, two heat treatment processes were required as shown in Figure 6.2.2 and described in the following sections.

6.3.2.1. Initial heat treatment to produce porous Ni substrate

The initial heat treatment was required to produce a mechanically robust porous Ni substrate. This also comprised two stages, a low temperature stage \((T_L)\) and a high temperature stage \((T_H)\).
The purpose of the low temperature heating, carried out under air atmosphere, is mainly to remove the polymers (PVA, PEO and PEG) with the conditions determined by the thermal decomposition of the polymers.

After the low temperature step, a porous Ni substrate is obtained, with a higher temperature sintering (under N\textsubscript{2}/5%H\textsubscript{2}) then being used to give the substrate sufficient mechanical strength to allow subsequent handling whilst still keep the porous microstructure. Investigations were carried out to find the optimum temperature (T\textsubscript{H}) for this process. Four temperatures were investigated: 600°C, 700°C, 800°C and 900°C. A heating rate of 5°C/min was used throughout the complete heat treatment and the cooling stage.

6.3.2.2. Final heat treatment of two-layer/impregnated oxide cathode

The final heat treatment was required to facilitate the BaSr(CO\textsubscript{3})\textsubscript{2} to BaSr(CO\textsubscript{3})\textsubscript{2} conversion and to promote further sintering of both the Ni and BaSrO\textsubscript{2} to obtain the cathode with proper mechanical and microstructural properties. Again, this final heat treatment also comprised two stages, a low temperature stage (T\textsubscript{L}) and a high temperature stage (T\textsubscript{H}).

The low temperature stage heating was required to remove the processing additives where dispersant is added to the suspension, the conditions being decided by whether dispersant is used and the thermal analysis of the dispersant.

The high temperature heating is to provide sufficient temperature for BaSr(CO\textsubscript{3})\textsubscript{2} conversion to take place and also generate a porous microstructure, with the conditions being determined from the thermal analysis of BaSr(CO\textsubscript{3})\textsubscript{2} conversion process and the required properties of the heated cathode material. Again, a heating and cooling rate of 5°C/min was used.
6.3.3. Changes of thermally obtained BaSrO$_2$ when exposed to air

After the final stage heat treatment during which, the BaSr(CO$_3$)$_2$ was converted to BaSrO$_2$, the resultant material was removed from the protective atmosphere for further investigations. As introduced in Section 3.4, these oxides are very sensitive to H$_2$O and CO$_2$ that will react rapidly with them to form the alkaline earth hydroxides, BaSr(OH)$_2$.

To trace the changes occurring during the air exposure, the thermally converted BaSrO$_2$ cathode was placed on a balance for weighing immediately after being taken out of the furnace and following exposure time of 1 hour.
6.4. **Characterisation**

6.4.1. Scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX)

Both the macrostructure and microstructure of the two new designed cathodes were investigated before and after heat treatment by Scanning Electron Microscopy (SEM) using a Leo 1530 VP FEGSEM. Except for the Ni substrate, all the materials were prepared by vacuum coating with a gold conductive coating before SEM examination to limit specimen-charging effects.

6.4.1.1. Macrostructure and microstructure of the resultant products

For the BaSrO₂ containing cathode materials, samples were put into the SEM for investigation immediately after being taken out of the heat treatment furnace in order to minimize any effects caused from reactions with the ambient atmosphere (as mentioned in Section 3.5).

For the two-layer/impregnated cathode, the microstructure of the interfacial material between two layers were investigated after heat treatment with the coating layer being scraped from the cathode after being taken out from the furnace to reveal the interface.

6.4.1.2. Morphology of BaSr(CO₃)₂ powder

As introduced in Section 6.2.2.2, different BaSr(CO₃)₂ suspensions were prepared to investigate the effects of various process conditions on the BaSr(CO₃)₂ particle size and dispersion. In order to prepare the samples for SEM, 1 ml of each suspension was taken and then diluted 5 times with water. A drop of each suspension was then put on a plastic film and left at room condition to dry. SEM studies of the morphology and size of the particles could then be made directly on the resultant coated film.
6.4.1.3. Cross-section of the cathodes

Cross-sections of the two-layer/impregnated oxide cathode were also investigated by SEM to study the distribution and penetration of Ba and Sr into the porous Ni base and thickness of the two layers respectively. Samples were prepared as follows:

(a). The sample was impregnated into Struers’ SpeciFix-20 epoxy resin prepared according to the manufacture’s instructions;

(b). The resin-impregnated sample was ground and polished down to 1μm grade.

The EDX maps of Ba, Sr and Ni in the sample cross-section both before and after heat treatment were collected over 15 minutes.

6.4.2. Thermal analysis

Thermogravimetric analysis was used here mainly to study the thermal decomposition of the polymer additives, the thermal conversion of \( \text{BaSr(CO}_3\text{)}_2 \) and any other reactions occurring during heat treatment. In addition, Differential Thermal Analysis (TDA), which detects the heat release or absorbed during heating/cooling, was also used to provide additional information on the processes occurring and to provide supplementary data on the reaction temperatures.

A combined DTA-TGA system (simultaneous thermal analysis: STA) was employed using a TA instruments SDT 2960 Simultaneous DTA-TGA apparatus. Both the composite cathode materials and their individual components were characterised. The thermal analyses conditions of various materials were chosen to be exactly the same as the heat treatment conditions used during the manufacturing process.

6.4.3. Image analysis

Image-Pro Plus is a commercial software package which was used in this investigation to analyse the porosities of the microstructure of the cathode material from the SEM photomicrographs. This software detects the pore area and particles by differential contrast. The dark areas are automatically regarded as pores and the bright
areas as particles. Two pictures showing a SEM image and the image after analysis are shown in Figures 6.4.2(a) and (b) to show more clearly how this image analysis work. To eliminate the effect of different brightness or contrast of each SEM image to the analysis result, all the SEM images were adjusted to the same contrast before being used for analysis.

Fig 6.4.2(a),(b), Two SEMs showing (a), a normal SEM images and (b), SEM image after Image-Pro Plus analysis.
Part Four

The Integrated Oxide Cathode

Results and Discussion
Chapter 7

Results I--The Integrated Oxide Cathode

The integrated oxide cathode developed in this project comprises a mixture of BaSrO$_2$ and Ni, as shown in Fig 1.2(a). As introduced in Section 6.2.1 and 6.3.1, the cathode was produced by casting the BaSr(CO$_3$)$_2$/Ni/polymer composite film and stamping the cathode component from the cast film, followed by thermal conversion to BaSrO$_2$/Ni. In this section, the resultant products produced by the manufacturing process will be described step by step.

7.1. As cast BaSr(CO$_3$)$_2$/Ni/polymer composite film

The first stage of the manufacturing process comprised a casting process, the aim of which was to produce a dry composite film with suitable properties. Flatness and structural integrity were the two main requirements. Two common problems were encountered: a), distortion/ warping of the films; b), the formation of cracking in the films, which could, in some circumstances, be so serious that the whole film would break into several pieces.

As introduced from Sections 6.2.1.1.1 to 6.2.1.1.3, in order to develop a suitable process to provide a cast film with satisfactory macrostructure, a range of various casting suspensions with different formulations were trialled. The results of these investigations are shown in the following sections (Sections 7.1.1—7.1.3).

Two parameters were chosen to provide an assessment of the quality of the cast composite films. These are: (a), the extent of distortion, which is denoted as “ED”; and (b), the extent of cracking, which is denoted as “EC”. A standardised semi-quantitative notation is used throughout to describe these two parameters on a scale of 0 to 5, where 0 represents the lowest level and 5 represents the highest level. Table 7.1(a) is the description of distortion of level 0 to 5 and Table 7.1(b) is a summary of the description of cracking of level 0 to 5.
Table 7.1(a). Description of distortion of level 0 to 5

<table>
<thead>
<tr>
<th>Level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No distortion at all</td>
</tr>
<tr>
<td>1</td>
<td>The whole film appears flat although very little distortion may exist</td>
</tr>
<tr>
<td>2</td>
<td>Some significant distortion at the edge of the sample only with the main body remains generally flat</td>
</tr>
<tr>
<td>3</td>
<td>Some distortion in the main body of the film</td>
</tr>
<tr>
<td>4</td>
<td>Significant distortion happens to the film</td>
</tr>
<tr>
<td>5</td>
<td>The whole film distorted and curled up</td>
</tr>
</tbody>
</table>

Table 7.1(b). Description of cracking from level 0 to 5

<table>
<thead>
<tr>
<th>Level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No visible cracks present</td>
</tr>
<tr>
<td>1</td>
<td>Limited cracks only at the edge of the film with no cracks on the main body</td>
</tr>
<tr>
<td>2</td>
<td>Small amount of cracks begin to appear on the main body</td>
</tr>
<tr>
<td>3</td>
<td>Increased amount of cracks on the main body and at the edge</td>
</tr>
<tr>
<td>4</td>
<td>Large amount of cracks distributed in the film but film remains intact</td>
</tr>
<tr>
<td>5</td>
<td>The film breaks into pieces because of the cracks</td>
</tr>
</tbody>
</table>
7.1.1. Effect of the polymer compositions on the properties of the cast composite film

The effects of the type and addition level of the various polymer additives on the macrostructure of the cast composite films are described in this section. In the first section, the effects of the individual polymer additives are reported, whilst the subsequent sections report the effect of various combinations of these additives.

7.1.1.1. As cast films with PVA, PEO and PEG as individual polymer additive

In this first series of experiments, aimed at determining the effect of the various polymer additives used, PVA, PEO and PEG were mixed individually with BaSr(CO$_3$)$_2$/Ni to form cast films. The proportions of the components were as listed in Table 6.2.1.1.1. The macrostructures obtained in these cast films are described in Table 7.1.1.1.

It was found that the cast film with only PVA present as the polymer additive underwent a high level of distortion to a concave shape and shrinkage. There was also some transparent polymer segregated to the surface of the as cast film.

The cast BaSr(CO$_3$)$_2$/Ni/polymer film with PEO alone as polymer additive showed very different macrostructure to the PVA containing material. There was almost no polymer could be observed on the surface of the resultant material. The PEO containing material showed a slightly convex distortion of the whole film. A few cracks appeared at the edge of the PEO containing cast material.

It was not possible to produce a solid film when PEG was used as polymer additive on its own.

Table 7.1.1.1. Descriptions of the appearances of cast BaSr(CO$_3$)$_2$/Ni films containing PVA, PEO and PEG used as individual additives.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>50 wt%</th>
<th>Solid content 13.3 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymer additives</strong></td>
<td>PVA: 50wt%</td>
<td>PEO: 50wt%</td>
</tr>
<tr>
<td>Appearance of cast films</td>
<td>ED</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>EC</td>
<td>0</td>
</tr>
</tbody>
</table>
7.1.1.2. As cast films with PVA/PEG as polymer additive

The following results report the effects of combinations of PVA and PEG in different proportions on the macrostructures of the cast films in terms of distortion (ED) and cracking (EC) in Table 7.1.1.2. The various compositions are as introduced in Table 6.2.1.1.1.2. A typical example of the resultant product is also illustrated in Figure 7.1.1.2.

The results showed that all the PVA/PEG containing films exhibited very low levels of distortion and shrinkage. However, more negatively, the cast film with PVA/PEG exhibited significantly worse inhomogeneity, with a very bright and glossy polymer rich surface layer formed at the top surface and edges with this region being quite weak as indicated by the presence of the edge cracks in the cast film. Although PEG improved the distortion resistance, it also generally reduced the mechanical strength of the cast material resulting in increased number of small cracks.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>50 wt%</th>
<th>45wt%</th>
<th>35wt%</th>
<th>25wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer additives</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid content</td>
<td>13.3 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cast films</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ED</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>EC</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>
7.1.1.3. As cast films with PVA/PEO as polymer additive

The addition of PEO to produced combined PVA/PEO formulations also changed the macrostructures of the cast films. The effect on the appearance of the resultant materials of various combinations of PEO mixed with PVA in the casting suspension are described in Table 7.1.1.3 with selected examples illustrated in Figures 7.1.1.3 (a) and (b). The various formulations investigated were as introduced in Table 6.2.1.1.1.3.

The results of the investigations showed that PEO could also improve the resistance to distortion in the cast films compared to that with PVA alone although the effect was not as obvious as obtained with PEG addition. Optimum properties were obtained when the amount of PEO added was equal to that of PVA with the resultant film in this case being generally flat and crack free.

By contrast with the PEG additive, PEO additive appeared to improve the homogeneity of the cast films with the polymer rich glossy surface observed with PVA and PEG not occurring with this system, however, some polymer rich regions could still be observed on the top surface and edges of the films with lower PEO addition levels.
Fig 7.1.1.3. Descriptions of the appearances of cast BaSr(CO\textsubscript{3})\textsubscript{2}/Ni films containing PVA and PEO with various polymer compositions.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>50 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer composition</td>
<td>PVA</td>
</tr>
<tr>
<td></td>
<td>PEO</td>
</tr>
<tr>
<td>Solid content</td>
<td></td>
</tr>
<tr>
<td>Appearance of cast</td>
<td>ED</td>
</tr>
<tr>
<td>films</td>
<td>EC</td>
</tr>
</tbody>
</table>

Fig 7.1.1.3(a). Appearance of as cast BaSr(CO\textsubscript{3})\textsubscript{2}/Ni/polymer film containing 45wt%PVA/5wt%PEO.

Fig 7.1.1.3(b). Appearance of as cast BaSr(CO\textsubscript{3})\textsubscript{2}/Ni/polymer film containing 25wt%PVA/25wt%PEO.
7.1.1.4. As cast films with PVA/PEO/PEG as polymer additive

In these experiments, the effects of combined additions of all three polymer additives, PVA, PEO and PEG, in different proportions were investigated. The formulations of the components including these three polymers were introduced in Table 6.2.1.1.4. The conditions of the as cast BaSr(CO₃)₂/Ni/polymer films with all three polymers (PVA, PEO and PEG) as additives are described in Table 7.1.1.4, an example of one such film being shown in Fig 7.1.1.4.

There were relatively few differences between these films obtained for all the compositions investigated which contained these three polymers in combination. All the cast films exhibited generally good macrostructures with little distortion and being completely crack free in the main body of the films although the material containing the highest level (40wt%) of PVA still had the highest level of distortion. The homogeneity was improved compared to the PVA/PEG containing film, although some polymer segregation could still be observed both around the edge and on the surface of the cast films, as shown in Figure 7.1.1.4.

Table 7.1.1.4. Descriptions of the appearances of cast BaSr(CO₃)₂/Ni films containing PVA, PEO and PEG with various polymer compositions.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>50 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer composition</td>
<td>PVA</td>
</tr>
<tr>
<td></td>
<td>PEO</td>
</tr>
<tr>
<td></td>
<td>PEG</td>
</tr>
<tr>
<td>Solid content</td>
<td>13.3 wt%</td>
</tr>
<tr>
<td>Appearance of cast films</td>
<td>ED</td>
</tr>
<tr>
<td></td>
<td>EC</td>
</tr>
</tbody>
</table>
Fig 7.1.1.4. Appearance of as cast BaSr(CO₃)₂/Ni/polymer film containing 20wt%PVA/20wt%PEO/10wt%PEG.

7.1.1.5. Microstructure of polymer cast films

To provide a better understanding of the behaviour of the various polymer additives and their effects on the cast films, experiments were carried to study the film forming ability and resultant structure of films obtained from various solutions of the polymers, both individually (described in Section 7.1.1.5.1) and in combination (from Section 7.1.1.5.2 to Section 7.1.1.5.5) but with no other solid additives present. The compositions investigated and their proportions are described in Section 6.2.1.1.5.

7.1.1.5.1. As cast individual polymer films

The microstructures of individual polymer films obtained from PVA, PEG and PEO are shown in Figures 7.1.1.5.1(a) to (c).

Macrostructurally, the PVA cast film is a transparent, and highly distorted material with smooth surface. From SEM as shown in Figure 7.1.1.5.1(a), the PVA cast film exhibited an apparently amorphous matrix, taking up about 95% of the total area, with small opaque areas visible. Higher magnification studies by SEM at the micron scale could not determine any obvious structure from these areas, suggesting that any phase separation or crystallisation must have been present at a very fine scale if at all.
The as cast PEO film is an opaque and much less distorted material. Significant roughness and inhomogeneity appeared on the surface with ripple-like patterns on some areas. Microstructurally, the SEM image of PEO film (Figure 7.1.1.5.1(b)) contained extensive distributed cracks and voids of various sizes.

Attempts to investigate PEG films by SEM (Figure 7.1.1.5.1(c)) were less successful as the PEG film melted during the coating operation needed for SEM imaging leading to unrepresentative changes in the structure.

Fig 7.1.1.5.1(a). SEM showing the microstructures of as cast PVA film.
Fig 7.1.5.1(b). SEM showing the microstructures of as cast PEO film.

Fig 7.1.5.1(c). SEM showing the microstructures of as cast PEG film (note structure is modified by melting during SEM preparation procedure and may not be representative).
7.1.1.5.2. As cast PVA/PEG films

In contrast to pure PVA films, all the as cast polymer films containing PVA and PEG appeared opaque with the opacity increased with increasing PEG content.

Figures 7.1.1.5.2(a) and (b) are SEM images showing the microstructure of the as cast films obtained containing two different mixed PVA/PEG compositions, these being 90wt% PVA/10wt%PEG (i.e. PVA:PEG=45wt%:5wt% in Table 7.1.1.2) and 70wt%PVA/30wt%PEG (i.e. PVA:PEG=35wt%:15wt% in Table 7.1.1.2) respectively. It was not possible to image the microstructure for the materials with higher PEG content (>30wt%) because the material started to crack and melt under the SEM.

The material with 10wt%PEG showed essentially homogeneous and featureless microstructure with no evidence of any phase separation. Some small white spots appeared in the material with higher PEG content (30wt%PEG) and more surface inhomogeneity also started to appear as shown in Figure 7.1.1.5.2(b).

Fig 7.1.1.5.2(a). SEM showing the microstructure of polymer cast film with 90wt%PVA/10wt%PEG.
7.1.1.5.3. As cast PVA/PEO films

The microstructures obtained in the polymer cast films containing two different combinations of PVA and PEO are shown in Figures 7.1.1.5.3(a) and (b). As the PVA/PEG polymer films, these PVA/PEO films all appeared opaque. The compositions used in these polymer films were 90wt%PVA/10wt%PEO and 50wt%PVA/50wt%PEO. These formulations were equivalent in polymer additive compositions to the cathode composition containing 45wt%PVA/5wt%PEO and 25wt%PVA/25wt%PEO, with the remaining 50wt% comprising the Ni and BaSr(CO$_3$)$_2$ in these.

In the compositions, two phases can be readily identified. The main, or matrix, phase comprises a relatively featureless microstructure, with this containing a second phase distributed as discrete “spherical” regions. The sizes of these second phase regions increased with increasing amount of PEO, with the diameter of the regions being approximately 5 ~ 10μm for 10wt%PEO formulation increasing to 8~15μm for 50wt%PEO formulation. As the PEO content was increased (50wt%), the matrix phase developed some small cracks as shown in Figure 7.1.1.5.3(b).
Fig 7.1.5.3(a). SEM showing the microstructure of as cast polymer films containing 90wt% PVA/10wt% PEO.

Fig 7.1.5.3(b). SEM showing the microstructure of as cast polymer films containing 50wt% PVA/50wt% PEO.
7.1.1.5.4. As cast PEO/PEG film

The PEO-PEG material containing 66.6wt%PEO/33.3wt%PEG is shown in Figure 7.1.1.5.4, with this formulation was equivalent in polymer additive compositions to the cathode composition containing 20wt%PVA/20wt%PEO/10wt%PEG with the remaining 50wt% comprising the Ni and BaSr(CO₃)₂ in these. As with the PVA/PEG material, attempts to investigate the material containing more than 40wt%PEG was not successful because the material was damaged under SEM.

As shown in SEM, the material showed evidence of the formation of crystalline spherulites and extensive cracked areas and breaking up of the material. Some small white spots similar to these shown in the 70wt%PVA/30wt%PEG material in Figure 7.1.1.5.2(b) also appeared.

![SEM image of as cast polymer films containing 66.6wt%PEO 33.3wt%PEG.](image)

Fig 7.1.1.5.4. SEM showing the microstructure of as cast polymer films containing 66.6wt%PEO 33.3wt%PEG.
7.1.1.5.5. As cast PVA/PEO/PEG films

Figures 7.1.1.5.5 (a) and (b) are two SEM images showing the microstructures of the polymer composite cast films containing combinations of the three polymers (PVA/PEO/PEG) with different compositions. As described in Table 6.2.1.1.1.5 the compositions used were 60wt%PVA/20wt%PEO/20wt%PEG and 40wt%PVA/40wt%PEO/20wt%PEG, these being equivalent to the polymer formulations used in the cathode composite materials with 30wt%PVA/10wt%PEO/10wt%PEG and 20wt%PVA/20wt%PEO/10wt%PEG, with the remaining 50wt% comprising the BaSr(CO₃)₂ and Ni phase.

In the microstructure of 20wt%PEO containing material (Figure 7.1.1.5.5(a)), the film appeared to be primarily amorphous with some small regions of cracks, possibly regions of phase separation or incipient crystallisation. When the amount of PEO was increased to 40wt% (Figure 7.1.1.5.5(b)), very obvious changes took place. Three discrete phases could be identified comprising a featureless, amorphous phase, an extensively cracked phase and a small amount of a third phase distributed as “spherical” regions in the microstructure.

Fig 7.1.1.5.5(a), SEM showing the microstructures of the as cast polymer film containing 60wt%PVA/20wt%PEO/20wt%PEG.
Fig 7.1.5.5(b), SEM showing the microstructures of the as cast polymer film containing 40wt%PVA/40wt%PEO/20wt% PEG.

7.1.6. Summary

On the basis of these experiments, in particular the resistance to cracking and distortion, it was concluded that the optimum composition for the polymer additives were two systems, which being either 30wt%PVA/10wt%PEO/10wt%PEG or 20wt%PVA/20wt%PEO/10wt%PEG with 50wt% of BaSr(CO₃)₂/Ni. The composition 20wt%PVA/20wt%PEO/10wt%PEG was initially chosen as the basis for further investigations into the effect of the other two variables (solids contents and ratios between carbonate/Ni).
7.1.2. Effect of the solid content on the properties of the cast composite films

The purpose of this series of experiments was to investigate the effect of the solid content (amount of liquid) in the initial suspension on the appearance and behaviour of the as cast BaSr(CO$_3$)$_2$/Ni/polymer films. The determination of concentrations of solid contents and range of compositions investigated were described in Section 6.2.1.1.2.

The macroscopic appearance of the resultant BaSr(CO$_3$)$_2$/Ni films obtained from casting suspensions with various initial solid contents are summarised in Table 7.1.2. To supplement the information in this table, a representative selection of the cast films are illustrated in Figures 7.1.2(a)-(c), for solid contents from 9.8wt% to 17.5wt% respectively.

Two opposing effects can be observed in those experiments. The extent of distortion decreased with increasing solid content (decreasing liquid amount), whereas the tendency to cracking increased with solid content. Cast films with essentially no cracking and distortion could be produced from suspensions with intermediate solid content, with approximately 13 wt% solids found to be the optimum composition as shown in Figure 7.1.2(b).

Table 7.1.2: Descriptions of the appearances of cast BaSr(CO$_3$)$_2$/Ni films obtained with different suspension solid concentrations.

<table>
<thead>
<tr>
<th>Figure No</th>
<th>7.1.2(a)</th>
<th>7.1.2(c)</th>
<th>7.1.2(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content</td>
<td>9.8wt%</td>
<td>10.5wt%</td>
<td>11.0wt%</td>
</tr>
<tr>
<td>Polymer composition</td>
<td></td>
<td>20wt%PVA/20wt%PEO/10wt%PEG</td>
<td></td>
</tr>
<tr>
<td>Appearances of cast films</td>
<td>ED</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>EC</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Fig 7.1.2(a). Appearance of as cast BaSr(CO$_3$)$_2$/Ni/polymer film obtained with a suspension of 9.8wt% solid content.

Fig 7.1.2(b). Appearance of as cast BaSr(CO$_3$)$_2$/Ni/polymer film obtained with a suspension of 13.3wt% solid content.
7.1.3 Effect of the ratios of BaSr(CO$_3$)$_2$/Ni on the properties of the cast composite film

The appearances of the cast BaSr(CO$_3$)$_2$/Ni/polymer films obtained from the casting suspensions with different ratios of BaSr(CO$_3$)$_2$ to Ni, produced as described in Section 6.2.1.1.3 are summarised in Table 7.1.3. Figures 7.1.3(a) to (f) show the resultant cast BaSr(CO$_3$)$_2$/Ni/polymer films.

Table 7.1.3: Descriptions of the appearances of cast BaSr(CO$_3$)$_2$/Ni films with different ratios of BaSr(CO$_3$)$_2$ to Ni in suspension.

<table>
<thead>
<tr>
<th>Figure No</th>
<th>7.1.3(a),(b)</th>
<th>7.1.3(e),(f)</th>
<th>7.1.3(c),(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni compositions</td>
<td>2wt%</td>
<td>10wt%</td>
<td>2wt%</td>
</tr>
<tr>
<td>Solid content</td>
<td>9.8 wt%</td>
<td>13.3 wt%</td>
<td>17.5 wt%</td>
</tr>
<tr>
<td>Polymer composition</td>
<td>20wt% PVA/20 wt% PEO/10 wt% PEG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance of cast films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ED</td>
<td>4.5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>EC</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig 7.1.2(c). Appearance of as cast BaSr(CO$_3$)$_2$/Ni/polymer film obtained with a suspension of 17.5wt% solid content.
Fig 7.1.3(a),(b). Two as cast BaSr(CO$_3$)$_2$/Ni/polymer films produced from suspensions of 9.8wt% solid content.

Fig 7.1.3(c),(d). Two as cast BaSr(CO$_3$)$_2$/Ni/polymer films produced from suspensions of 13.3wt% solid content.
The experimental results revealed that variations in the proportion of Ni to ceramic in the casting suspension produced very limited effects in comparison with the effect of variations in the solid content. Samples produced with equivalent solid contents at casting had generally very similar properties in distortion and cracking irrespective of the Ni to ceramic content. Distortion occurred in the cast films with low solid content (Figures 7.1.3 (a) and (b)) and cracking appeared in the cast films with high solid content (Figures 7.1.3(e) and (f)). For all the BaSr(CO$_3$)$_2$/Ni ratios investigated, the suspension with 13.3wt% solid content, as seen in Fig 7.1.3(c) and (d), was found to be optimum, with this being unaffected by the proportions of Ni to ceramic. In all cases, the 2 wt% Ni composite films were pale grey in appearance whilst those with 10 wt% Ni appeared dark grey or black.
7.1.4. Summary

Based on the results of all the above experiments, it was decided that subsequent experiments should focus only on those material compositions identified as providing generally good qualities to the cast composite. Four candidate systems were thus chosen. The selected composition and casting conditions for these selected systems are listed below in Table 7.1.4.

Table 7.1.4: Selected compositions of cathode material casting suspension used in the following investigated.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>Polymer additive</th>
<th>Solid content</th>
</tr>
</thead>
<tbody>
<tr>
<td>2wt%Ni, 48wt%</td>
<td>30wt%PVA/10wt%PEO/10wt%PEG</td>
<td>13.3wt%</td>
</tr>
<tr>
<td>BaSr(CO₃)₂</td>
<td>20wt%PVA/20wt%PEO/10wt%PEG</td>
<td></td>
</tr>
<tr>
<td>10wt%Ni, 40wt%</td>
<td>30wt%PVA/10wt%PEO/10wt%PEG</td>
<td></td>
</tr>
<tr>
<td>BaSr(CO₃)₂</td>
<td>20wt%PVA/20wt%PEO/10wt%PEG</td>
<td></td>
</tr>
</tbody>
</table>

Note for brevity, the polymer compositions 30wt%PVA/10wt%PEO/10wt%PEG and 20wt%PVA/20wt%PEO/10wt%PEG are abbreviated to the 30wt%PVA and 20wt%PVA compositions respectively hereafter.
7.2. **As stamped integrated oxide cathode precursor**

The next step of the manufacturing process is the stamping of the cathode precursor from the cast film in the form of a pellet as introduced in Section 6.2.1.2. The macrostructure, dimensions and microstructures of the obtained stamped cathode precursors are described in this section.

### 7.2.1. Macrostructure of the stamped integrated cathode precursor

Based on the results described in the previous sections, all the integrated cathode precursors produced with the optimum material compositions shown in Table 7.1.4 could survive the mechanical stamping. Figures 7.2.1(a) and (b) are typical examples of as stamped cathode precursors with two different Ni contents.

The pictures showed that these cathode precursors were complete and round in shape with reasonably smooth edges at this stage, although the edge definition of the sample containing 2wt%Ni (Figure 7.2.1(a)) was not as good as that of the sample containing 10wt%Ni (Figure 7.2.1(b)).

![Macrostructure of the as stamped integrated cathode precursor](image)

**Fig 7.2.1(a).** Macrostructure of the as stamped integrated cathode precursor containing 2wt%Ni and a polymer composition of 20wt%PVA/20wt%PEO/10wt%PEG.
Fig 7.2.1(b). Macrostructure of the as stamped integrated cathode precursor containing 10wt%Ni and a polymer composition of 20wt%PVA/20wt%PEO/10wt%PEG.

In Figure 7.2.1(a), with 2wt% Ni, approximately 10% of the cathode surface area was occupied by visible pores with average size approximately 0.2–0.5mm with the surface being quite uneven. As is illustrated in Fig 7.2.1(b), the surface of the 10wt%Ni cathode precursor is significantly different to that obtained with 2wt%Ni addition, being generally smooth but exhibiting some significant inhomogeneity. Some discrete, lighter coloured regions are apparent with typical dimensions approximately 0.1–0.5 mm in diameter. No large pores can be seen on this cathode at this scale of magnification.

The polymer formulation of the two cathode precursors shown in the images is 20wt%PVA/20wt%PEO/10wt%PEG. The cathode precursors produced containing 30wt%PVA/10wt%PEO/10wt%PEG exhibited generally same macrostructures for the same BaSr(CO₃)₂/Ni ratio, so they are not shown and described again.
7.2.2. **Effect of polymer additive on the microstructure of the integrated oxide cathode precursor**

In these experiments, the effects of the two polymer formulations described in Table 7.1.4 were investigated for a fixed $\text{BaSr(CO}_3\text{)}_2/\text{Ni}$ composition. Figures 7.2.2(a) to (d) are the SEM images showing the microstructure of these cathode precursor materials. The Ni content of these two materials shown are both 10wt%Ni with the polymer formulations being based on 30wt%PVA and 20wt%PVA (plus PEO-PEG) respectively. In addition, the microstructure of the conventional cathode coating is displayed in Figure 7.2.2(e) for comparison purpose.

As shown in Figures 7.2.2(a) and (c), both polymer and inorganic phases can be clearly identified in the microstructures of the two cast films with different polymer compositions (30wt%PVA formulation and 20wt%PVA formulation). The polymer component being present between the $\text{BaSr(CO}_3\text{)}_2$ particles providing physical interconnection (binding) between them.

By adjusting the parameters of the SEM, images can be obtained to “hide” the organic phase and more clearly reveal the distribution and morphologies of the $\text{BaSr(CO}_3\text{)}_2$ particles shown in Figures 7.2.2(b) and (d). The particles of $\text{BaSr(CO}_3\text{)}_2$ appear as long columnar shapes with diameters typically less than 0.5μm and lengths typically around 5~8μm. The particles were mainly present as agglomerated units comprising around 5~10 particles.

The target at this stage of the project was to attempt to replicate as closely as possible the microstructure of the current (sprayed) oxide cathode. The microstructures of the new materials are compared with that of the conventional cathode especially in terms of porosity and pore size. The microstructure of current oxide cathode is shown in Figure 7.2.2(e). The particles of $\text{BaSr(CO}_3\text{)}$ appear as columnar shape with their lengths smaller than those in the new cathodes, being typically 3~5μm, and the same diameters. The particles also formed agglomerates with various sizes.
Fig 7.2.2(a). SEM showing the microstructure of integrated oxide cathode precursor containing 40wt%BaSr(CO₃)₂, 10wt%Ni and 30wt%PVA/10wt%PEO/10wt%PEG.

Fig 7.2.2(b). SEM showing the microstructure of integrated oxide cathode precursor containing 40wt%BaSr(CO₃)₂, 10wt%Ni and 30wt%PVA/10wt%PEO/10wt%PEG (same material as shown in Fig (a)).
Fig 7.2.2 (c). SEM showing the microstructure of integrated oxide cathode precursor containing 40wt% BaSr(CO\(_3\))\(_2\), 10wt%Ni, and 20wt%PVA/20wt%PEO/10wt%PEG.

Fig 7.2.2(d). SEM showing the microstructure of integrated oxide cathode precursor containing 40wt% BaSr(CO\(_3\))\(_2\), 10wt%Ni and 20wt%PVA/20wt%PEO/10wt%PEG (same material as shown in Fig (c)).
Fig 7.2.2(e). SEM showing the microstructure of conventional as sprayed cathode precursor coating material.

Generally the microstructures of both the new cathode materials and conventional material are broadly similar especially the 20wt% PVA material in terms of the porosity and pore sizes.

The porosities and pore size analyses of both new cathode materials and the current cathode material were obtained by image analysis (as introduced in Section 6.4.2) with the pore size analysis results being shown in Figures 7.2.2(f) to (h). The porosity analyses showed that in both new cathode materials, satisfactory porosities were obtained, with measured values being 54% in Figure(b) (30wt% PVA formulation) and 59% in Figure(d) (20wt% PVA formulation). In comparison, the measured porosity of the conventional material (Figure(e)) is 60%.
Fig 7.2.2(f). Pore area distribution in the cathode precursor containing 30wt% PVA/10wt% PEO/10wt% PEG.

Fig 7.2.2(g). Pore area distribution in the cathode precursor containing 20wt% PVA/20wt% PEO/10wt% PEG.

Fig 7.2.2(h). Pore area distribution in the conventional as sprayed cathode coating material.
From both the analysis results and the images, it can be seen that the cathode material with 30wt%PVA contained more small pores than the other two materials with the biggest pore area in the range of 500-1000µm. In comparison, the 20wt%PVA formulation material exhibited a more open structure with more large pores and with the biggest pore areas being in the range of 10000-50000µm. The distribution of pores and pore areas were also more uniform in this material. The conventional cathode material exhibited both small and large pores, the majority of the pore areas being in the 1000-10,000 size range.

7.2.3. Summary

The investigation in Section 7.2.2 showed that the cathode material obtained from the formulations containing 20wt%PVA/20wt%PEO/10wt%PEG had a generally homogeneous pore size distribution and a higher porosity, which can also provide an cathode precursor component with satisfactory macrostructure as shown in Section 7.2.1. Based on these findings, two compositions were therefore selected for further investigation as shown in Table 7.2.3.

Table 7.2.3. Selected composition of cathode material used in the following investigations.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>Polymer additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%wtNi / 48wt%BaSr(CO₃)₂</td>
<td>20wt%PVA / 20wt%PEO /10wt%PEG</td>
</tr>
<tr>
<td>10%wtNi / 40wt%BaSr(CO₃)₂</td>
<td></td>
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</tbody>
</table>
7.3 Thermal analysis of integrated cathode material

Thermal analysis (TGA and DTA) was used to investigate the reactions occurring for each component of the cathode material during the heat treatment as introduced in Section 6.4.3. The results of these investigations are reported below.

7.3.1 Polymer additives

7.3.1.1 Polyvinyl alcohol (PVA)

The results of the TGA and DTA investigations of the thermal decomposition of PVA between room temperature and 600°C in air are shown in Figures 7.3.1.1 (a) and (b) respectively.

In both TGA and DTA analysis, a series of multiple events were observed with the main weight loss occurring between 260°C and 540°C with approximately 0.5wt% residue in the sample. Generally, each of the mass changes (stages I and II in Figure 7.3.1.1(a)) was accompanied by corresponding thermal events (identified from A to G in Figure 7.3.1.1(b)).

Table 7.3.1.1(a) and (b) are the summaries of the events identified by TGA and DTA during thermal decomposition of PVA.
Fig 7.3.1.1 (a). TGA of the decomposition of PVA during heating in air.

Fig 7.3.1.1(b). DTA of the decomposition of PVA during heating in air.
Table 7.3.1.1(a), Summaries of the weight changes identified by TGA during PVA decomposition

<table>
<thead>
<tr>
<th>Stages</th>
<th>Sub-steps</th>
<th>Weight changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n/a</td>
<td>Gradual weight loss of 9 wt% during room temperature ~ 260°C</td>
</tr>
<tr>
<td>II</td>
<td>i</td>
<td>Rapid weight loss of a further 57 wt% between 260°C-355°C</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>A further weight loss of 9 wt% between 355°C-410°C</td>
</tr>
<tr>
<td></td>
<td>iii</td>
<td>A further weight loss of 9 wt% between 410°C-485°C</td>
</tr>
<tr>
<td></td>
<td>iv</td>
<td>Very sharp weight loss of 5 wt% at 485°C</td>
</tr>
<tr>
<td></td>
<td>v</td>
<td>A small weight loss of 2 wt% between 485°C-540°C</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No weight change between 540°C and 600°C with approximately 0.5 wt% material left</td>
</tr>
</tbody>
</table>

Table 7.3.1.1(b), Summary of the thermal events identified by DTA during PVA decomposition

<table>
<thead>
<tr>
<th>Stages</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A</td>
<td>An endothermic peak at 225°C</td>
</tr>
<tr>
<td>II</td>
<td>B</td>
<td>A broad endothermic peak at about 300°C</td>
</tr>
<tr>
<td></td>
<td>C-G</td>
<td>Several exothermic peaks at 375°C(C), 415°C(D), 455°C(E), 490°C(F) and 500°C(G)</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No thermal events between 540°C and 600°C</td>
</tr>
</tbody>
</table>
7.3.1.2 Polyethylene oxide (PEO)

The results of the TGA and DTA studies of the thermal decomposition of polyethylene oxide (PEO) used in the fabrication process between room temperature and 600°C are shown in Figure 7.3.1.2 (a) and (b) respectively.

Compared to the decomposition of PVA, that of PEO is simpler with less thermal events. There are generally three main stages of weight loss, which commenced at about 150°C and finished at 470°C with approximately 0.5 wt% of the total weight left.

A summary of the thermal events identified by TGA and DTA are given in Tables 7.3.1.2(a) and (b).

![Graph of TGA and DTA studies of the thermal decomposition of PEO](image)

Fig 7.3.1.2 (a). TGA of the decomposition of PEO during heating in air.
Table 7.3.1.2(a), Summaries of the weight changes identified by TGA during PEO decomposition

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sub-steps</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n/a</td>
<td>No weight loss</td>
</tr>
<tr>
<td>II</td>
<td>i</td>
<td>A rapid weight loss of 84wt% during 170°C - 310°C</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>A further weight loss of 10wt% during 310°C - 340°C</td>
</tr>
<tr>
<td></td>
<td>iii</td>
<td>A further weight loss of 5wt% during 350°C - 470°C</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>Weight decrease stops at 470°C and approximately 1wt% material remain</td>
</tr>
</tbody>
</table>

Table 7.3.1.2(b), Summary of the thermal events identified by DTA during PEO decomposition

<table>
<thead>
<tr>
<th>Stage</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A</td>
<td>One clear endothermic peak at 70°C</td>
</tr>
<tr>
<td>II</td>
<td>B-F</td>
<td>Several exothermic peaks at 160°C(B), 260°C(C), 310°C(D), 330°C(E) and 430°C(F) respectively</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No thermal events took place between 470°C and 600°C</td>
</tr>
</tbody>
</table>

Fig 7.3.1.2 (b). DTA of the decomposition of PEO during heating in air.
7.3.1.3 Polyethylene glycol (PEG)

The results of the TGA and DTA investigations into thermal decomposition of PEG between room temperature and 600°C in air are shown in Figures 7.3.1.3 (a) and (b).

The first stage of the thermal decomposition comprises a small weight loss of about 8 wt% in TGA, and in DTA there were two small endothermic peaks at 35°C and 105°C respectively.

The main decomposition process of PEG commenced at about 190°C with total decomposition by 460°C, which comprised three main weight loss stages denoted as i, ii and iii in Figure 7.3.1.3(a). The DTA graph deviated from the baseline between 160°C and 460°C, during which four exothermic peaks could be identified corresponding to different sub-stages of these processes, denoted as C to F.

Summaries of the thermal reactions identified by TGA and DTA are shown in Tables 7.3.1.3(a) and (b).

![Fig 7.3.1.3 (a). TGA of the decomposition of PEG during heating in air.](image-url)
Fig 7.3.1.3 (b). DTA of the decomposition of PEG during heating in air.

Table 7.3.1.3(a), Summary of the weight changes identified by TGA during PEG decomposition

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sub-steps</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n/a</td>
<td>Weight loss of about 8wt% between room temperature ~190°C</td>
</tr>
<tr>
<td>II</td>
<td>i</td>
<td>Main weight loss of 67wt% between 190°C ~320°C</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>A further weight loss of about 17wt% between 320°C ~370°C</td>
</tr>
<tr>
<td></td>
<td>iii</td>
<td>Final weight loss of about 8wt% between 370°C ~460°C</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>Weight decrease stops and no residue left after 460°C</td>
</tr>
</tbody>
</table>
Table 7.3.1.3(b), Summaries of the thermal events identified by DTA during PEG decomposition

<table>
<thead>
<tr>
<th>Stage</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A, B</td>
<td>Two endothermic peaks at 35°C(A) and 105°C(B) respectively</td>
</tr>
<tr>
<td>II</td>
<td>C~F</td>
<td>Several exothermic peaks at 310°C(C), 325°C(D), 380°C(E) and 425°C(F) respectively</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No thermal event took place above 460°C</td>
</tr>
</tbody>
</table>

7.3.1.4. Summary

From the thermal decomposition analysis results of the three polymers (PVA, PEO and PEG), the maximum temperature required for the first stage heating in air of the integrated cathode composite material was identified to be 500°C. This temperature was then used for the initial stage heating during the thermal investigation of the following materials which all comprised two stage heating process (Sections 7.3.2–7.3.4).
7.3.2 Nickel (Ni)

The TGA and DTA results showing the reactions of Ni occurring during heating under air from room temperature to 500°C and under N\(_2\)/5%H\(_2\) from 500°C to 1200°C are reported in Figures 7.3.2(a) and (b).

The TGA analysis comprised two main stages of weight change denoted as I and II and five sub-stages, denoted as i to v, in Figure 7.3.2(a). The DTA analysis showed two thermal events of the sample during heating, denoted as A and B in Figure 7.3.3(b).

The weight of the sample started to increase as shown in the TGA at about 240°C (sub-stage ii) with the DTA curve starting to deviate from the baseline at similar temperature. The endothermic peak(A) appeared at 500°C. Both the weight increase in TGA and the thermal event in DTA stopped at approximately 560°C. The total weight increase during this temperature range was 17wt%.

Between 560°C and 750°C, there were no reactions in both DTA and TGA(sub-step iii). At 750°C, the weight started to decrease rapidly at 780°C (sub-step iv) and the weight at 900°C was decreased back to the original weight (100wt%). Correspondingly, the DTA curve went up from the base line and a large exothermic peak appeared at 840°C(B). Between 900°C and 1200°C, no other reactions could be found in both TGA and DTA.

Table 7.3.2(a) and (b) are the summaries of the thermal reactions identified in both TGA and DTA of Ni during heating.
Fig 7.3.2(a), TGA of reactions of Ni filament during heating from room temperature to 500°C under air and from 500°C to 1200°C under N2/5%H2.

Fig 7.3.2(b), DTA of reactions of Ni filament during heating from room temperature to 500°C under air and from 500°C to 1200°C under N2/5%H2.
Table 7.3.3(a), Summaries of the weight changes identified by TGA during heating of Ni filaments.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sub-steps</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>i</td>
<td>No weight change from room temperature ~ 240°C</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>Weight increase to 117wt% between 240°C ~ 560°C</td>
</tr>
<tr>
<td></td>
<td>iii</td>
<td>No weight change between 560°C ~ 780°C</td>
</tr>
<tr>
<td>II</td>
<td>iv</td>
<td>Rapid weight loss of 17wt% between 780°C ~ 900°C</td>
</tr>
<tr>
<td></td>
<td>v</td>
<td>No weight change between 900°C ~ 1200°C</td>
</tr>
</tbody>
</table>

Table 7.3.3(a), Summaries of the thermal events identified by DTA during heating of Ni filaments.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A</td>
<td>A broad endothermic peak at 500°C</td>
</tr>
<tr>
<td>II</td>
<td>B</td>
<td>A large exothermic peak at 830°C</td>
</tr>
</tbody>
</table>
7.3.3 Barium strontium carbonate (BaSr(CO₃)₂)

Figures 7.3.3(a) and (b) are the TGA and DTA showing the thermal analysis results of BaSr(CO₃)₂ during heating. As with Ni filament, this decomposition process was also carried out under two different atmospheres. The thermal decomposition of BaSr(CO₃)₂ can be divided into two main stages, denoted as I and II in TGA with these including a number of sub-stages, evidenced by five peaks, denoted as A to E, in DTA.

The first stage comprised a small and gradual weight loss of 2wt% from room temperature to 600°C in TGA with the first endothermic peak (A) appeared at 150°C in DTA.

This was followed by a second stage, which included a period (sub-stage i) between 600°C and 865°C where no weight change was observed in TGA, but including a sharp endothermic peak appeared at 800°C in DTA (B). At 860°C, there began an abrupt and sharp weight loss in TGA and stopped at 1160°C (sub-stage ii). The total weight loss between 850°C and 1160°C was 26wt%. After 1160°C, there was no weight loss and the weight kept constant. In DTA graph, three endothermic peaks could be observed during this temperature range, which are at about 930°C, 960°C and a third broad one at 1060°C.

No weight change and thermal events took place after 1160°C in both TGA and DTA, denoted as region III in these figures.

Summaries of the thermal reactions discovered in both TGA and DTA are listed in Tables 7.3.3(a) and (b).
Fig 7.3.3(a). TGA of the thermal decomposition of BaSr(CO₃)₂ during heating from room temperature-500°C in air and 500°C-1200°C under N₂/5%H₂.

Fig 7.3.3(b). DTA of the thermal decomposition of BaSr(CO₃)₂ during heating from room temperature-500°C in air and 500°C-1200°C under N₂/5%H₂.
Table 7.3.3(a), Summaries of the weight changes identified by TGA during BaSr(CO₃)₂ decomposition

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sub-steps</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n/a</td>
<td>Small weight decrease of about 2 wt% during room temperature and 600°C</td>
</tr>
<tr>
<td>II</td>
<td>i</td>
<td>No weight change between 600°C and 860°C</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>Large weight loss of about 26.5wt% between 860°C and 1160°C</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No weight loss and weight kept constant after 1160°C</td>
</tr>
</tbody>
</table>

Table 7.3.3(b), Summaries of the thermal events identified by DTA during BaSr(CO₃)₂ decomposition

<table>
<thead>
<tr>
<th>Stage</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A</td>
<td>A endothermic peaks at 150°C</td>
</tr>
<tr>
<td>II</td>
<td>B-E</td>
<td>Several exothermic peaks at 800°C(B), 930°C(C), 960°C(D) and 1060°C(E) respectively</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No thermal events appeared after 1060°C</td>
</tr>
</tbody>
</table>
7.3.4 New cathode material

Figures 7.3.4(a) and (b) show the TGA and DTA results of the thermal analysis for the cathode composite material (BaSr(CO₃)₂/Ni/polymers). The Ni content in the material is 10wt%. As with BaSr(CO₃)₂ and Ni, the thermal analysis was carried out in two stages, these being from room temperature to 500°C in air and from 500°C to 1200°C in N₂/5%H₂ (same conditions as the cathode heat treatment developed in this project). As can be seen from TGA and DTA, a number of various weight changes (stages I to III in TGA) and thermal events (denoted as A to K in DTA) happened during the thermal analysis.

The TGA graph started with a small weight loss of 3wt% (sub-step i) up to about 140°C. Correspondingly, there were two endothermic peaks at 60°C (A) and 120°C (B) in DTA graph. From 140°C to 500°C, there were several stages of weight loss in TGA (sub-step ii) and four exothermic peaks (C to F) identified by DTA. The total weight loss up to 500°C was approximately 46wt%. With increasing temperature, there was a small weight increase of about 0.62wt% in TGA (sub-step iii) between 500°C and 575°C and a corresponding endothermic peak identified by DTA at 510°C (G).

A constant weight stage (sub-step iv) was followed from 570°C to 830°C in TGA. However, an endothermic peak appeared over this temperature range in DTA at 800°C(H). The next significant weight loss in TGA started at 830°C and finished at about 1115°C giving a 13.5wt% weight loss. There was a big endothermic event during this temperature range with three endothermic sub-stages at 930°C(I), 960°C(J) and 1030°C(K) respectively. There were no reactions in DTA and TGA between 1115°C and 1200°C (stage IV).
Fig 7.3.4(a). TGA of the cathode composite material during heating from room temperature to 500°C in air and from 500°C to 1200°C in N₂/5% H₂.

Fig 7.3.4(b). DTA of the cathode composite material during heating from room temperature to 500°C in air and from 500°C to 1200°C in N₂/5% H₂.
The summary of the thermal reactions as identified by TGA and DTA are listed in Tables 7.3.4(a) and (b).

Table 7.3.4(a), Summaries of the weight changes identified by TGA during heating of BaSr(CO₃)₂/Ni/polymers.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sub-steps</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>i</td>
<td>Small weight loss of 3wt% from room temperature to 140°C</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>Large weight loss of 46wt% between 140°C ~ 500°C (including several processes)</td>
</tr>
<tr>
<td>II</td>
<td>iii</td>
<td>Small weight increase by 0.62wt% between 500°C ~ 575°C</td>
</tr>
<tr>
<td>III</td>
<td>iv</td>
<td>No weight change between 575°C ~ 830°C</td>
</tr>
<tr>
<td></td>
<td>v</td>
<td>Weight loss by 13.5wt% between 830°C ~ 1115°C</td>
</tr>
<tr>
<td>IV</td>
<td>n/a</td>
<td>No weight change from 1115°C to 1200°C</td>
</tr>
</tbody>
</table>

Table 7.3.4(b), Summaries of the thermal events identified by DTA during heating of BaSr(CO₃)₂/Ni/polymers.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A, B</td>
<td>Two endothermic peaks at 60°C(A) and 120°C(B) respectively</td>
</tr>
<tr>
<td></td>
<td>C-F</td>
<td>Four exothermic peaks at 175°C(C), 250°C(D), 385°C(E) and 405°C(F) respectively</td>
</tr>
<tr>
<td>II</td>
<td>G</td>
<td>An endothermic peak at 510°C</td>
</tr>
<tr>
<td>III</td>
<td>H-K</td>
<td>Four endothermic peaks at 800°C(H), 930°C(I), 960°C(J) and 1030°C(K) respectively</td>
</tr>
<tr>
<td>IV</td>
<td>n/a</td>
<td>No thermal events appeared between 1115°C ~ 1200°C</td>
</tr>
</tbody>
</table>
7.3.5. Summary

The conditions of the heat treatment are initially decided according to the thermal analysis results shown previously in this section and are shown schematically in Figure 7.3.5. As mentioned in Section 7.3.1.4, 500°C was chosen as the first stage temperature.

For the second heating stage required for the carbonate decomposition, three temperatures ($T_H$), 950°C, 1050°C, and 1150°C, were initially chosen based on the thermal analysis of the cathode material for further investigation into how they affect the properties of the final cathode.

![Diagram of heat treatment process]

Fig 7.3.5. Two stage heat treatment process and the conditions for the integrated cathode
7.4. **Integrated oxide cathode after heat treatment**

The results reported in this section refer to the structure and properties of the resultant integrated oxide cathode after the heat treatment stage of the manufacturing process developed. The results reported here are all refer to components subjected to this two stage heat treatment as previously shown in Section 7.3.5 with the compositions investigated as summarised in Section 7.2.3.

7.4.1. **Macrostructure of the integrated oxide cathode after heat treatment**

Figures 7.4.1(a) to (d) show the macrostructures of integrated oxide cathode components with different Ni contents at two different heating temperatures, 950°C (Figures 7.4.1(a) and (b)) and 1150°C (Figures 7.4.1(c) and (d)), which revealed the effects of various heating temperatures and material compositions on the macrostructures and mechanical properties of the cathode components.

![SEM showing an integrated oxide cathode with 2wt%Ni after heat treatment to 950°C.](image)

Fig 7.4.1(a). SEM showing an integrated oxide cathode with 2wt%Ni after heat treatment to 950°C.
Fig 7.4.1(b). SEM showing an integrated oxide cathode with 10wt%Ni after heat treatment to 950°C.

Fig 7.4.1(c). SEM showing an integrated oxide cathode with 2wt%Ni after heat treatment to 1150°C.
Fig 7.4.1(d). SEM showing an integrated oxide cathode with 10wt%Ni after heat treatment to 1150°C.

Generally the results were disappointing at this stage. The results indicated that the mechanical strength of the cathode components after heat treatment increased with increasing heating temperature and Ni content. The cathode components heated at 950°C generally had lower mechanical strength than those at 1150°C, showing either serious spallation (Figure 7.4.1(b)) of the cathode containing 10wt%Ni or total fracture in the case of sample with lower Ni content (Figure 7.4.1(a)). The mechanical integrity was improved by increasing temperatures, especially in the case of 2wt%Ni content material (Figure 7.4.1(c)), which exhibited a complete macrostructure although some serious cracks presented. The cathode component containing 10wt%Ni also showed evidence of spallation on the surface. Generally, all the heated cathode components showed good porosity.
7.4.2. Microstructure of the new cathode component after heat treatment

Considering both the thermal analysis and the macrostructure results for the cathode component, 1150°C was chosen as the heating temperature \( T_h \) for the second-stage heat treatment for the following investigations. The results of SEM and image analysis investigations into the microstructure and porosity of the resultant integrated oxide cathode material after the two-stage heat treatment as shown in Figure 7.4 are reported in this section. The microstructure of the cathode component depicted in Fig 7.4.1(d) is shown in Fig 7.4.2.

![Figure 7.4.2](image)

**Fig 7.4.2.** SEM showing the microstructure of the integrated cathode containing 10wt%Ni after two stage heat treatment.

Porosity can be detected from the SEM with the image analysis results giving the total porosity to be 50% and the pore size to be 3-10μm in diameter. The microstructure showed evidence of significant agglomeration and fusion. Some cracks were apparent in the fused regions. No evidence of Ni filaments can be obviously detected in this material.
7.4.3. Distribution and morphology of Ni filaments in the thermally treated new cathode component

Although simple microstructural analysis by SEM did not initially reveal the presence and distribution of the Ni, the use of EDX mapping technique did enable this. EDX dot maps of the two oxide cathode components with different Ni contents and after heat treatment with a highest temperature of 1150°C are illustrated in Figures 7.4.3(a) and (b).

It is apparent that in the as heated material with 2wt%Ni, the Ni filaments remain discrete with no connectivity apparent between them. By contrast, in the 10wt%Ni material, the Ni particles appear to be largely connected to each other within the composite to form an interconnected Ni skeleton or framework within the material. Very little agglomeration of Ni can be detected in 2wt%Ni containing material, but the sizes and numbers of these agglomerates increased with increasing Ni content.

Fig 7.4.3(a) SEM dot mapping showing Ni distribution in the heat treated integrated oxide cathodes containing 2 wt% Ni.
Fig 7.4.3(b). SEM dot mapping showing Ni distribution in the heat treated integrated oxide cathodes containing 10 wt% Ni.

To further investigate the morphology of these Ni filaments, high magnification image of the EDX mapped regions having large Ni concentration as shown in Figure 7.4.3(b) was obtained as shown in Figure 7.4.3(c). Close examination reveals the Ni filaments and shows that these largely retained their filamentary morphologies in the heated material with the diameters being typically 2μm.

Fig 7.4.3(c). SEM image showing the microstructure of a cathode component with 10 wt% Ni after heat treatment. Ni filaments identified for clarify.
7.4.4. Atmospheric reactions of the as heated integrated oxide cathode

The effect of atmospheric exposure on the heated integrated oxide cathode was studied by direct measurements of the mass change of the material on air exposure.

The cathode prepared as described in Section 6.3.3 was exposed to air after being taken out of the furnace. The weight changes of the material with increasing time are shown in Fig 7.4.4. For the first 10 minutes, there was a relatively rapid weight increase which was followed by a further weight increase with exposure time which occurred at a gradually decreasing rate. A total weight increase of 16.3wt% was obtained during 60 minutes of air exposure.

Fig 7.4.4. Weight increase of heat treated integrated oxide cathode after exposure in air.
Chapter 8. Discussion I-The Integrated Oxide Cathode

8.1. Features of the integrated oxide cathode and its manufacturing process

The concept and features of the newly designed structure for the integrated cathode, together with the manufacturing process developed are discussed respectively in Section 8.1.1 and 8.1.2.

8.1.1. Design concept of the integrated oxide cathode

The integrated oxide cathode designed in this project has a relatively simple structure as shown in Figure 1.2(a), which is a mixture of Ni filament and BaSrO$_2$ in the form of a composite pellet, with the metallic and oxide components intimately mixed to provide a much higher interfacial area. Such a cathode structure was initially expected to provide some advantages to the conventional cathode, in particular:

(i). Improvement to the electron conductivity.

As introduced in Section 2.1, although the emission principle is based on the Richardson-Dushman equation$^{15,16}$ (equation 2.1.1(i)), the emission property is also largely dependent on the conductivity of electrons inside the coating layer$^{35,38}$ which comprised three different mechanisms, pore conduction, surface conduction and grain boundary conduction.$^{35}$ Among these three, the latter two mechanisms are both decided largely by the conductivity of the solid material. In the integrated oxide cathode, Ni filaments are incorporated with BaO, which as a metallic conductor will provide enhanced solid state conductivity, particularly where the metallic material forms a continuous percolating network, similarly to the principles discussed by Al-Ajili, Ray and Hodgson.$^{37}$
(ii). Improvement to the reactions between activators and BaO.

In terms of the activation of the oxide cathode, because the activators are envisaged to be alloyed in the Ni filaments and mixed with BaSrO$_2$ in the integrated cathode, instead of needing to travel through the Ni base (thickness 400$\mu$m) to reach the BaO,$^{[6,31]}$ the activator will, in this case, have a much shorter diffusion path length to reach the BaO, this being essentially the diameter of the Ni filaments which after heat treatment is about 10$\mu$m as described in Section 7.4.3(c). This shortening of the required diffusion path length for the activator species should provide much quicker activation for the electron emission of the oxide cathode, according to the reactions described in Section 2.4.2.$^{[41]}$

(iii). Reduction of the formation of continuous interfacial layer and its subsequent damage to the cathode.

As described in Section 2.5, the interfacial layer between Ni alloy substrate and spray deposited coating can result in serious problems in the conventional oxide cathode both mechanically, in terms of lack of adhesion,$^{[48]}$ and electrically, by the build up of a high resistance layer of reactive products of the activation process.$^{[40]}$ In the case of the integrated oxide cathode, because the Ni and activators are separately distributed throughout the cathode, the oxidation and reduction of activator and BaO is also more homogeneous. Therefore, the effect of building up of the reaction products to inhibit the further diffusion of the other activators and hence the suppressing of the production of free Ba can be greatly reduced. The mixed Ni and BaSrO$_2$ structure of the integrated oxide cathode should also largely eliminate the possibility of debonding between the emissive coating and the base metal.
8.1.2. Main features of the newly developed manufacturing process

To produce the newly designed integrated cathode, a corresponding manufacturing process has also been developed. As with the conventional oxide cathode (described in Section 2.3),[32] the manufacturing process developed for the integrated oxide cathode comprises two basic steps, (i), the manufacturing of integrated cathode precursor, and (ii), subsequent heat treatment to produce the required appropriate macro- and micro-structure and chemical transformations.

The main improvement of the new manufacturing process focused on the preparation of cathode precursor, which was designed to achieve the main aim of the project, i.e. low material wastage and low environmental impact. The preparation rate for the cathode precursor in the new cathode was envisaged to offer several advantages to that of the conventional cathode, in particular:

(i). A reduction in the number of process operations.

During the manufacture of the conventional cathode introduced in Section 2.3, the Ni cap and BaSr(CO₃)₂ are prepared separately in advance using different techniques with both requiring several stages of preparation.[32]

The manufacturing of the cathode precursor for the integrated cathode is essentially based on a variant of a ceramic tape casting process and was chosen to be relatively easy and straightforward. The process comprised mixing the cathode precursor components (Ni, BaSr(CO₃)₂, polymer additives and water) in the required amounts to form a well-mixed suspension which was then cast to form a film. The cathode precursor component is then obtained by mechanical cutting from the film.

(ii). Lower wastage

The new design, together with the casting process developed for it resulted in a process which had much lower wastage of the BaSr(CO₃)₂ than the spray processing of the conventional cathode.

A simple estimate of process wastage can be determined as follows.

For a cast film as shown in Figure 7.1.1.4 being used with planar dimensions 50mm*50mm, it was found that practically if cathode pellets with diameter 2.9mm
are cut from it, then for each row/column, 13 pellets could be stamped leading to 169 pellets in total. The waste of the material can thus be calculated as follows:

Number of cathode pellet can be cut from a film ($N_{op}$) = $13 \times 13 = 169$

Surface area of each cathode component ($A_p$) = \( \left( \pi \times 2.9 \times 2.9 \right) / 4 = 6.6 \text{mm}^2 \)

Surface area of total cathode pellet in a film:

\( (A_{tp}) = N_{op} \times A_p = 169 \times 6.6 = 1115 \text{mm}^2 \)

Surface area of a film ($A_f$) = $50 \times 50 = 2500 \text{mm}^2$

Waste of the material ($W\%$) = $100\% - \left( \frac{1115}{2500} \right) = 55\%$

Whilst there is undoubtedly scope to further enhance this by automated production processes for the stamping allowing closer spacing of the stamped components, the above figure of 55% wastage of the material during manufacturing the integrated oxide cathode is already much lower compared with more than 90% for the conventional oxide cathode manufacturing process (Section 2.5).\(^{34}\)

(iii). Less environmental impact.

Firstly, the new cathode casting method is based on an aqueous system which, compared with the organic solution of nitrocellulose binder used in the conventional material,\(^{32}\) is preferable because of its low toxicity, environmental impact and price, as introduced in Section 4.1.3.1.\(^{89,175}\)

Moreover, the residual scrap material left after the cathode pellets are cut out is in the form of a solid film, which can easily be collected and subsequently cause much less damage to the environment. Significantly, these materials may potentially also be recycled by redissolving the cast film and reused in oxide cathode production which will cause even less wastage.
8.2. Effects of the casting process on the properties of the as cast cathode precursor material

The experimental results in Sections 7.1 and 7.2 showed that casting step is one of the most crucial processes in producing the integrated oxide cathode. The production of the cast cathode precursor material in the form of a composite film with satisfactory properties (macro- and micro-structure) is an essential precondition for the subsequent manufacturing steps. This "as-cast" cathode precursor material has significant effect on the subsequent production processes and final properties of the final resultant integrated oxide cathode. The essential requirements for this as cast cathode precursor include good flatness, freedom from cracking and homogeneity of material distribution as well as the appropriate microstructure.

8.2.1. Effects of the casting parameters on the macrostructure of the as cast cathode precursor material

In terms of the macrostructure, the investigations showed that distortion and cracking were the two most significant problems encountered during casting, thus, the prevention of these defects was a major goal in the development of the process. From the mechanisms of drying discussed in Section 4.2, it is evident that both distortion and cracking are likely to be produced by the generation of various stresses inside the cast material during drying of the cast film.\cite{82,95}

The experiment results described in Section 7.1 showed that the appearances of distortion and cracking in the cast film were largely determined by the compositions of the casting suspensions. In particular, the combination and proportion of the polymer additives and the solid content in the casting suspension had very significant and obvious effects on the properties of the cast film, while the relative proportions of the two active constituents (BaSr\((\text{CO}_3)_2\) and Ni) produced little apparent influence. The development of the necessary understanding of the influences of these different materials is required to allow the required properties to be engineered and this is discussed in the following sections 8.2.1.1 to 8.2.1.3.
8.2.1.1. Effects of polymer additives on the macrostructure of the as cast films

Previous studies of stress development during drying between suspensions with and without polymer additives have shown that polymer additives can lead to very large effects.\textsuperscript{[98,100]} These findings appear to mirror those observed in this work, where with the presence of polymers in the casting suspension, high levels of residual stress were generated in the dried product with these stresses increasing with increasing amount of polymer additives. These can be explained in terms of the capillary stress\textsuperscript{[97-99]} and shrinkage of the binder\textsuperscript{[98,100,102]} as described in Section 4.2.2.

In comparison with more conventional ceramic casting process,\textsuperscript{[80,81]} the 50% by weight content of polymer additives in the cathode precursor material in this project was very high. This high content of polymer additives was necessary to achieve the high levels of porosity required in the cathode material. Unfortunately this is generally counter-productive in terms of stress development leading to relatively large amount of stresses generated inside the cast material during drying.\textsuperscript{[98,100,102]} This led to the need to investigate a range of potential polymer additives to attempt to control the resultant distortion. The effects of these polymers on the stress development and other macrostructural properties of the cast cathode materials are discussed in this section.

8.2.1.1.1. Effects of the individual polymer on the cast films

As reported in Section 7.1.1.1, the macrostructure of the various as cast materials containing PVA, PEO and PEG as individual polymer additives showed different characteristics.

The large amount of distortion in the PVA containing material described in Table 7.1.1.1 was due to the large internal stress generated by PVA. The high stress generated with PVA additives during casting is consistent with previous work as described in Section 4.2.2,\textsuperscript{[100]} this being caused by the relatively high glass transition
temperature \((T_g)\) of PVA.\textsuperscript{[120]} The \(T_g\) of a polymer is mostly determined by the mobility of its polymer chain, which, in turn, is determined primarily by the flexibility of the polymer backbone and the pendant groups present in the polymer.\textsuperscript{[175]} PVA has a back-bone of C-C-C, which has a relatively high strength.\textsuperscript{[119]} Moreover, the hydrogen bonding provided by the side groups of PVA further reduce the chain mobility of the PVA.\textsuperscript{[119]} Both these properties of PVA thus give rise to the high internal stress to the polymer film, and subsequently resulted in high distortion in the as cast film. This high glass transition temperature of PVA was also responsible for the high shrinkage of the cast film since polymers with a high \(T_g\) normally contain more solvent at the solidification point than a polymer with a low \(T_g\) and thus shrink more.\textsuperscript{[100]}

By comparison, PEO has a much lower \(T_g\) than that of PVA because of its (C-O-C) backbone, which has a much higher flexibility than the PVA backbone.\textsuperscript{[119]} The lower \(T_g\) of PEO also results from the absence of pendant groups of PEO.\textsuperscript{[119]} These properties of the PEO molecule were responsible for the much lower distortion and shrinkage of the PEO containing material. However, the convex distortion of the resultant material mentioned in Section 7.1.1.1 and together with the extensive cracking of the microstructure of the PEO as shown in Figure 7.1.1.5.1(b) are both thought to result from the semi-crystalline property of PEO with crystallites being created during the precipitation from the solution.\textsuperscript{[137]} These so-formed crystallites separate into discrete regions during drying with the higher density of the crystalline regions also leading to higher localised shrinkage and the associated formation of shrinkage cracks and distortion. These crystallites are also thought to be responsible for the inhomogeneity on the surface of the PEO containing composite material.

Casting suspensions with PEG as the only polymer additive could not form a proper cast film after drying the liquid. This is because of the very low melting temperature and low strength of PEG at room temperature. In fact the melting temperature of PEG \((\approx 50^\circ C)\)\textsuperscript{[155]} is so low that attempts to carbon or metal coat the material for SEM examination were unsuccessful leading to melting and distortion of the structure as shown in Figure 7.1.1.5.1(c).
On the basis of the high distortion associated with the use of PVA as a binder, the serious surface inhomogeneity and convex distortion with the use of PEO and the inadequate strength of PEG, it can be concluded that none of these three polymers are suitable to be used individually as the binders and processing additives for the casting of the cathode materials in this work and it was therefore decided to investigate combinations of these polymers to attempt to combine the best attributes of each.

8.2.1.1.2. Effects of combined polymer additives on the as cast films

8.2.1.1.2.1. The combination of PVA and PEG

The addition of relatively small amounts of PEG to PVA produced substantial effects on the macrostructure of the as cast material compared to the cast film with only PVA as can be seen from Section 7.1.1.2. The resultant cast films obtained for all PEG additions investigated (5wt% -25wt%) exhibited significantly decreased distortion which indicated significantly decreased internal stress generated during drying of the material. The PEG additives can be considered to act as plasticisers to the PVA in this case. The decrease of stress can be explained by equation 4.2.2(iii)\(^{[103]}\) which showed that the glass transition temperature of the polymer additives present has a decisive influence on the internal stress developed in a cast film.\(^{[103-107]}\) When PEG was added as a plasticiser, equation 4.2.2(iii) can be written as following:

\[
T_g = \frac{w_{PVA}T_{gPVA} + k w_{PEG}T_{gPEG}}{w_{PVA} + k w_{PEG}}  \quad 8.2.1.1.2.1
\]

with \(k, w\) and \(T\) being as described in Section 4.2.2.\(^{[103]}\)

The glass transition temperature of the combined polymer system is thus determined by the respective properties and addition levels of both PVA and PEG. As discussed in the previous section, PVA has a relatively high glass transition temperature, which results in high internal stress. Although a precise value of \(T_g\) was not available for the PEG used in the project, it is known that PEG generally has a very low glass transition temperature, well below 0°C(-67°C to -27°C)\(^{[151]}\) and the low
Tg of PEG in equation 8.2.1.2.1 can thus explain the significant improvement of distortion level achieved with even quite small additions (5wt%) of PEG. The low glass transition temperature of PEG comes from many aspects, such as the low molecular weight and chain length of PEG. In addition, the (C-O-C) backbone of PEG, (C-O-C) is the same as that of PEO and hence also induces great flexibility.\textsuperscript{119}

The cracks which appeared at the edge of the PVA/PEG composite film (Figure 7.1.1.2) indicated that the mechanical strength of the composite film with PEG additions was much lower than that achieved with only PVA addition. This could again be attributed to the decrease of the glass transition temperature. Above the glass transition temperature the polymer chains are able to slide against each other and take up strain. Thus the addition of PEG can increase the flexibility of PVA but at the cost of a reduction in strength. Determining an optimum composition between these two parameters was one of the main goals in developing this process.

Another characteristic of the cast film brought by the addition of PEG is the increase in the extent of the polymer segregation of the surface and around the edge of the cast film. This can be attributed to the plasticisation effect of the PEG. As described in Section 4.1.3.2 the addition of plasticiser can cause the polymers to migrate or flow in a way similar to the flow of solvent during drying.\textsuperscript{81} It is believed that the small size of PEG molecules allow them to act as a plasticiser, penetrating into the long PVA molecules and decrease the hydrogen bonding between the PVA molecules, effectively lubricating the PVA chains and resulting in easier migration of the PEG and PVA polymer.

8.2.1.2.2. The combination of PVA and PEO

The results reported in Section 7.1.1.3 show that the addition of PEO into PVA can also reduce the tendency for distortion of the products although the effect is not as obvious as for PEG addition. The improvement brought by PEO can also be similarly explained by equation 4.2.2(iii)\textsuperscript{103} where the glass transition temperature of polymer combination(Tg) is decreased by the addition of PEO, which also has a lower glass
transition temperature (-62°C--67°C) than that of PVA, leading to reduced generation of internal stress.\textsuperscript{176-178}

However, the effectiveness of PEO as a plasticiser was not as great as PEG. In this case, the optimum flatness could only be obtained when the amount of PEO was increased to 50wt% of the organic binder, PVA:PEO=1:1 (wt%). This is most probably because of the much higher molecular weight of PEO (100,000) compared to that of PEG (1000), leading to a smaller effect on the glass transition temperature compared to that of PEG in the PVA/PEG binder system. The higher molecular weight and strength of PEO also explains why the mechanical strength of the PVA/PEO containing films did not decrease as significantly as the PVA/PEG containing cast film.

Another characteristic brought by the addition of PEO was the reduction in the extent of polymer segregation on the surface and at the edge of the film with increasing PEO amount (Figures 7.1.1.3(a) and (b)). This property of PEO is the exact opposite to that observed with addition of PEG, which promoted the polymer surface segregation as shown in Section 7.1.1.2. The mechanisms responsible for these two contradictory effects are unclear and would require further investigation to determine.

8.2.1.1.2.3. The effect of the combination of three polymers

The optimum macrostructure of the as cast material could be obtained when the three polymer additives were used in combination as shown in Section 7.1.1.4. Two promising candidate systems 30wt%PVA/10wt%PEO/10wt%PEG and 20wt%PVA/20wt%PEO/10wt%PEG were identified from these experimental results, as shown in Table 7.1.4. The effect of each polymer in the tri-polymer material could be considered to be essentially the same as for the bi-polymer materials discussed in the previous two sections (Section 8.2.1.1.2.1 and 8.2.1.1.2.2) producing complementary effects.

In these systems, PVA was used as the main binder and the addition of PEO, PEG was designed to decrease the internal stress generated and subsequently the distortion of the as cast film. PEG was also used to improve the flexibility of the cast
film for facilitating the stamping process whilst PEO was used primarily to decrease the polymer segregation. The macro-properties of the as cast film were then determined by the respective proportions of these three polymers.

8.2.1.2. Effect of solid content of the casting suspension on the macrostructure of the cast films

The results reported in Section 7.1.2 showed that the solid content of the casting suspension had significant influence on the macrostructures of the cast films. These results are summarised in Figure 8.2.1.2.

![Graph showing effect of solid content on distortion and cracking properties of cast cathode precursor films.]

For the cast material obtained from low solid content suspension, the high tendency for distortion is believed to be caused by the polymer segregation. Low solid content infers that the suspensions contained relatively large amounts of liquid and thus would undergo a longer constant rate period for drying which, in accordance with previous studies\[107-109\] as described in Section 4.2.3, might be expected to result in large amount of polymer segregation. During the drying process, these polymers formed a visible polymer rich coating over the top surface of the cast material and at the edge of it, as shown in Figure 7.1.2(a). The shrinkage of these polymer rich regions of the cast films would be expected to be higher than that of the rest of the
material, and this differential shrinkage would in turn therefore be expected to lead to the generation of differential stress and hence distortion of the cast film, in accordance with other studies (Section 4.2.2). \[^{80,81,95}\]

The cast film obtained from high solid content suspension exhibited substantial cracking but little and/or no polymer segregation. As described in Section 4.2.2 the formation of such cracking implies that during the drying process, the capillary force that generated these cracks must have exceeded the cohesive strength of the material, \[^{95,106}\] so it can be inferred that in this case, either the capillary force increased or the cohesive strength of the material decreased.

The value of the capillary force can be estimated according to equation 4.2.2(v). \[^{95}\] As introduced in Section 4.2.1 the evaporation rate during constant rate period is mainly dependent on the external conditions \[^{80,81,94}\] which were kept constant during these experiments and thus \(V_E\) can be considered to be broadly the same for the cast material obtained from both suspensions. It is also unlikely that there would be a significant change in the permeability (D) of the samples which were of similar thickness and microstructure. It is then reasonable to conclude that it was not the increase in capillary force that caused the cracking, and that the cracking is more probably attributable to a reduction in cohesive strength.

For the casting suspension with very high solid content, the constant rate period was so short that almost no polymer segregation took place and all polymer additives were blended and left inside the cast material. Although the presence of the polymers was expected to provide enhanced binding to the material, the experimental results in Sections 7.1.2 and 7.1.3 (Figures 7.1.2(c), 7.1.3(e) and 7.1.3(f)) indicated decreased strength of the material. This suggests that the bonding between the polymer and inorganic material is impaired. This effect is consistent with the findings of Annika et al \[^{106}\] described in Section 4.2.2 who suggested that a similar effect in casting system with latex binder was due to the fact that the polymers didn’t have enough time to form effective bonds between themselves and the other solid materials because of the short constant drying period.
8.2.1.3. Effects of the proportion of BaSr(CO₃)₂ and Ni on the macrostructure of the cast films

The experimental results (Section 7.1.3) showed no perceptible change in the distortion of the cast films with different ratios of BaSr(CO₃)₂ to Ni as the cathode material.

This phenomenon can be explained referring to the stress development process during drying in a cast film with polymer additive discussed in Section 4.2.2 (Figure 4.2.2(b)) which showed that the overall stress in such a system is dominated by the effects of the polymer. The internal stress generated by the solid materials (BaSr(CO₃)₂ and Ni) is developed at the very start of the drying process and then released by the subsequent stress-relaxation stage.

8.2.2. Effects of the casting conditions on the microstructure of the cast films

The microstructure of the cathode precursor material can, to a large extent, decide that obtained in the cathode after conversion and during operation. The three polymers used in preparing the cathode material casting suspension were added not only as the binder/plasticiser, but also crucially as microstructural template to provide the necessary pores in the cathode after they are thermally burned out. The results reported in Section 7.2.2 confirmed these polymers did indeed have a significant influence on the microstructure and especially pore size and structure of the cathode precursor material.

8.2.2.1. Effects of the polymer composition to the microstructure of the cast films

For the two polymer compositions chosen (as shown in Table 7.1.4), the cathode precursor material containing 30wt%PVA/10wt%PEO/10wt%PEG (Figures 7.2.2(a)
and (b)) had a less open microstructure with lower porosity and smaller pore size than the material containing 20wt%PVA/20wt%PEO/10wt%PEG (Figures 7.2.2(c) and (d)) with the latter material found to be preferable for the production of the cathode precursor material with the necessary porous microstructure after heating and during operation.

The different microstructure of cathode material is related to the microstructure produced by the polymer phases as shown in Figures 7.1.1.5.5 (a) and (b). To understand the microstructure of the tri-polymer material, individual polymer and bi-polymer materials are also investigated as shown in Sections 7.1.1.5.1 to 7.1.1.5.4.

SEM images showed that the tri-polymer material with the composition 20wt%PVA composition exhibited obvious phase separation as shown in Figure 7.1.1.5.5(b) as compared to Figure 7.1.1.5.5(a) which is for material with the composition 30wt%PVA. The phase separation is accompanied by the occurrence of the cracks, with these effects is thought to be introduced by the addition of PEO. Evidence to support this is given by the similarity of these cracks to those observed in both pure PEO (Figure 7.1.1.5.1(b)) and the two PEO containing bi-polymer systems (PVA/PEO (Figure 7.1.1.5.3(b) and PEO/PEG (Figure 7.1.1.5.4)). These cracked regions are thus believed to be PEO-rich area. The phase separation in both PVA/PEO and PEO/PEG systems were both consistent with the findings of other investigations as described in Section 5.4.1 and 5.4.2.

It can be concluded that it is the PEO which generated the more serious and obvious phase separation in the cathode material containing 20wt%PVA and subsequently generated the more open and porous microstructure than the material containing 30wt%PVA. So, besides the polymer-segregation-reduction function to the as cast film, the addition of PEO was also significantly helpful in producing larger pores and more open microstructure of the cathode material by causing the phase separation between the polymers. The optimum formulation will be determined by a compromise between these two factors.
8.2.2.2. Comparison to that of the conventional cathode

The importance of the microstructure of the cathode material to the performance of the cathode has been mentioned many times. So, to initially produce the new oxide cathode with comparable emission performance to that of the conventional cathode, it is required to duplicate the microstructure of the conventional cathode to the new cathode as far as practicable.

The microstructure in the conventional cathode is mainly determined by the spraying process, which generates the porous structure for the conventional cathode. The microstructure of the integrated cathode, especially the large amount of pore, is by contrast designed to be provided by the large amount of polymers, which, after burning out during heating will leave the pores inside the material. Despite the different controlling parameter of these two microstructures, experimental results (Section 7.2.2) showed similarity of the new cathode material to that of the conventional cathode material which proved the suitable composition and amount of the polymers used in the integrated cathode material.
8.3. The investigations to the thermal analysis of the cathode material and their effects on the properties of the as heated integrated oxide cathode

Following on from the casting process, the heat treatment is another critical stage in the newly developed manufacturing process for the integrated oxide cathode which determines many significant properties, including proper composition, macrostructure and microstructure. These properties will largely decide the emission behavior of the cathode during operation.

8.3.1. Reactions of the cathode material during heating

Since many reactions are involved during the heat treatment, these processes were separately investigated and reported in Section 7.3.1-7.3.3 to provide as complete understanding as possible of the overall processes occurring during heat treatment. The thermal analysis results obtained for the individual components of the cathode are discussed in the subsequent Sections 8.3.1.1 to 8.3.1.3 with the thermal analysis results of the combined cathode material developed for the casting process being discussed in Section 8.3.1.4.

8.3.1.1. Thermal decomposition of polymer additives

It is important for the development of the integrated cathode that the various polymer additives used as process aids and microstructure formers can be effectively removed during heat treatment prior to sealing in the CRT assembly where they might contaminate the device during operation. The complete burnout of these polymer additives under the experiment conditions is one of the main purposes of the initial heating stage with this being studied in the thermal analysis experiments discussed in the following sections.
8.3.1.1.1. Polyvinyl Alcohol (PVA)

Similarly as those introduced in Section 5.1.3.1,\textsuperscript{[119–128]} the thermal analysis results reported in Section 7.3.1.1 also showed two main stages in the thermal decomposition of PVA. The TGA decomposition curve is quite similar to the findings of previous studies\textsuperscript{[122]} as described in Figure 5.1.3.1(b) with the DTA results also being in accordance with the other DTA investigations of PVA decomposition in air reported in Section 5.1.3.2 which identified similar exothermic reactions for the decomposition of PVA in air.\textsuperscript{[129,130]}

The first stage (Stage I) comprising 9wt\% weight loss (TGA) and the corresponding small endothermic reaction (A) identified by DTA can be attributed to the removal of water trapped within PVA or other dehydration process as mentioned in Section 5.1.3.1.\textsuperscript{[120–126]} Although the glass transition temperature of PVA is normally between 60°C–80°C as introduced in Section 5.1.1,\textsuperscript{[120]} no corresponding thermal event was found in the DTA results over this temperature range. The reason for this is not clear and further investigation is then needed to clarify this. Possibly the glass transition temperature of the PVA sample used here was below the temperature range used for the thermal analysis.

Closer inspection of the second stage (Stage II) identified in the TGA results (Figure 7.3.1.1(a)) shows that this actually comprised several sub-steps of weight loss between 260°C and 540°C during the decomposition of the PVA polymer. These various decomposition reactions in TGA and DTA are thought to be related to the oxidation and further dehydration reactions of the unsaturated polymer chains as described in Section 5.1.3.1\textsuperscript{[126,127]} over a number of (unidentified) different reactions although no information is available for each specific reactions. With increasing temperature, the PVA sample decomposition stopped by 540°C with approximately 0.5wt\% residual material as indicated by the TGA.

Although according to many researchers that PVA is a semi-crystalline material with the melting temperature in the range of 210°C–250°C,\textsuperscript{[120]} peak B is attributed to
the melting temperature of PVA in this case, with melting being closely followed by further dehydration and decomposition reactions.

A summary of the decomposition behaviours of PVA in air is listed in Table 8.3.1.1.1.

Table 8.3.1.1.1. Summary of thermal decomposition behaviour of PVA during thermal analysis.

<table>
<thead>
<tr>
<th>Stage</th>
<th>TGA</th>
<th>DTA</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>A</td>
<td>Elimination of water and dehydration process</td>
</tr>
<tr>
<td>II</td>
<td>i-v</td>
<td>B-G</td>
<td>Melting and main decomposition stage of PVA over a series of oxidation and further dehydration processes</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>n/a</td>
<td>No decomposition of PVA after 540°C in air and approximately 0.5wt% residue left</td>
</tr>
</tbody>
</table>

8.3.1.1.2. Polyethylene oxide (PEO)

The thermal decomposition results for PEO in air are reported in Section 7.3.1.2. Although previous reported studies of the thermal decomposition of PEO in nitrogen atmosphere as shown in Figures 5.2.3.1(a) and (b) both showed one step, the TGA results (Figure 7.3.1.2(a)) of PEO in air in this project showed weight loss of several steps indicating by various slopes of TGA curve, which is thought to indicate the different decomposition mechanisms brought by the different heating atmosphere used.

The first endothermic event (A) identified by DTA corresponds with a region of stable mass in TGA (Region I), and can be attributed to melting of the crystallites in PEO, which is generally in agreement with the other findings as mentioned in Section 5.2.2.\textsuperscript{[137]}

The subsequent higher temperature thermal events commencing at approximately 170°C, comprising several stages of weight loss (i~iv) in TGA with corresponding exothermic peaks (B~F) in DTA, represented a series of stages of
thermal decomposition of PEO. As for the decomposition of PVA, no information is available for each specific reactions of PEO decomposition. So these weight loss steps in TGA and high temperature peaks identified by DTA were all tentatively ascribed to the degradation by the oxidation reaction\[136,137\] of the molecular chains of PEO. The decomposition of PEO in air stopped at 470°C with approximately 0.5wt% residue remaining after that.

A summary of the decomposition reactions of PEO is listed in Table 8.3.1.1.2.

**Table 8.3.1.1.2. Summary of the thermal decomposition behaviour of PEO during thermal analysis.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>TGA</th>
<th>DTA</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>A</td>
<td>Melting of crystallites</td>
</tr>
<tr>
<td>II</td>
<td>i–iii</td>
<td>B–F</td>
<td>Degradation of PEO by various oxidation reactions of molecular chains</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>n/a</td>
<td>Decomposition of PEO stopped at 470°C in air and approximately 0.5wt% residue left</td>
</tr>
</tbody>
</table>

**8.3.1.1.3. Polyethylene Glycol (PEG)**

The thermal analysis results reported in Section 7.3.1.3 identified a number of discrete steps in the thermal decomposition of PEG in air, which is in accordance with the results of a previous decomposition study in air shown in Figure 5.3.3.1(b).\[156\]

The first endothermic peak at 40°C (A) in DTA can be attributed to the melting of crystallites in PEG because of its semi-crystalline property and is generally consistent with other reported DSC investigation results as shown in Figure 5.3.2.\[155\]

The endothermic peak at 105°C (B) identified by DTA is accompanied by a corresponding weight loss in TGA (Stage I) and can be attributed to the removal of chemically and physically bound water from the material.

The main decomposition processes of PEG identified between 190°C and 460°C by TGA (Stage II) with corresponding exothermic events (C–F) in DTA can be
attributed to complex multi-step decomposition and oxidation of the PEG molecules. On the basis of this data, it is not possible to separately identify the cause of each separate sub-step of these decompositions. However, for the purpose of this work, this is not of major significance. Complete burnout of PEG was obtained by 460°C with no residue.

A summary of the decomposition reactions of PEG is listed in Table 8.3.1.1.3.

Table 8.3.1.1.3. Summary of thermal decomposition behaviour of PEG during thermal analysis.

<table>
<thead>
<tr>
<th>Stage</th>
<th>TGA</th>
<th>DTA</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>A</td>
<td>Melting temperature of PEG crystalline</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>B</td>
<td>Elimination of water in PEG</td>
</tr>
<tr>
<td>II</td>
<td>i-iii</td>
<td>C-F</td>
<td>Thermal decomposition of PEG in several sub-steps and completed at 460°C</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>n/a</td>
<td>Decomposition of PEG completed at 460°C and no residue left after that</td>
</tr>
</tbody>
</table>

8.3.1.2. Reaction of Ni filaments

For the purpose of the development of the new cathode manufacturing processes in this work, it was important to understand how the metallic nickel additives behaved during heating under the different atmospheres (air and N₂/H₂) and temperatures used. In particular it was of interest to determine if the temperatures required for burnout of the organic additives in air up to 500°C resulted in the simultaneous (and undesirable) oxidation of the metallic Ni, and whether any oxidation could be reversed by subsequent heat treatment in reducing atmosphere.

The reactions identified for the Ni filaments under heating conditions used in the project were reported in Section 7.3.2. Both DTA and TGA analysis showed evidence of expected oxidation of nickel (Ni) to the corresponding nickel oxide (NiO) during heat treatment in air at temperatures from room temperature to 500°C as evidenced by the weight increase (sub-step ii) in TGA and the endothermic peak (A) in DTA with
the rate increasing with increasing temperature in this range as might be anticipated. As described in Section 3.2.2 this oxidation is expected according to thermodynamics.\textsuperscript{[192]}

In these experiments, the heating atmosphere was switched from air to a protective \textit{N$_2$/H$_2$} atmosphere at 500°C. It can be noted in these results that oxidation continued at a reduced rate during further heating to 560°C, presumably whilst residual oxygen was eliminated from the system-leading to total increase of mass of 17wt%, which is 63wt% of the theoretical weight enhancement (27wt%) which would be anticipated according to reaction 3.2.2(i) for the oxidation of Ni, thus implying that the Ni phase is substantially, but not completely, oxidised. Although as mentioned the oxidation of Ni is supposed to be an exothermic process,\textsuperscript{[196,197]} the DTA graph reported in Section 7.3.2 indicated the endothermic characteristics of the Ni oxidation process in this project. The reason for this is not clear and further investigation is needed into fully understands this. One possibility is that there has been some special treatment to the Ni material used in the project that led to the endothermic reaction during heating, such as the reaction 3.2.2(ii) mentioned in Section 3.2.2.\textsuperscript{[195]}

As the temperature was further increased under the \textit{N$_2$/H$_2$} atmosphere, a second stage of reactions started from 780°C evidenced by weight loss (sub-step iv) in TGA and the thermal peak(B) in DTA, which is in consistent with other researchers introduced in Section 3.2.3\textsuperscript{[184]} that the reduction of NiO by H$_2$ is exothermic, indicating the occurrence of reduction of NiO back to Ni. By 900°C, the weight loss of sample was the same as the weight increase during low temperature heating in air (17wt\%) and the weight of Ni went back to the original value shown in TGA graph, indicating that the oxidation process occurring at lower temperatures in air could be completely reversed.

It is noticed that although \textit{N$_2$/H$_2$} was provided at 500°C, the reduction of NiO didn’t take place until the temperature was raised to 780°C. Given that this reduction of NiO by H$_2$ is thermodynamically anticipated at all temperatures as introduced in Section 3.2.3,\textsuperscript{[192]} This requires some further explanation. The delay in the onset of the reduction reaction can be explained according to the investigations of James and
Rodriguez et al\textsuperscript{[184,191]} as introduced in Section 3.2.3. As suggested by these researchers, there is an induction time before the commencement of the reduction during which many processes, such as the creation of the oxygen vacancies, the adsorption of the hydrogen and the migration of oxygen take place. The commencement of the reduction at 780°C is also thought to be partially due to the low content of H\textsubscript{2}, only 5%, in the atmosphere used here which is in agreement with the investigations of different researchers as shown in Section 3.2.3.\textsuperscript{[184,191]} It is thus expected that the reduction reaction might be promoted to occur at lower temperature when H\textsubscript{2} content is increased.

A summary of the thermal reactions of the Ni material during the two stages of heating is listed in Table 8.3.1.2.

Table 8.3.1.2. Summary of the behaviour of Ni during thermal analysis

<table>
<thead>
<tr>
<th>Stage</th>
<th>TGA</th>
<th>TGA</th>
<th>Atmosphere</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>n/a</td>
<td>air</td>
<td>No reaction</td>
</tr>
<tr>
<td>ii</td>
<td>A</td>
<td></td>
<td></td>
<td>Partial oxidation of Ni to NiO</td>
</tr>
<tr>
<td>III</td>
<td>iii</td>
<td>n/a</td>
<td>N\textsubscript{2}/H\textsubscript{2}</td>
<td>No reaction</td>
</tr>
<tr>
<td>iv</td>
<td>B</td>
<td></td>
<td></td>
<td>Reduction of NiO to Ni</td>
</tr>
</tbody>
</table>

8.3.1.3. Thermal decomposition analysis of BaSr(CO\textsubscript{3})\textsubscript{2}

The thermal analysis results of BaSr(CO\textsubscript{3})\textsubscript{2} are reported in Section 7.3.3. The main purpose of this investigation was to determine the onset and completion temperatures for the conversion reaction of BaSr(CO\textsubscript{3})\textsubscript{2}, in order that this could be compared with the decomposition temperatures for the polymer additives to determine if polymer burnout could be accomplished without converting the BaSr(CO\textsubscript{3})\textsubscript{2} to the less stable oxide phase.

(i). Thermal reactions of the thermal analysis

The small weight loss (Stage I) in TGA and the corresponding endothermic peak (A) in DTA graph were attributed to the thermal removal of water absorbed in
no literature shown any reactions of BaSr(CO$_3$)$_2$ over this temperature range.

No further reactions were identified in either TGA or DTA until about 800°C at which point the endothermic peak identified by DTA (B) can be attributed to the phase transformation of BaSr(CO$_3$)$_2$ from orthorhombic to hexagonal form, this being in agreement with the finding of other workers as described in Section 3.1.3.$^{[71]}$ The following two endothermic peaks (C,D) at 930°C and 960°C can be attributed to the phase transformation of SrCO$_3$ and BaCO$_3$ from hexagonal to cubic, although compared to the findings in other studies$^{[71,74]}$ those two reactions occurred at somewhat lower temperatures. This discrepancy may be due to the lower heating rate used in this project (5°C/min) compared to those used in the other studies by Arvanitidis et al$^{[70]}$ which as showed, normally resulted in lower phase transformation temperatures.

The decomposition of BaSr(CO$_3$)$_2$ according to reaction 2.4.1(i)+(ii) or 2.4.1(iii)$^{[23]}$ commenced at 860°C as indicated by the mass loss identified in TGA and the changes in DTA curve.

It is significant that although as introduced in Section 3.1.2$^{[84-86]}$ the expected decomposition temperatures of BaCO$_3$ and SrCO$_3$ are different under the same conditions, only a single endothermic peak could be identified in the DTA. This strongly suggest that the BaSr(CO$_3$)$_2$ material supplied for use in the project comprised a solid solution of these two constituents rather than a simple mechanical mixture. So the decomposition reaction occurred as described in reaction 2.4.1(iii).$^{[24]}$ The decomposition reaction was apparently completed by 1170°C. The total mass loss between 860°C and 1170°C was 26.5wt% with no further mass change. These temperatures are approximately consistent with the decomposition temperatures in Ar reported by Arvanitidis$^{[70,71]}$ The slightly lower completion temperature can be attributed to the use of a mixed oxide preventing the effect discussed in Section 3.1.4.$^{[71]}$
(2). Compositional calculation

To confirm if the conversion reaction had indeed gone to completion, the percentage of the decomposition of BaSr(CO$_3$)$_2$ under the heating conditions can be calculated according to the reaction 2.4.1(iii).$^{[23]}$

For a 100% BaSr(CO$_3$)$_2$ sample, the theoretical weight loss of the decomposition of BaSr(CO$_3$)$_2$ is approximately 28 wt% as calculated from reaction 2.4.1(iii). However, the sample used in the thermal analysis comprised only 97wt% BaSr(CO$_3$)$_2$, the remaining being water. The theoretic weight loss of the sample can thus be calculated as:

\[ \Delta W\% = 97 \times 28\text{wt}\% = 27.16\text{wt}\% \]

8.3.1.3

The actual mass loss of 26.5wt% in these experiments is thus very close to the theoretical weight loss suggesting that the BaSr(CO$_3$)$_2$ had indeed decomposed completely by this temperature. The minor discrepancy can be attributed to measurements in the instrument and for the presence of impurities in the sample.

A summary of the reactions of BaSr(CO$_3$)$_2$ during thermal analysis was listed in Table 8.3.1.3.

Table 8.3.1.3. Summary of thermal decomposition behaviour of BaSr(CO$_3$)$_2$ during thermal analysis.

<table>
<thead>
<tr>
<th>Stage</th>
<th>TGA</th>
<th>DTA</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n/a</td>
<td>A</td>
<td>Thermal removal of water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i</td>
<td>Phase transformation of BaCO$_3$ from orthorhombic to hexagonal</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>C</td>
<td>Phase transformation of SrCO$_3$ from orthorhombic to hexagonal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ii</td>
<td>Phase transformation of BaCO$_3$ from hexagonal to cubic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thermal decomposition of BaSr(CO$_3$)$_2$ to BaSrO$_2$</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>n/a</td>
<td>BaSr(CO$_3$)$_2$ completely decomposed to BaSrO$_2$ by 1160°C</td>
</tr>
</tbody>
</table>
8.3.1.4. Experiment reaction of BaSr(CO₃)₂/Ni/polymer composite

The aim of the experiments reported in Section 7.3.4 was to determine how the thermal degradation processes occurred during heating of the combined polymer/inorganic constituents of the new composite integrated cathode.

In this section, the reactions occurring during the heating step of the new cathode manufacturing process (Section 7.3.4) identified in both DTA and TGA are explained and identified based on the thermal analysis results obtained for the individual components as discussed in Sections 8.3.1.1-8.3.1.3. Secondly, the effect of the various stages of heating on the composition of the cathode material is calculated to check the selection of the heat treatment conditions for final confirmation and/or adjustment.

(i). Thermal reactions of the thermal analysis

The initial stage of heating led to a small weight loss (sub-step i) in TGA and two endothermic peaks (A and B) identified by DTA. One of these peaks should be related to the removal of water together with the weight loss (sub-step i) with the other peak mostly likely to be due to the transition of the polymer phase (glass transition or melting). Similar effects were identified for the impregnated oxide cathode discussed in Section 10.1.3.1.

The second stage (step ii) of reactions identified by TGA in Figure 7.3.4(a) comprising several sub-stages of weight loss with four corresponding exothermic peaks (C,D,E,F) in DTA (Figure 7.3.4(b)) can be attributed to the thermal decomposition of the various polymers according to the previous results and discussion (Section 7.3.1 and 8.3.1.1). As many of these degradation reactions occur over similar temperatures for the PVA, PEO and PEG additives, the separate identification of each sub-stage cannot be ascertained.

The weight reduction due to loss of polymer would be expected to be partially balanced by the Ni oxidation reaction which also took place during this temperature range according to both the thermal analysis of pure Ni (Section 7.3.2) showing the
oxidation of Ni starting at about 250°C as discussed in Section 8.3.1.2 and the deviation of DTA curve of the cathode composite material from baseline downwards at 440°C in the composite material shown in Figure 7.3.4(b).

Because the polymer is essentially removed after heating in air to 500°C, it is reasonable to assume that after the switch of atmosphere to N₂/H₂ at 500°C, the weight increase in TGA (step iii) and the endothermic peak in DTA (G) can therefore both be attributed to the oxidation of Ni. Compared to the pure Ni (Section 7.3.2), the temperatures corresponding to the maximum rate and completion of Ni oxidation both raised slightly most probably because the mixing of Ni with other materials impeded the ability of oxygen to penetrate into the material to react with Ni thereby reducing the reaction rate. The oxygen necessary to cause this reaction is most probably residual gas not purged from the system. The endothermic peak of Ni oxidation mirror those obtained for the pure Ni material discussed in Sections 8.3.1.2 and no further explanation is given here.

The endothermic peaks (H.I.J) identified between 800°C and 960°C by DTA are due to the phase transformation of BaCO₃ and SrCO₃ as has been discussed in Section 8.3.1.3. The final stage weight loss (v) in TGA occurred between 840°C and 1115°C. It would be anticipated that this would comprise both NiO reduction and decomposition of BaSr(CO₃)₂ according to the thermal analysis results obtained for both individual components. However, the exothermic peak (B) in Figure 7.3.2(b) representing the reduction reaction in the DTA of pure Ni filament is not apparent in the DTA plot obtained for this composite material. This could indicate either that the reduction did not occur in this case, or that the thermal effect was masked by the large endothermic peak (K) due to the decomposition of BaSr(CO₃)₂. This can be obtained by the calculation later.

Compared to the results for BaSr(CO₃)₂, the decomposition of BaSr(CO₃)₂ in the composite material happened at the slightly lower temperatures in terms of the starting and completion temperatures. Although the reasons for this are uncertain, one possibility is that the Ni additives acted as a catalyst for this reaction.
(ii). Compositional calculation

Besides a knowledge of the process as occurring during heat treatment of the composite material, it is also important to know the composition in the final product after heating in the cathode material by calculation of the weight loss of each stage. This information can be used to determine the correct heat treatment conditions for cathode processing. The compositional requirements of the heat treatment and the aims of these calculations are thus to establish that: (1), the polymer additives are completely removed during the low temperature heat treatment; (2), that Ni is present in the form of metal rather than NiO in the final material; (3), that BaSr(CO$_3$)$_2$ is fully converted at the heat treatment conditions used to BaSrO$_2$. For simplicity in the following calculations, there are some assumptions that are necessary to make:

(1). That the distribution of every component is assumed to be homogeneous, so that the compositions of each component in the sample examined was 40wt%BaSr(CO$_3$)$_2$, 10wt%Ni and 50wt% polymer.

(2). That the oxidation of Ni in the composite was the same as the pure Ni. That means the onset temperature and approximate speed of oxidation were the same as for the pure Ni filament as reported in Figure 7.3.2(a).

With these assumptions, the loss of the components and the final products in the composite can then be calculated as follows.

(i). Step ii

First, from the TGA graph of the composite (Figure 7.3.4(a)), it can be estimated that the as cast cathode material comprised 96wt% solid constituent with the remaining 4wt% being water which was removed on heating below 170°C. Given that the proportions of the solid components were 40wt%BaSr(CO$_3$)$_2$, 10wt%Ni, 50wt%polymer as described in Section 7.3.4. The overall composition of all the components in the cast cathode material can thus be corrected to an assumed 38.4wt% BaSr(CO$_3$)$_2$, 9.6wt% Ni, 48wt% polymer and 4wt% water.

By 500°C, the weight loss of the sample was 46wt%, which comprised the weight loss caused by the decomposition of polymer and weight increase by the oxidation of Ni. It can be calculated from Figure 7.3.2(a) that by 500°C, the weight
increase due to oxidation of the pure Ni material was 14wt% assuming that the Ni oxidation behaviour in the composite was the same as for the individual Ni. Then the expected mass increase due to oxidation of the 9.6wt% Ni present in the composite is thus as follows:

\[ \Delta W_{\text{Ni}} = 9.6 \times 14\text{wt\%} = 1.344\text{wt\%} \]  

Compensating for the additional mass due to oxidation of the Ni, then the calculated weight loss due to removal of the polymers in the composite material is:

\[ \Delta W_{\text{polym}} = 46\text{wt\%} + 1.344\text{wt\%} = 47.344\text{wt\%} \]

This calculated mass loss accounts to nearly 99% of the total mass of the polymers in the sample, suggesting that at least the large majority of the polymers (>98.6wt%) could be removed by the heat treatment at 500°C in air, although there is some chance that a small amount of polymer residue (∼1wt%) could left in the cathode material. It is difficult to be more specific than this as the discrepancy between the observed and theoretical mass loss is within the likely range of experimental error of the measurements and assumptions made.

The thermal analysis of the individual polymers (Section 7.3.1) showed that while PEG decomposed completely, both PVA and PEO did leave small residues (0.5wt%) after heating at 500°C in air. As just calculated, the residue of the polymer combination in the cathode composite is approximately 1wt%, which can be due to the experimental error of the measurements and assumptions made. So, at this stage, there is no clear evidence showing if the presence of the Ni and ceramic material (BaSr(CO₃)₂) have any catalytic effect on the decomposition of the polymers as mentioned in Section 4.3.1.2. More detailed study would be needed to determine fully the effect of these inorganic material on the decomposition of the polymers in the cathode material. However, it still can be concluded from the calculation results that the temperature chosen (500°C), for the low temperature stage heating of the process is adequate to generally satisfying the requirement of the heat treatment process.
(ii). Step iii

Accounting for the further weight increase of 0.6wt% obtained during heating between 500°C and 560°C due to the Ni oxidation by residual oxygen after the atmosphere was changed to N2/H2, gives a total weight increase due to Ni oxidation during heating:

\[ \Delta W_{Ni} = 1.344\text{wt\%} + 0.6\text{wt\%} = 1.944\text{wt\%} \]

8.3.1.4(iii)

(iii). Step v

The weight loss of almost 13.5% observed during heating between 840°C and 1115°C under N2/H2 suggests that this comprised both NiO reduction and BaSr(CO3)2 decomposition.

As calculated in Section 8.2.1.3 that the theoretical mass loss due to decomposition of a 100wt% BaSr(CO3)2 is 28wt%, so for 38.4wt% BaSr(CO3)2 in the sample, the theoretical decomposition percentage should be calculated as:

\[ \Delta W_{carbonate} = 38.4 \times 28\text{wt\%} = 10.752\text{wt\%} \]

8.3.1.4(iv)

The additional mass loss can thus be attributed to reduction of NiO although the 13.5% mass loss recorded during heating at these temperatures is in fact rather higher than would be anticipated from 8.3.1.4(iv) and the 1.944wt% attributed to oxidation/reduction of Ni.

\[ \Delta W_{r} = 10.752\text{wt\%} + 1.944\text{wt\%} = 12.696\text{wt\%} \]

8.3.1.4(v)

Despite the discrepancy which is probably due to a combination of errors in the measurements and underlying assumptions and sample homogeneity, comparing the theoretical weight loss, 12.696wt%, and the practical weight loss, 13.5wt%, it can reasonably be assumed that by 1125°C, both complete BaSr(CO3)2 decomposition and NiO reduction took place in the cathode composite material under the conditions used during thermal analysis.

A summary of the thermal events occurring during the heat treatment of the cathode composite material is given in Table 8.3.1.4.
Table 8.3.1.4. Summary of thermal decomposition behaviour of cathode composite during thermal analysis.

<table>
<thead>
<tr>
<th>Stage</th>
<th>TGA</th>
<th>DTA</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>i</td>
<td>A</td>
<td>Melting of crystalline structure in polymer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>Elimination of water</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>C~F</td>
<td>Decomposition reaction of three polymers and oxidation of Ni</td>
</tr>
<tr>
<td>II</td>
<td>iii</td>
<td>G</td>
<td>Oxidation of Ni</td>
</tr>
<tr>
<td></td>
<td>iv</td>
<td>H</td>
<td>Phase transformation of BaCO₃ from orthorhombic to hexagonal</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>I,</td>
<td>Phase transformation of SrCO₃</td>
</tr>
<tr>
<td></td>
<td>v</td>
<td>J</td>
<td>Phase transformation of BaCO₃ from hexagonal to cubic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K</td>
<td>Thermal decomposition of BaSr(CO₃)₂</td>
</tr>
<tr>
<td>IV</td>
<td>n/a</td>
<td>n/a</td>
<td>Thermal decomposition of BaSr(CO₃)₂ completed and no reaction happen after this</td>
</tr>
</tbody>
</table>

8.3.2. Summary and application of the thermal analysis on results

The thermal analysis results were of considerable significance in the development of the process route for the new integrated cathode, allowing both the feasibility of the proposed process route to be demonstrated with regard to the thermal compatibility of the constituents to be demonstrated, and allowing the optimum heat treatment conditions to be determined.

For the heat treatment of the integrated oxide cathode, the object of the initial stage heating is to remove polymer additives (PVA, PEO and PEG) as complete as possible whilst try to depressing the undesirable oxidation of the Ni component. First, the thermal analysis results of the three polymers (PVA, PEO and PEG) provided
useful information of the low temperature heating stage, with the atmosphere and temperature, air and 500°C, being initially chosen. Air was chosen as the atmosphere for the initial heat treatment to allow the most effective removal\textsuperscript{[81,89]} with this being confirmed by these measurements of the polymer binder. The thermal analysis of pure Ni provided information on what would be expected for the Ni phase during heating and help to calculate the final composition of the cathode composite material as discussed in Section 8.3.1.4. 500°C is also chosen because it can be confirmed from the thermal analysis that this temperature is not high enough for the unstable oxide to be produced.

Finally, the thermal analysis of the composite material helped to confirm the optimum process conditions. As outlined in Section 8.3.1.4, 500°C and air were found to be suitable during the low temperature stage from the thermal analysis which demonstrated that nearly 99wt% of the polymer can be burnout at this temperature. The protective/reducing atmosphere, N\textsubscript{2}/5%H\textsubscript{2}, is also proved to be a suitable medium allowing both the conversion reaction to take place and at the same time allowing any oxidation of the Ni at lower temperatures to be reversed. The thermal analysis also provided information to initially decide the temperature range for the high temperature heating stage. However, the temperature of the high heating stage will be finally decided by both macrostructure and microstructure of the as heated cathode material.
8.4. Practical properties and problems of the as heated integrated oxide cathode

Whilst the basic concept of the design of the integrated oxide cathode discussed in Section 8.1.1 offers many potential benefits, it is the practical properties of the integrated oxide cathode, particularly after heat treatment, which must ultimately decide the feasibility of this new cathode design and the performance during operation. These properties which were reported in Sections 7.3 and 7.4 are discussed in the following sections, together with their implications for the viability of the new cathode design and manufacturing process.

8.4.1. Macrostructure of the as heated integrated oxide cathode

In order to produce a viable cathode, the manufacturing process is required to be able to produce components of consistent size and shape, with the required degree of flatness and with sufficient mechanical strength to allow the component to be mounted into the electron gun assembly as introduced in Section 2.3.

One of the most obvious problems of the macrostructure of the as heated integrated oxide cathode as shown in Section 7.4.1 is the poor mechanical properties. This is evidenced by either missing material (Figures 7.4.1(b) and (d)) in the as produced components and/or by the presence of cracks (Figure 7.4.1 (c)) and even the break down of the whole cathode (Figure 7.4.1(a)). Clearly apart from impacting on the viability of the manufacturing process, such defects may cause failure of the cathode during operation and thus prevent the practical application of the design.

To try and determine whether these problems could be overcome, various experiments aimed at understanding the source of these defects were carried out as described in Sections 7.4.2 to 7.4.4. Generally these showed that the poor mechanical properties of the cathode could result from many aspects, which are discussed in more detail below.
(i). The structural transformation of the converted BaO/SrO oxide material

The cracks shown in the microstructure of the as heated integrated oxide cathode material (Figures 7.4.2 and 7.4.3(c)) are one of the main reasons responsible for the low mechanical strength. It is believed that these cracks are largely caused by the effects of the reactions of the BaSrO2 with H2O and CO2 as introduced in Section 3.1.5 and equation 3.1.5(i) to (iii)\(^{39,71}\) when the cathode was taken out of the furnace.

These various reactions of BaSrO2 and H2O, CO2 were evidenced by the weight increase reported in Section 7.4.4 when the as heated cathode was exposed to air. The weight increase of more than 16wt% observed after exposure of the as heated cathode to air for 60 minutes showed that these reactions were both rapid and extensive. Assuming that the composition in both BaSrO2 is 50wt%/50wt%, it can be calculated that the density of BaSrO2 is 5.55g/cm\(^3\) according to the data in Table 3.1.5,\(^{179}\) which is substantially higher than the density of BaSr(CO\(_3\))\(_2\) (4g/cm\(^3\)).\(^{169}\) The reconversion of the oxide to the carbonate would therefore be expected to result in a large volume change and expansion of the particles inside the cathode. These effects are thought to be responsible for the cracking observed in the cathode materials and subsequently the very poor mechanical strength.

Although such effects would be expected to be avoided in practical production provided the cathode could be assembled into the electron gun before thermal conversion in vacuum as is the case in current CRT manufacture (conditions which could not be practically replicated in these experiments),\(^{32}\) it still could be suspected that the mechanical strength of the integrated oxide cathode would remain low due to the following reasons.

(ii). The effect of thermal removal of polymer binders

The loss of mechanical support after the cathode has been heat-treated can be also attributed to the burnout of polymers which, as discussed in Section 8.1.2, provided mechanical support to the cathode precursor material. Not only does the binding between materials disappear with removal of polymer, this also generates hollow pores inside the material, which impair the mechanical robustness of the as
heated cathodes.

The effect of the removal of polymer can also result in a further lack of integrity especially for the top layer of the cathode as seen in Fig 7.4.2(a) and (c), which can be largely attributed to the segregation of polymers toward the top surface during casting resulting in extensively low density of the cathode material (BaSrO₂) in these surface regions after burnout of the polymers.

(iii). The inhomogeneous distribution of Ni filaments

The formation of an interconnected Ni structure formed by sintering of the Ni filaments was envisaged to be useful as a means to provide good mechanical strength to the heat treated cathode after removal of the binder, however, the poor distribution of Ni filaments as shown by SEM dot mapping investigations (Figures 7.4.4(a) and (b)) indicates that in practise, process was not fully successful in forming this skeleton. The absence of such interconnection in 2wt%Ni cathode is probably caused by the amount of Ni being inadequate to achieve necessary interconnection, leading to the very poor mechanical strength. Much improved results were obtained by increasing the Ni content to 10%, presumably due to much improved interconnectivity between these Ni filaments which was observable in the SEM results (Figure 7.4.3(b)). However, the uneven distribution of Ni must also have resulted in areas with low Ni content and hence poor interconnectivity and low strength. Moreover, these results indicated that a homogeneous distribution of Ni could not be obtained easily by simply mixing these materials. This inhomogeneity could also be a problem as regards the provision of the necessary electrical conductivity during cathode operation.

Apart from the low mechanical strength, the as heated integrated cathode also showed inhomogeneity on the topography as shown by comparison between different cathodes formed by this process as shown in Figures 7.4.1(a) to (d) where it can be seen that some cathodes had rough surfaces whilst others had relatively flat surfaces.
The inhomogeneity is thought to be caused by the random polymer distribution on the surface of the cast materials caused by polymer surface segregation. These differences in surface topography between the cathode components are thought likely to make the cathode surface properties and thus the cathode operational behaviour hard to reproduce and control.

8.4.2. Microstructure of the as heated integrated oxide cathode

Whilst the process route developed for the integrated oxide cathode was successful in allowing a suitable porous microstructure of appropriate composition to be obtained, a number of other problems were identified at the microstructural scale, these problems mainly coming from the Ni phase.

(i). The morphologies of Ni filaments in the cathode material

As described in previous section and in Section 8.1, the aims of the addition of Ni filaments to the cathode material were to enhance both the mechanical strength as previously discussed and also to enhance the emission behaviour of the cathode by increasing the conductivity in the cathode material. In both cases, the optimum effectiveness can be imagined to be obtained by a homogeneous distributed and interconnected Ni structure.

However, the lack of interconnection between the Ni filaments suggests that Ni additions at the 2-10wt% level would be unlikely to lead to the desired results. The likely causes and implications of this failure to achieve the desired interconnected, percolating Ni skeleton within the cathode are discussed below.

(2). The poor distribution of Ni

The poor distribution of Ni filaments in the cathode material would be expected not only to lead to impaired mechanical strength of the cathode, but also to have other detrimental effects on the cathode behaviour. As with the conventional oxide cathode, it is necessary for the operation of the cathode to introduce activators into the
structure in the form of alloying additives in the metallic phase. In the integrated cathode, these activators are envisaged to be mixed with Ni filaments. The inhomogeneous distribution of the Ni filament would therefore be expected to lead to the poor distribution of the activators, which means in some areas there would be little activators, whilst in other areas there would be a much higher content of activators. During operation, this would be expected to lead to activator deficient regions requiring further diffusion in order for the activators to migrate to these areas to react and generate electrons, thus decreasing the cathode performance.

8.5. Summary—Viability of the integrated cathode design

As discussed, the properties of the integrated oxide cathode were found to be limited by various problems, including mechanical and microstructural, which the experimental results suggest are likely to be inherent in the design and the manufacturing process and which would therefore not be easy to eliminate. Whilst the development of the integrated cathode was successful in many aspects, most notably in demonstrating that the required porous structure could be replicated without the need for the wasteful spray deposition process currently used, it was ultimately decided these problems of the integrated oxide cathode prevent it from practical implication in this form.

For this reason it was decided to build on the knowledge gained during the development of the integrated cathode design and manufacturing process and apply this toward the development of another alternative form cathode, the two-layer/impregnated oxide cathode. The development of this cathode design thus formed the basis for the second half of the investigation and is reported and discussed in the following parts of the thesis (Part 5).
Part Five

The Two-Layer/Impregnated Oxide Cathode

Results and Discussions
Chapter 9

Results II-- The Two-Layer/Impregnated Oxide Cathode

Due to the practical limitations discussed in Section 8.4 for the integrated oxide cathode, it was decided that this approach was not practically viable. For this reason, an alternative design of cathode, the two-layer/impregnated oxide cathode, was designed and investigated. This section of the thesis is concerned with development of this alternative cathode design with its manufacturing process introduced previously in Sections 6.2.2 and 6.3.2.

The basic design of the two-layer/impregnated cathode illustrated in Figure 1.2(b) comprises a porous Ni substrate with BaSr(CO₃)₂ applied both as a coating on this substrate and embedded/impregnated into the pore structure with this subsequently resulting in the formation of BaSrO₂ in and on the porous Ni matrix after appropriate heat treatment. In this chapter, the resultant products obtained after each of the various stages of the manufacturing process outlined in Section 6.2.2 and 6.3.2 are reported in the following sections.

I. Porous Ni substrate (Section 9.1)
   i. As cast Ni/polymer composite film (Section 9.1.1)
   ii. As stamped Ni substrate component before heat treatment (Section 9.1.2)
   iii. Ni substrate component after heat treatment (Section 9.1.3)

II. Complete two-layer/impregnated oxide cathode emitter component (Section 9.2)
   i. Cathode emitter component before heat treatment (Section 9.2.1)
   ii. Cathode emitter component after heat treatment (Section 9.2.2)
9.1. Porous Nickel(Ni) Substrate

As described in Sections 6.2.2 and 6.3.2.1, the porous Ni substrate of the two-layer/impregnated cathode is prepared by casting, stamping and heat treatment, similarly to the process used for the integrated oxide cathode.

9.1.1. As cast Ni/polymer composite film

Figures 9.1.1(a) ~ (d) show the effects of different compositions of Ni/polymer in the cast suspensions on the macrostructures of the as cast Ni/polymer films. The compositions of each individual material, including ratios of Ni to polymers, the composition of polymers and the solid content, have been previously described in Table 6.2.2.1.1.

As shown in all the images, the cast films obtained were generally flat and crack-free for all ratios of Ni/polymers investigated indicating that the mechanical strength is acceptable.

Fig 9.1.1(a). As cast Ni/polymer film with 10wt%Ni/90wt%polymer.
Fig 9.1.1(b). As cast Ni/polymer film with 15wt% Ni/85wt% polymer.

Fig 9.1.1(c). As cast Ni/polymer film with 20wt% Ni/80wt% polymer.
The films did exhibit some inhomogeneity with some areas of the films exhibiting a reasonably consistent transparent polymer rich surface, whilst a small proportion of the cast material exhibited some lighter coloured (grey) regions of opaque polymer segregation. The amount of these opaque polymer rich regions decreased with increasing Ni content in the formulation. The surface roughness of the film increased as the Ni content decreased, as shown in Figures 9.1.1(a) to (d).

The thickness of these cast films were also measured with the results listed in Table 9.1.1. For equivalent mass additions of solid in the casting suspensions, the samples with the lowest Ni contents exhibited the lowest thickness, with a gradual increase in thickness as the Ni content was increased.

<table>
<thead>
<tr>
<th>Ni composition in the film</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>10wt%Ni (0.2g Ni/1.8g polymer)</td>
<td>0.60 ~ 0.62 mm</td>
</tr>
<tr>
<td>15wt%Ni (0.3g Ni/1.7g polymer)</td>
<td>0.68 ~ 0.72 mm</td>
</tr>
<tr>
<td>20wt%Ni (0.4g Ni/1.6g polymer)</td>
<td>0.70 ~ 0.72 mm</td>
</tr>
<tr>
<td>25wt%Ni (0.5g Ni/1.5g polymer)</td>
<td>0.70 ~ 0.74 mm</td>
</tr>
</tbody>
</table>
9.1.2. As stamped Ni substrate component before heat treatment

9.1.2.1. Macrostructure of the Ni substrate component before heat treatment

An indicative example of an as stamped Ni substrate component before heat treatment is shown in Figure 9.1.2.1 below. The Ni substrates containing all four Ni/polymer compositions exhibit very similar macrostructures.

The stamped substrate component exhibits generally smooth and well defined edges. The size of the component was defined by the stamping tool, being 2.9mm in diameter. Significant porosity is apparent on the surface of the component although the pore sizes cannot easily be measured at this magnification. However, some inhomogeneity can be observed. Generally, the central area exhibits greater porosity, whilst the regions around the circumference of the component show less visible porosity, suggesting a high density in these regions adjacent to the area impacted by the cutting tool.

![SEM showing an as stamped Ni substrate with 15wt%Ni/85wt%polymer before heat treatment.](image)
9.1.2.2. Microstructure of the Ni substrate component before heat treatment

SEM pictures of the Ni/polymer substrate precursor with three compositions of Ni filament (as shown in Figures 9.1.1(b) to (d)) are shown in Figures 9.1.2.2(a) to (c) to investigate their effects on the microstructures before heat treatment and Figure 9.1.2.2(d) is a SEM image with high magnification showing the morphology of the Ni filaments. The 10wt%Ni containing material (Figure 9.1.1(a)) was not chosen for further investigation because of its poor mechanical strength and macrostructure. All the SEM images in this and the following sections were taken in the central area of the samples. The microstructure investigations were supported by porosity analysis (as introduced in Section 6.4.2), with these results being shown in Table 9.1.2.2 and Figures 9.1.2.2(e)–(g).

Fig 9.1.2.2(a). SEM showing microstructure of the as cast Ni/polymer film with 15wt%Ni/85wt%polymer.
Fig 9.1.2.2(b). SEM showing microstructure of the as cast Ni/polymer film with 20wt% Ni/80wt% polymer.

Fig 9.1.2.2(c). SEM showing microstructure of the as cast Ni/polymer film with 25wt% Ni/75wt% polymer.
Fig 9.1.2.2(d). SEM showing microstructure of as cast Ni/polymer composite film with 15wt% Ni/85wt% polymer (higher magnification).

The SEM images in Figures 9.1.2.2(a) to (d) allow the polymer and Ni filament components of the films to be clearly distinguished. As in the BaSr(CO₃)₂/Ni/polymer composites (Figures 7.2.2(a) and (c)), polymer is distributed between the solid particles, in this case the Ni filament phase, providing a continuous matrix connecting the Ni. No discernible structure can be resolved within the polymer phase at the magnification used in these images. A reduction in the proportion of polymer phase present can be observed as the proportion of Ni in the casting formulation is increased.

As shown in Figure 9.1.2.2(d), the Ni filaments before heat treatment are very thin with diameters in the range of 0.3-0.5μm and a wide range of length varying from about 3μm to > 10μm. Some of the Ni filaments remain separate whilst others appear to be agglomerated together. The surface of these Ni filaments is not smooth, with each Ni filament being composed of “strings” of smaller, roughly spherically shaped particles with the sizes of these individual particles being around 0.3~ 0.5μm
in diameter.

The porosities of the three Ni/polymer materials shown in Figures 9.1.2.2(a) to (c) obtained from the image analysis are listed in Table 9.1.2.2. As revealed, the porosity of these materials decreased with increasing Ni content from 69% for the 15wt% Ni formulation material to 40% porosity when the Ni content was increased to 25wt%.

Table 9.1.2.2. Porosities of the as cast materials containing various Ni/polymer compositions

<table>
<thead>
<tr>
<th>Material composition</th>
<th>15wt%Ni</th>
<th>20wt%Ni</th>
<th>25wt%Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosities</td>
<td>69%</td>
<td>61%</td>
<td>40%</td>
</tr>
</tbody>
</table>

Figures 9.1.2.2(e) and (g) are the pore area distribution analyses of the as cast Ni substrate materials reported in Figures 9.1.2.2(a) to (c) with various Ni/polymer compositions. It can be observed that in all three compositions, most of the pore areas are comprised by large pores, with area in the range of 1000-10000μm². It can also be seen that the percentages of these large pores decrease with increasing amount of Ni in the composition.

Fig 9.1.2.2(e). Pore area distribution in 15wt%Ni containing as cast Ni/polymer film.
9.1.2.3. Summary

From the investigations above, it can be concluded that the Ni/polymer composite films containing 15wt% and 20wt% Ni provide both mechanical integrity and reasonably satisfactory porosity (69% and 61% respectively) which are expected to result in a porous Ni substrate after the heat treatment. These two materials were therefore chosen as the basis for the following investigations.
9.1.3. Nickel(Ni) substrate component after heat treatment

The purpose and the process of the heat treatment of the Ni substrate material have been generally introduced in Sections 6.3.2.1. As with the integrated cathode, this heat treatment was carried out in two stages, with the optimum conditions used during these two heating stages being determined from the various investigations reported in the following sections.

The thermal analysis results of the Ni/polymer material are reported in Section 9.1.3.1 and the properties of the resultant porous Ni substrate are reported in Section 9.1.3.2 and 9.1.3.3. A summary is then given in Section 9.1.4.

9.1.3.1. Thermal analysis of the as cast Ni/polymer composite

The thermal analysis results presented in this section comprise two parts. The first refers to thermal analysis during continuous heating at 5°C/min from room temperature to 700°C, whilst the second refers to the effect of heating for different periods at a fixed temperature.

9.1.3.1.1. Under increasing temperature

One of the purposes for the initial stage heating of the Ni substrate material is to decompose polymers completely as mentioned in Section 6.3.2.1. Based on the heat treatment developed for the integrated oxide cathode discussed in Section 8.3.1.4 and 8.3.2, it is expected that the polymer additives used in Ni/polymer film can be decomposed completely in air by 500°C. So in this thermal analysis, 500°C was initially decided as the highest temperature for the first stage heating in air, followed by a second stage heating at higher temperature under a N₂/5%H₂ atmosphere to both avoid the further oxidation of the Ni filaments and reduce NiO generated during the first stage as discussed in Section 8.3.1.2.
The thermal analysis results obtained from the Ni/polymer material containing 15wt%Ni/85wt%polymers are shown in Figures 9.1.3.1.1(a) and (b). The processes occurring can be divided into three main stages (stages I ~ III), with a number of sub-stages.

The first stage (I) from room temperature to about 490°C comprised several sub-steps of weight loss (i ~ iii) in TGA and both endothermic peaks (A, B, D) and exothermic peaks (C, E~H) in DTA at various temperatures. The total weight loss at the end of this stage was 84wt%.

The second stage (II) was between 490°C and 550°C comprising a small weight increase in TGA and an endothermic peak (I) at about 510°C in DTA. The weight increase obtained during this temperature range was 1.2wt%.

After the weight increase, there was no reaction in both DTA and TGA during the final stage (III) from 550°C to 700°C.

![TGA analysis of Ni/polymer composite during heating from room temperature to 500°C in air and from 500°C to 700°C in N₂/5%H₂.](image)

Fig 9.1.3.1.1(a), TGA analysis of Ni/polymer composite during heating from room temperature to 500°C in air and from 500°C to 700°C in N₂/5%H₂.
Fig 9.1.3.1.1(b), DTA analysis of Ni/polymer composite during heating from room temperature to 500°C in air and from 500°C to 700°C in N2/5% H2.

Summaries of the thermal events happened during heating in TGA and DTA are listed in Tables 9.1.3.1.1(a) and (b).

Table 9.1.3.1.1(a). Weight changes identified in TGA during heating of Ni/polymer composite material

<table>
<thead>
<tr>
<th>Stages</th>
<th>Sub-steps</th>
<th>Weight changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>i</td>
<td>Small weight loss of 2wt% between room temperature ~ 80°C</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>No weight change between 80°C ~ 125°C</td>
</tr>
<tr>
<td></td>
<td>iii</td>
<td>Large weight loss of about 82wt% between 125°C ~ 490°C</td>
</tr>
<tr>
<td>II</td>
<td>n/a</td>
<td>Small weight increase of 1.2wt% between 490°C ~ 550°C</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No weight change between 550°C ~ 700°C</td>
</tr>
</tbody>
</table>
Table 9.1.3.1.1(b). The thermal events identified by DTA during the thermal analysis of Ni/polymer composite material

<table>
<thead>
<tr>
<th>Stages</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A, B</td>
<td>Two endothermic peaks at 60°C(A) and 120°C(B)</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>One exothermic peak at 160°C</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>One endothermic peak at 215°C</td>
</tr>
<tr>
<td></td>
<td>E – H</td>
<td>Four exothermic peaks at 280°C (E), 320°C (F), 390°C (G), and 430°C (H) respectively</td>
</tr>
<tr>
<td>II</td>
<td>I</td>
<td>One endothermic peak at 510°C</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No thermal event happened between 550°C - 700°C</td>
</tr>
</tbody>
</table>

9.1.3.1.2. Under isothermal conditions

The thermal analysis of Ni substrate at the fixed temperature after the continuous increasing temperature is also investigated mainly to identify the timescale for the onset and completion of the NiO reduction process. A temperature of 700°C was used in these experiments, which was also used during the heat treatment of the Ni substrate during cathode manufactur. Figures 9.1.3.1.2 (a) and (b) are the DTA and TGA results showing the thermal events and mass changes recorded whilst the material was heated at a constant 700°C for 30 minutes with time, instead of temperature, being used as the X-axis in this case.

Both TGA and DTA can be divided into three main stages (I to III) with the first (I) and the final stages(III) both comprised stable weight as shown in TGA and no thermal events identified by DTA. A weight loss (stage II) appeared in TGA after the sample was heated at 700°C for about 12.5 minutes and was finished after a further 15 minutes. The total weight loss is about 2.4wt%. Correspondingly, an exothermic peak (A) appeared in DTA for the similar time at this temperature.
Fig 9.1.3.1.2(a), TGA analysis of the Ni substrate during heating at 700°C in N₂/5%H₂ for 30 minutes.

Fig 9.1.3.1.2(b), DTA analysis of the Ni substrate during heating at 700°C in N₂/5%H₂ for 30 minutes.
Summaries of the thermal events happened during heating in TGA and DTA are listed in Tables 9.1.3.1.2(a) and (b).

Table 9.1.3.1.2(a). Weight changes identified in TGA during the isothermal heating of Ni substrate material

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sub-steps</th>
<th>Weight changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n/a</td>
<td>No weight change</td>
</tr>
<tr>
<td>II</td>
<td>n/a</td>
<td>A weight decrease of 2.4wt% after being heated at 700°C for approximately 12.5 minutes</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>Weight loss stopped and no weight change after that</td>
</tr>
</tbody>
</table>

Table 9.1.3.1.2(b). Thermal events identified in DTA during isothermal heating of Ni substrate material

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sub-steps</th>
<th>Weight changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n/a</td>
<td>No thermal events</td>
</tr>
<tr>
<td>II</td>
<td>A</td>
<td>An exothermic peak started to occur after heated at 700°C for approximately 12.5 minutes</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>No thermal events after that</td>
</tr>
</tbody>
</table>
9.1.3.1.3. Summary

According to the thermal analysis results of the Ni/polymer substrate material shown in Sections 9.1.3.1.1 and 9.1.3.1.2, the conditions of the two-stage heat treatment are initially decided as shown schematically in Figure 9.1.3.1.3. As mentioned in Section 6.3.2.1, four temperatures, 600°C to 900°C, are selected initially as the highest temperature for the second-stage (stage H) to investigate their effects on the properties of the Ni substrate.

Fig 9.1.3.1.3. Two stage heat treatment process and the conditions for the Ni substrate.
9.1.3.2. Macrostructure of the as heated Ni substrate

The results reported in this and the following sections all refer to the structure and properties of the resultant Ni substrate after the two-stage heat treatment process as summarised in Section 9.1.3.1.3.

The experiment results showed that an intact Ni substrate with enough mechanical strength could only be obtained when the heating temperature was at least 700°C. However, determination of the optimum temperature required more detailed investigations into the effects of sintering at 700°C, 800°C and 900°C as reported in the following sections.

Figure 9.1.3.2 is an SEM photomicrograph showing a typical Ni substrate component obtained after heat treatment at 700°C. A key difference to the integrated oxide cathode is that these cast and heat treated Ni substrate components have enough mechanical strength to remain intact and also retain a well defined edge. Porosity can be observed from the picture and although the pores are too small to be quantitatively measured at this magnification, it is apparent from comparison with Figure 9.1.2.1 that there is some reduction in both pore size and porosity after heat treatment. The diameter of the Ni pellet is 1.5±1mm after this heat treatment, which represents a shrinkage of 48% compared to the Ni precursor before heat treatment (2.9mm as shown in Fig 9.1.2.1).
9.1.3.3. Microstructures of the as heated Ni substrate

In this section, the results of investigations into the effects of material composition and sintering temperature on the microstructures of the Ni substrate after heat treatment are reported. These experiments aimed to determine a suitable material composition and sintering conditions.

9.1.3.3.1. Effect of Ni/polymer composition in the suspension

As summarised in Section 9.1.2.3 the Ni substrate materials with 15wt%Ni and 20wt%Ni were both chosen as the most promising for further study into the effect of heat treatment due to their higher and larger initial porosity. SEM images showing the typical microstructure of these two Ni substrate materials after heat treatment at 700°C for 30 minutes under N₂/5%H₂ are shown in Figures 9.1.3.3.1(a) and (b).
Fig 9.1.3.3.1(a). SEM image showing microstructure of a 15wt%Ni substrate after heat treatment of 700°C in N₂/5%H₂ for 30 minutes.

Fig 9.1.3.3.1(b). SEM image showing microstructure of a 20wt%Ni substrate after heat treatment of 700°C in N₂/5%H₂ for 30 minutes.
Generally, compared with the material before heat treatment (Section 9.1.2.2), there is little evidence of significant coarsening of the Ni filaments, with their diameter being about 0.6–0.8μm in both as heated materials (the diameter of the Ni filaments before heat treatment is 0.3–0.5μm). The 15wt%Ni formula material showed a much more homogeneous microstructure than the 20wt%Ni containing composition. Fewer agglomerates were apparent in the 15wt%Ni formulation material with the sizes of those present being around 3–5μm. By comparison a much greater number of and larger sized (>10μm) agglomerates occurred in the 20wt%Ni containing material.

Table 9.1.3.3.1 is the summary of the porosities of the two as heated Ni substrates and their comparison to those before heat treatment and Figures 9.1.3.3.1(c) and (d) are the pore area distribution results from the image analysis (Section 6.4.2). These analysis results are indicative of some densification in the materials after heat treatment compared to the un-heated materials leading to a reduction in both porosity and pore size/area compared to the unheated samples (Section 9.1.2.2) although a porous Ni network was still obtained in each case as shown in the SEM images.

The porosities of these two materials decreased from 69% and 61% before heating (Section 9.1.2.2) to 59% and 45% respectively after heating.

Table 9.1.3.3.1. Porosities of the unheated and heated Ni substrate material with 15wt% and 20wt%Ni.

<table>
<thead>
<tr>
<th>Porosities</th>
<th>15wt%Ni</th>
<th>20wt%Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before heating</td>
<td>69%</td>
<td>61%</td>
</tr>
<tr>
<td>After heating</td>
<td>59%</td>
<td>45%</td>
</tr>
</tbody>
</table>

The pore area analyses in Figure 9.1.3.3.1(c) and (d) revealed that the pore size distribution and largest pore size also decreased in the heat treated Ni substrate material, with the largest pore decreasing from an area of 1000–1000μm² in un-heated material to 500–1000μm² in the after-heated material. The pores in the 15wt%Ni substrate have a more homogeneously distributed pore size with similar proportions.
of pores in each size category, whereas the substrate material containing 20wt% Ni (Figure 9.1.3.3.1(d)) showed a very inhomogeneous distribution, with most of the pore areas occupied by either large pores (500–1000μm²) or small pores (1–10μm²). These results are consistent with observation of the SEM images in Figures 9.1.3.3.1(a) and (b).

![Graph showing pore area distribution](image)

**Fig 9.1.3.3.1(c).** Pore area distribution in the 15wt%Ni substrate material after heat treatment at 700°C in N₂/5%H₂ for 30 minutes.

![Graph showing pore area distribution](image)

**Fig 9.1.3.3.1(d).** Pore area distribution in the 20wt%Ni substrate material after heat treatment at 700°C in N₂/5%H₂ for 30 minutes.

Based on these results it can be concluded that the Ni substrate with 15wt% Ni with a more homogenous distributed microstructure and higher porosity was the optimum composition, and this was therefore chosen as the base material for subsequent investigations.
9.1.3.3.2. Effect of sintering temperature

This series of investigations studied the effects of various sintering temperatures (700°C, 800°C, 900°C) on the microstructures of the selected Ni substrate material (15wt%Ni). The resulting SEM images are shown in Figures 9.1.3.3.2 (a) to (c). The results of the image analysis (Image-Pro Plus) carried out on these SEM images are shown in Table 9.1.3.3.2 and Figures 9.1.3.3.2(d)-(f).

The results confirmed that for all sintering temperatures in this range, porous Ni networks could be produced and the Ni phase would still retain the filamentary morphology. A slight increase in the sizes of the Ni filaments from 0.6–0.8μm to 0.8–1μm was determined when the sintering temperature increased from 700°C to 800°C. However after heat treatment at 900°C, the Ni filaments became very coarse with a diameter of 2μm. Agglomerates of various sizes were apparent in samples heated at all temperatures.

Fig 9.1.3.3.2(a). SEM image showing microstructure of 15wt% Ni substrate after heat treatment of 700°C under N₂/5%H₂ atmosphere for 30 minutes.
Fig 9.1.3.3.2(b). SEM image showing microstructure of 15wt%Ni substrate after heat treatment of 800°C under N₂/5%H₂ atmosphere for 30 minutes.

Fig 9.1.3.3.2(c). SEM image showing microstructure of 15wt%Ni substrate after heat treatment of 900°C in N₂/5%H₂ atmosphere for 30 minutes.
The image analysis results confirmed this, showing a gradual reduction in porosity and pore area after heat treatment at 700°C and 800°C, but with a significant change in the material after 900°C heat treatment as shown in Table 9.1.3.3.2 and Figures 9.1.3.3.2(d) to (f). As revealed in the pore area distribution graphs, the 700°C heated material exhibited the widest pore size distribution with pore areas from 1~10μm² to 500~1000μm², while the maximum pore area material decreased to 100~250μm² after heating to 800°C. In the material heat treated to 900°C, only pores with area 1~25μm² remain after heating.

Table 9.1.3.3.2. Porosities of the 15wt%Ni substrate after heat treatment of various temperatures.

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>15wt%Ni substrate</td>
<td>59%</td>
<td>49%</td>
<td>31%</td>
</tr>
</tbody>
</table>

Fig 9.1.3.3.2(d). Pore area distribution in the 15wt%Ni substrate material after heat treatment at 700°C under N₂/5%H₂ for 30 minutes.
Fig 9.1.3.3.2(e). Pore area distribution in the 15wt%Ni substrate material after heat treatment at 800°C under N₂/5%H₂ for 30 minutes.

Fig 9.1.3.3.2(f). Pore area distribution in the 15wt%Ni substrate material after heat treatment at 900°C under N₂/5%H₂ for 30 minutes.
9.1.4. Summary

The selected processing parameters chosen for the next stages in the investigation together with the resultant properties of the material after each stage of heat treatment are summarised in Table 9.1.4.

Table 9.1.4. Summary of the processing parameter and properties of the porous Ni substrate

<table>
<thead>
<tr>
<th>Materials composition</th>
<th>15 wt% Ni / 85wt% polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treatment</td>
<td></td>
</tr>
<tr>
<td>conditions</td>
<td></td>
</tr>
<tr>
<td>Initial stage</td>
<td>Room temperature ~ 500°C (air)</td>
</tr>
<tr>
<td>Second stage</td>
<td>500°C ~ 700°C</td>
</tr>
<tr>
<td></td>
<td>holding at 700°C for 30 minutes and cool down (N₂/5%H₂)</td>
</tr>
<tr>
<td>Properties of the</td>
<td></td>
</tr>
<tr>
<td>resultant heated</td>
<td></td>
</tr>
<tr>
<td>Macrostructure</td>
<td>Diameter: 1.5±1mm;</td>
</tr>
<tr>
<td></td>
<td>Thickness: 400 μm</td>
</tr>
<tr>
<td>Microstructure</td>
<td>Porosity: 59%</td>
</tr>
</tbody>
</table>
9.2. **Two-layer/impregnated oxide cathode**

The next stage in the manufacturing process of the two-layer/impregnated cathode after a porous Ni substrate is the impregnation process as described in Sections 6.2.2.2 and 6.2.2.3. Appropriate heat treatment, as described in Section 6.3.2.2, is then applied to the cathode to generate the oxide cathode with required properties. In this section, the resultant products of the two-layer/impregnated oxide cathode after the impregnation process (before heat treatment) and the final heat treatment are reported and described in Section 9.2.1 and 9.2.2 respectively.

9.2.1. **Two-layer/impregnated oxide cathode before heat treatment**

9.2.1.1. **Effect of the BaSr(CO₃)₂ suspension preparation conditions on the BaSr(CO₃)₂ particles and agglomerates**

9.2.1.1.1. **Effect of the addition of dispersant on the BaSr(CO₃)₂ agglomerates**

As introduced in Section 6.2.2.2, BaSr(CO₃)₂ suspensions containing water and water/dispersant (Darvan821A) (suspensions (a) and (b)) were prepared to investigate the effect of the dispersant on the morphology and size of the BaSr(CO₃)₂ particles when subjected to a simple mixing process. SEM images showing the BaSr(CO₃)₂ particles obtained from these two suspensions are shown in Figures 9.2.1.1.1(a) and (b). The preparation of these samples for SEM investigation was described in Section 6.4.1.2.
Fig 9.2.1.1.1(a), SEM image showing the \( \text{BaSr}(\text{CO}_3)_2 \) agglomerates obtained from water suspension.

Fig 9.2.1.1.1(b), SEM image showing the \( \text{BaSr}(\text{CO}_3)_2 \) particles and agglomerates obtained from water/dispersant suspension.
When water was used as the liquid to disperse BaSr(CO$_3$)$_2$ (Figure 9.2.1.1.1(a)), the BaSr(CO$_3$)$_2$ comprised rod like forms with typical dimensions approximately 0.25$\mu$m diameters and 2-5$\mu$m length. These particles were agglomerated to form larger particles comprising several of the primary particles with the agglomerates sizes being of the order of 10-15$\mu$m.

When Darvan821 was added to the suspension as dispersant (Figure 9.2.1.1.1(b)), fewer agglomerates were formed and their sizes were much smaller compared with the material obtained without dispersant, with the agglomerate size in this case being typically 2-6$\mu$m. Some small unagglomerated rod-like BaSr(CO$_3$)$_2$ particles of about 1-2$\mu$m in diameter can also be observed.

9.2.1.1.2. Effect of the ultrasonic treatment on the BaSr(CO$_3$)$_2$ particles and agglomerates

As introduced in Section 6.2.2.2, ultrasonic treatment was carried out on some BaSr(CO$_3$)$_2$ casting suspensions to investigate the effect on the BaSr(CO$_3$)$_2$ particles and agglomerates (suspensions (c) and (d)). SEM images showing the BaSr(CO$_3$)$_2$ particles obtained from these two suspensions after ultrasonic treatment are shown in Figures 9.2.1.1.2(a) and (b). The preparation of these samples for SEM investigation was as described in Section 6.4.1.2.

Figure 9.2.1.1.2(a) shows an SEM image of the BaSr(CO$_3$)$_2$ particles obtained from aqueous suspension after ultrasonic treatment from which it showed that the BaSr(CO$_3$)$_2$ agglomerates obtained from water suspension were essentially unchanged after ultrasonic treatment (compared to Figure 9.2.1.1.1(a)).

Figure 9.2.1.1.2(b) shows the effect of the same ultrasonic treatment on BaSr(CO$_3$)$_2$ agglomerates obtained from the water/dispersant suspension in which significant changes occurred to the BaSr(CO$_3$)$_2$ agglomerates. No large agglomerates remain in these suspensions although some small agglomerates with size around 3$\mu$m remain. In some cases the agglomerates were broken down completely to discrete rod-like or cub-like BaSr(CO$_3$)$_2$ particles with sizes around 1 - 2$\mu$m.
Fig 9.2.1.2(a), SEM image showing the BaSr(CO$_3$)$_2$ agglomerates in water suspension after ultrasonic treatment for 15 minutes.

Fig 9.2.1.2(b), SEM image showing the BaSr(CO$_3$)$_2$ particles and agglomerates obtained with water/dispersant suspension after ultrasonic bath for 15 minutes.
9.2.1.1.3. Summary

From the investigations above, it can be concluded that the BaSr(CO$_3$)$_2$ containing suspensions without dispersant (Figures 9.2.1.1.1(a) and 9.2.1.1.2(a)) could not be efficiently de-agglomerated by mechanical stirring or ultrasonic treatment and remain as very large agglomerates, which is thought not to be suitable for the impregnated structure designed for the new cathode. This approach was thus not adopted for subsequent investigation.

The suspension with addition of dispersant but no ultrasonic treatment (Figure 9.2.1.1.1(b)) showed better dispersion of the BaSr(CO$_3$)$_2$ particles with smaller agglomerates and some single particles. The morphologies and sizes of the particles in this suspension are similar as those of the conventional as sprayed cathode material as shown in Figure 7.2.2(e). Significantly improved dispersion and break up of agglomerates was achieved when ultrasonic treatment was applied to the suspensions containing dispersant (Figure 9.2.1.1.2(b)) leading to very small agglomerates and discrete particles. These two suspensions were thought to be more promising for the required impregnated structure of the cathode to be produced.

However, at this stage, it was not clear whether mechanical or ultrasonic deagglomeration of the dispersant containing suspensions (suspension (b) and (d) in Section 6.2.2.2) was most suitable for the development of the desired structure and microstructure of the two-layer/impregnated oxide cathode, so both were investigated as potential routes for the subsequent production of the two-layer/impregnated cathode precursor.
9.2.1.2. Macrostructure of the two-layer/impregnated oxide cathode precursor before heat treatment

Based on the results reported in the previous section, all the subsequent results were obtained from the dispersant(Darvan821A) containing BaSr(CO₃)₂ suspension. The resultant cathode components are illustrated in Figure 9.2.1.2(a) and (b). Figure 9.2.1.2(a) shows the cathode component obtained from the BaSr(CO₃)₂/Darvan821A suspension without ultrasonic treatment, whilst Figure 9.2.1.2(b) shows the cathode precursor obtained from the BaSr(CO₃)₂/Darvan821A suspension with ultrasonic treatment.

![SEM image showing a two-layer/impregnated oxide cathode with the coating material obtained from the BaSr(CO₃)₂/Darvan821A suspension without ultrasonic treatment.](image)

Fig 9.2.1.2(a). SEM image showing a two-layer/impregnated oxide cathode with the coating material obtained from the BaSr(CO₃)₂/Darvan821A suspension without ultrasonic treatment.
Fig 9.2.1.2(b). SEM image showing a two-layer/impregnated oxide cathode with the coating material obtained from the BaSr(CO$_3$)$_2$/Darvan821A suspension with ultrasonic treatment.

As shown from the images, both the resultant cathode components comprised a relatively homogeneous layer coating surface of primarily BaSr(CO$_3$)$_2$ with some small pores although the sizes of these cannot be estimated at this scale of magnification. Although the images shown here indicate some difference in the surface flatness, this was not a general phenomenon associated with the suspension treatment.
9.2.1.3. **EDX dot mapping of cross-section of the cathode before heat treatment**

The cross-sections of the two cathode components as shown in Figures 9.2.1.2(a) and (b) were examined by EDX compositional (dot) mapping to determine the elemental distribution across their thickness before heat treatment. The preparation of these samples was described in Section 6.4.1.3.

9.2.1.3.1. **Cross-section of the cathode precursor obtained from BaSr\((CO_3)\_2/Darvan821A suspension without ultrasonic treatment**

The SEM image showing the cross-section of the two-layer/impregnated cathode obtained from the BaSr\((CO_3)\_2/Darvan821A suspension without ultrasonic treatment is illustrated in Figure 9.2.1.3.1(a) with the distribution maps of Ni, Ba and Sr in the cathode precursor are shown in Figures 9.2.1.3.1(b), (c) and (d) respectively.

![SEM image of cross-section of two-layer/impregnated cathode precursor produced from BaSr\((CO_3)\_2/Darvan821A suspension without ultrasonic treatment.](image-url)
Fig 9.2.1.3.1(b). SEM dot mapping showing the distribution of Ni along the cross-section of the cathode precursor produced from BaSr(CO$_3$)$_2$/Darvan821A suspension without ultrasonic treatment.

Fig 9.2.1.3.1(c). SEM dot mapping showing the distribution of Ba along the cross-section of the cathode precursor produced from BaSr(CO$_3$)$_2$/Darvan821A suspension without ultrasonic treatment.

Fig 9.2.1.3.1(d). SEM dot mapping showing the distribution of Sr along the cross-section of the cathode precursor produced from BaSr(CO$_3$)$_2$/Darvan821A suspension without ultrasonic treatment.
The cathode component produced, shown in Figure 9.2.1.3.1(a), was generally flat and exhibited a relatively homogeneous porous structure. The cathode component also showed enough strength to remain intact after the sample preparation steps. The thickness of the whole cathode component was determined to be approximately 400µm. The uncoated bottom side of the cathode was relatively rough whilst the top surface of the cathode component was coated by an approximately 50µm thick, relatively smooth (under this magnification) layer of the BaSr(CO₃)₂ material. The thickness of the Ni structure can be more easily estimated from the EDX map in Figure 9.2.1.3.1(b) which can be determined as 350µm.

The dot map images of the Ba and Sr components are shown in Figures 9.2.1.3.1(c) and (d). It is apparent from these images that the Ba and Sr are located at the top surface of the cathode as a surface coating with both the thickness of approximately 55µm. No obvious evidence can be found for the penetration of Ba and Sr to the porous Ni substrate from these results.

9.2.1.3.2. Cross-section of the cathode precursor obtained from BaSr(CO₃)₂/Darvan821A suspension with ultrasonic treatment

The SEM images showing the cross-section of the two-layer/impregnated cathode component obtained from the BaSr(CO₃)₂/Darvan821A suspension with ultrasonic treatment is illustrated in Figure 9.2.1.3.2(a) with the EDX maps of the distribution of Ni, Ba and Sr across the cross section shown in Figures 9.2.1.3.2(b), (c) and (d) respectively.

As with the previously described materials, the cathode shown in Figure 9.2.1.3.2(a) exhibited homogeneous microstructure and porosity and remained flat, intact and crack free. The total thickness of the cathode in this case was determined as 410µm from this image, including the coating which can be observed as a brighter layer on the surface of the cathode. The thickness of Ni substrate was estimated to be 350µm from the EDX map for nickel in Figure 9.2.1.3.2(b) from which it can be determined that the thickness of the surface coating is 60µm (410µm - 350µm).
The distribution of Ba and Sr in the component produced from the suspension with ultrasonic treatment is obviously changed compared to that obtained without ultrasonic treatment. The thickness of Ba and Sr rich regions determined from Figures 9.2.1.3.2(c) and (d) were about 180μm, this being both much higher than the thickness of Ba and Sr layer in Figures 9.2.1.3.1(c) and (d) for the samples produced without ultrasonic treatments and also being significantly greater than the 60μm thickness determined for the top coating, thus confirming the partial penetration of Ba and Sr into the upper structure of the porous Ni substrate in the component produced by this route.

Fig 9.2.1.3.2(a). SEM image of cross-section of two-layer/impregnated cathode precursor produced from BaSr(CO₃)₂/Darvan821A suspension with ultrasonic treatment.
Fig 9.2.1.3.2(b). SEM dot mapping showing the distribution of Ni along the cross-section of two-layer/impregnated cathode precursor produced from BaSr(CO$_3$)$_2$/Darvan821A suspension with ultrasonic treatment.

Fig 9.2.1.3.2(c). SEM dot mapping showing the distribution of Ba along the cross-section of two-layer/impregnated cathode precursor produced from BaSr(CO$_3$)$_2$/Darvan821A suspension with ultrasonic treatment.

Fig 9.2.1.3.2(d). SEM dot mapping showing the distribution of Sr along the cross-section of two-layer/impregnated cathode precursor produced from BaSr(CO$_3$)$_2$/Darvan821A suspension with ultrasonic treatment.
9.2.1.3.3. Summary

In view of the improved "impregnation" of the cathode achieved following ultrasonic treatment of the carbonate suspension, this process containing use of both dispersant(Darvan821A) and ultrasonic treatment was chosen as the basis for subsequent investigations.

9.2.1.4. Microstructure of the as impregnated two layer cathode surface before heat treatment

Figures 9.2.1.4(a), (b) and (c) are SEM images showing the microstructure of the top surface of the two-layer/impregnated cathode precursor after the impregnation process obtained from BaSr(CO3)2-water/dispersant suspension after ultrasonic treatment. Figures 9.2.1.4(a) and (b) show images from the same area of the surface but with different magnifications, whilst Figure 9.2.1.4(c) shows another area of the surface. The results obtained from the porosity analysis of this surface are shown in graphical form in Figure 9.2.1.4(d).

As shown in Figures 9.2.1.4(a), most of the coating material comprised discrete BaSr(CO3)2 particles and small agglomerates as described in Section 9.2.1.1.2 (Figure 9.2.1.1.2(b)). The coating comprised a largely homogeneous distribution of these particles and pores. However, some regions of inhomogeneity were present as shown in Figure 9.2.1.4(c), typically comprising very large pores and consequently increased surface roughness. Also, in comparison with the similarly produced material in Figure 9.2.1.1.2(b), the particles were apparently less columnar in morphology.

The image analysis showed a porosity of 50% in the coating material as shown and the pore area distribution as plotted in Figure 9.2.1.4(d). The majority of the pores in the coating material as shown in Figures 9.2.1.4(a) to(c) comprised a mixture of relatively small pores (1–25μm) plus some larger pores (500–10000μm), with relatively few pores of intermediate size.
Fig 9.2.1.4(a). SEM image showing the microstructure of the coating material of the two-layer/impregnated oxide cathode precursor.

Fig 9.2.1.4(b). SEM image showing the microstructure of the coating material of the two-layer/impregnated oxide cathode precursor (with higher magnification).
Fig 9.2.1.4(c). SEM image showing the microstructure of the coating material of the two-layer/impregnated oxide cathode precursor (another area showing inhomogeneity).

Fig 9.2.1.4(d). Pore area distribution in the coating material of a two-layer/impregnated cathode precursor.
9.2.2. Two-layer/impregnated oxide cathode after heat treatment

In this section the results of the analyses of the two-layer/impregnated cathode after the final heat treatment (as described in Section 6.3.2.2) are reported, focusing on measurements to determine the removal of the process additives, the conversion of the BaSr(CO₃)₂ to BaSrO₂ and the development of microstructure in the resultant cathodes.

9.2.2.1. Thermal analysis of coating material

9.2.2.1.1. Thermal analysis of Darvan821A dispersant

The results of the TGA and DTA investigation of the thermal decomposition of Darvan821A, used as dispersant in the cathode material suspension, between room temperature and 150°C are shown in Figures 9.2.2.1.1(a) and (b) respectively.

The decomposition of Darvan821A comprises two main steps as shown from the TGA graph in Figure 9.2.2.1.1(a). The first weight loss period is from room temperature to about 32°C (sub-step i) during which a total weight loss of 62.5wt% was obtained. Correspondingly, there are two small and overlapping endothermic peaks (denoted as A and B) identified by DTA over the same temperature range.

The second weight loss period in TGA (sub-step ii) started from 32°C to about 115°C during which the weight loss slowed and a total weight loss of 37.5wt% is obtained. Another two overlapping endothermic peaks (C and D) were identified by DTA over this temperature range as shown in Figure 9.2.2.1.1(b).

Both TGA and DTA results indicate that the decomposition of Darvan821A was completed by about 115°C with no residue left after that.

The summaries of the thermal events in TGA and DTA during heating of Darvan821A in air are listed in Tables 9.2.2.1.1(a) and (b).
Fig 9.2.2.1.1(a). TGA of decomposition of Darvan821A during heating in air from room temperature to 150°C.

Fig 9.2.2.1.1(b). DTA of decomposition of Darvan821A during heating in air from room temperature to 150°C.
Table 9.2.2.1.1(a). Weight changes identified by TGA during heating of Darvan821A in air.

<table>
<thead>
<tr>
<th>Stages</th>
<th>Sub-step</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>i</td>
<td>Rapid weight loss of 62.5wt% from room temperature to 32°C</td>
</tr>
<tr>
<td></td>
<td>ii</td>
<td>Slower weight loss of 37.5wt% from 32°C to 115°C</td>
</tr>
<tr>
<td>II</td>
<td>n/a</td>
<td>Decomposition completed and no residue after 115°C</td>
</tr>
</tbody>
</table>

Table 9.2.2.1.1(b). Thermal events identified by DTA during heating of Darvan821A in air.

<table>
<thead>
<tr>
<th>Stages</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A, B</td>
<td>Two endothermic peaks at 9°C(A) and 16°C (B) respectively</td>
</tr>
<tr>
<td></td>
<td>C, D</td>
<td>Two endothermic peaks at 49°C(C) and 90°C (D) respectively</td>
</tr>
<tr>
<td>II</td>
<td>n/a</td>
<td>No thermal events after 115°C</td>
</tr>
</tbody>
</table>

Based on the results of the thermal decomposition analysis of Darvan821A, the maximum temperature of the first stage heating of the BaSr(CO₃)₂/Darvan821A mixture is then initially decided to be 150°C. This is then used in the thermal analysis of the cathode material (Section 9.2.2.1.2) and the other investigations of the properties of the as heated cathodes.
9.2.2.1.2. Thermal analysis of BaSr\((\text{CO}_3)\)_2/Darvan 821A

The results of the TGA and DTA investigations of the thermal analysis of cathode coating material, which comprises BaSr\((\text{CO}_3)\)_2 and Darvan821A, are shown in Figures 9.2.2.1.2(a) and (b), which showed four discrete regions.

The first stage (stage I) is a relatively small weight decrease from room temperature to 560°C, during which 3wt% of the total weight is lost. Correspondingly, the DTA graph showed two endothermic peaks at 40°C (A) and 100°C (B) respectively (Figure 9.2.2.1.2(b)) with a further endothermic event from 205°C to approximately 405°C (denoted as C).

During the second region (stage II) from 560°C to 780°C, the sample was apparently thermally stable with no mass loss in TGA or thermal events in DTA. A large weight loss commenced at 780°C, indicating the third stage of the TGA (stage III), with this being completed by 1130°C. A further 25% of the total weight was lost in this region. The DTA results in this temperature range showed a number of endothermic events (D–G). Above 1130°C (IV in Figure 9.2.2.1.2(a)), the weight of the sample stayed constant. The total mass loss over this heat treatment was thus 28wt%.

The summaries of the thermal events from the thermal analysis results (TGA and DTA) for the BaSr\((\text{CO}_3)\)_2/Darvan821A composite are listed in Tables 9.2.2.1.2(a) and (b).
Fig 9.2.1.2(a). TGA of reactions of cathode material during heating from room temperature to 150°C under air and from 150°C to 1200°C under N₂/5% H₂.

Fig 9.2.1.2(b). DTA of reactions of cathode material during heating from room temperature to 150°C under air and from 150°C to 1200°C under N₂/5% H₂.

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Table 9.2.1.2(a). Weight changes by TGA during heating of cathode coating material (BaSr(CO$_3$)$_2$/Darvan821A).

<table>
<thead>
<tr>
<th>Stages</th>
<th>Sub-steps</th>
<th>Weight changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n/a</td>
<td>Small weight loss of about 3wt% from room temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sim$ 560°C</td>
</tr>
<tr>
<td>II</td>
<td>n/a</td>
<td>No weight change between 560°C $\sim$ 780°C</td>
</tr>
<tr>
<td>III</td>
<td>n/a</td>
<td>Big weight loss of about 25wt% from 780°C $\sim$ 1130°C</td>
</tr>
<tr>
<td>IV</td>
<td>n/a</td>
<td>No weight change after 1130°C</td>
</tr>
</tbody>
</table>

Table 9.2.1.2(b). Thermal events identified by DTA during heating of cathode coating material (BaSr(CO$_3$)$_2$/Darvan821A).

<table>
<thead>
<tr>
<th>Stages</th>
<th>Thermal peaks</th>
<th>Thermal events</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A $\sim$ C</td>
<td>Three endothermic peaks at 40°C(A), 100°C(B) and 405°C(C).</td>
</tr>
<tr>
<td>II</td>
<td>n/a</td>
<td>No thermal events</td>
</tr>
<tr>
<td>III</td>
<td>D $\sim$ G</td>
<td>Four endothermic peaks at 800°C(D), 910°C(E), 955°C(F) and 1045°C(G) respectively.</td>
</tr>
<tr>
<td>IV</td>
<td>n/a</td>
<td>No thermal events</td>
</tr>
</tbody>
</table>
9.2.2.1.3. Summary

The heat treatment to the two-layer/impregnated oxide cathode can be initially decided according to the thermal analysis with the heat treatment process used for the two-layer/impregnated oxide cathode in the following investigations are shown in Figure 9.2.2.1.3.

The first stage heating temperature is decided as shown in Section 9.2.2.1.1 to be 150°C in air. The second stage heating is decided according to the thermal analysis results of the BaSr(CO₃)₂/Darvan821A which showed that the decomposition of BaSr(CO₃)₂ started at about 750°C and was largely completed by 1130°C under the atmosphere used (N₂/5%H₂). So, during the following investigations, two temperatures, 1100°C and 1150°C, were chosen as the maximum temperature (Tₜ) for the final heat treatment.

![Fig 9.2.2.1.3. Heat treatment for the two-layer/impregnated oxide cathode](image-url)
9.2.2.2. Microstructure of the two-layer/impregnated oxide cathode after heat treatment

All the results that reported in the following sections refer to the samples after the two-stage heat treatment process as described in Section 9.2.2.1.3.

9.2.2.2.1. Effect of the sintering temperature on the coating material of cathode

In this section, the microstructures of the coating material of the two-layer/impregnated oxide cathode obtained after heat treatment at two selected temperatures, 1100°C and 1150°C, are reported and described. These experiments aimed to investigate the effects of these heat treatments on the microstructure and composition of the as-heated cathode material and to determine the optimum temperature for this heat treatment.

Figures 9.2.2.2.1(a) and (b) are the SEM images showing the microstructure of the coating material of a two-layer/impregnated oxide cathode after heat treatment of 1100°C under two magnifications with Figure 9.2.2.2.1(c) showing corresponding EDX analysis results obtained from this coating material. Figures 9.2.2.2.1(d) and (e) are the SEM images showing the microstructure of the same material after heat treatment at 1150°C under two different magnifications with Figure 9.2.2.2.1(f) showing the EDX analysis results for this material. All the EDX analyses were carried out on an area of 1mm² on the surface of the cathode (approximately 65% of the total surface area of the cathode). The porosity analysis results for these two materials are illustrated in Figures 9.2.2.2.1(g) and (h).
Fig 9.2.2.1(a). SEM image showing microstructure of two-layer/impregnated cathode top material after heat treatment at 1100°C.

Fig 9.2.2.1(b). Higher magnification SEM image showing microstructure of two-layer/impregnated cathode top material after heat treatment at 1100°C.
Heat treatment at 1100°C produced significant microstructural changes in the material compared to the un-heated material as shown in Section 9.2.1.4, with evidence of partial sintering to form larger aggregates shown in Figures 9.2.2.1(a) and (b). The majority of these aggregates were 5–8μm in size with some large aggregates up to 10μm also being present. From the images at higher magnification, it can be seen that these aggregates comprise partially sintered single particles of 1–2μm.

The EDX elemental analysis of the material is illustrated in Figure 9.2.2.1(c). Ba, Sr, and O were all identified in the EDX analysis of as-heated material. Two small peaks of Ni were also present. It can be assumed that these Ni filaments were detected through the pores as the coating thickness is rather high for this to be directly detected through the coating. No carbon was detected in this material after heating to 1100°C, although according to the thermal analysis, in Figures 9.2.2.1.2(a) and (b), only about 98wt% of the total decomposition was completed at this temperature. Au from the coating process used for SEM imaging was also detected.

![Graph showing EDX analysis of two-layer/impregnated cathode top material after heat treatment at 1100°C.](image-url)
The microstructure of the coating after heat treatment at 1150°C as shown in Figure 9.2.2.2.1(d) was very similar to that obtained after heating to 1100°C. However, the former material exhibited evidence of more sintering, with the average size of aggregates increasing to 8~10μm, and with the size of the larger ones being circa 15μm. The single particles of 1~2μm which comprised these aggregates could still be identified in this material as with the material heated at 1100°C. The EDX analysis of this material also did not detect any residual carbon in Figure 9.2.2.2.1(f), whilst the other elements identified were the same as in the material obtained at the lower heating temperature (Figure 9.2.2.2.1(c)).

Fig 9.2.2.1(d). SEM image showing microstructure of two-layer/impregnated cathode top material after heat treatment at 1150°C.
Fig 9.2.2.2.1(e). SEM image showing microstructure of two-layer/impregnated cathode top material after heat treatment at 1150°C.

Fig 9.2.2.2.1(f). EDX Analysis of two-layer/impregnated cathode top material after heat treatment at 1150°C.

The images of these two materials showed that porous structures could be obtained after heat treatment at both temperatures. The porosity analysis determined the total porosity to be very similar at 58% in the 1100°C material and 56% in the
1150°C heated material, the difference between these figures being within the probable margins of errors of these measurements. However, the pore area analyses reported in Figures 9.2.2.1(g) and (h) show more significant effects on the pore size distribution. These results showed that the materials contained a broad range of pores, from 1–1000μm in area, with the numbers of the largest pores falling significantly after heating to the higher temperature.

From the above results it can be concluded that although very similar microstructures are obtained, the material obtained after heating to 1100°C had slightly smaller aggregates, and broader range of pore sizes, including larger pores, with these being considered beneficial for the cathode, this temperature was thus chosen to be the maximum heat treatment of the two-layer/impregnated oxide cathode in the subsequent experiments.

![Fig 9.2.2.1(g). Pore area distribution in the two-layer/impregnated cathode top material after heat treatment at 1100°C.](image1)

![Fig 9.2.2.1(h). Pore area distribution in the two-layer/impregnated cathode top material after heat treatment at 1150°C.](image2)
9.2.2.2.2. Comparison of the microstructure of the coating material to the conventional oxide cathode

As mentioned in Section 7.2.2, one target of the project was to replicate the microstructure of the conventional oxide cathode as closely as possible. In this section, the microstructure of the coating material of the conventional oxide cathode after heat treatment is reported and compared with that of the two-layer/impregnated oxide cathode (Figures 9.2.2.2.1(a) and (b)).

Figures 9.2.2.2.2 (a) is the SEM image showing the conventional oxide cathode after heat treatment under equivalent conditions (1100°C) to those used for the two-layer/impregnated cathode developed here. The corresponding pore size analysis results are shown in Figure 9.2.2.2.2(b).

As in the two-layer/impregnated oxide cathode, aggregates of different sizes were similarly present after heat treatment in the conventional cathode material, as can be observed from Figures 9.2.2.2.2(a) and (b). The sizes of these aggregates were in the range of 3-10μm, which are similar to those obtained in the new cathode designs under the same heat treatment conditions. As with the materials obtained from the two-layer/impregnated cathodes, the BaSrO₂ material comprised partially sintered agglomerates of smaller particles. In this case, there was also some evidence of partial fusion of the material.
Fig 9.2.2.2.2(a), SEM showing microstructure of conventional oxide cathode after heat treatment at 1100°C under N\textsubscript{2}/5% H\textsubscript{2} for 30 minutes.

The pore analysis of the conventional oxide cathode after heat treatment at 1100°C is illustrated in Figure 9.2.2.2.2(b). The analysis also indicated a total porosity of 60%. The pores in the cathode material exhibited a wide range of areas, with the percentage of the large pore area being higher than that of the two-layer/impregnated cathode after the same heat treatment.

Fig 9.2.2.2.2(b). Pore area distribution of the conventional cathode coating material after heat treatment of 1100°C.
9.2.2.2.3. Microstructure of the interface of two-layer/impregnated oxide cathode after heat treatment

The results of the SEM observations of interfacial material of the two-layer/impregnated oxide cathode after heat treatment at 1100°C is shown in Figures 9.2.2.2.3(a) and (b) with the preparation process by which these samples were obtained being as described in Section 6.4.1.1. The EDX analysis result for this material is shown in Figure 9.2.2.2.3(c), with the pore analysis result of the material in this interface region reported in Figure 9.2.2.2.3(d).

As in the coating material shown in Section 9.2.2.2.1, the BaSrO₂ was present as aggregates of various sizes. However, in this case, unlike the corresponding images of the top surface under equivalent conditions shown in Figures 9.2.2.2.1(a) and (b), both Ni filaments and the BaSrO₂ phase can be distinguished in these images although the very limited contrast difference between them makes this difficult. The Ni particles generally retain their filamentary morphology after heating to this temperature (1110°C) although some coarsening could be observed, evidenced by an increase in the diameter of the Ni filaments increasing from approximately 0.8μm (as identified after heating at 700°C shown in Section 9.1.3.2.2.) to 2μm (after heating to 1100°C). EDX analysis (Figure 9.2.2.2.3(c)) detected Ba, Sr, O and Ni from the surface of the sample as pointed in the image.
Fig 9.2.2.3(a), SEM image showing microstructure of the interface of two-layer /impregnated cathode after heat treatment of 1100°C.

Fig 9.2.2.3(b), SEM image showing microstructure of the interface of two-layer /impregnated cathode after heat treatment of 1100°C.
Fig 9.2.2.3(c). EDX Analysis of the interfacial material of the two-layer cathode material after heat treatment at 1100°C.

The pore area analysis in Figure 9.2.2.3(d) showed that compared to the material at the coating surface (Figure 9.2.2.1(g)), the material at interface had a slightly higher porosity (61% according to the analysis result) and higher proportion of the large pore areas, this confirms the results of visual observation of the SEM image.

Fig 9.2.2.3(d), Area percentage of the pore size distribution of the interface of two-layer/impregnated cathode after heat treatment of 1100°C.
9.2.2.4. **EDX dot mapping of cross-section of the two-layer/impregnated oxide cathode after heat treatment**

SEM and EDX were used to investigate the effect of the heat treatment on the distribution of Ba and Sr through the cathode. Figure 9.2.2.2.4(a) is an SEM image of the cross-section of a two-layer/impregnated oxide cathode after heat treatment of 1100°C and Figures 9.2.2.2.4(b) to (d) are the EDX dot maps showing the distribution of Ni, Ba and Sr on the cross-section of this sample.

The thickness of the cathode after heat treatment as shown in Fig 9.2.2.2.4(a) was about 360μm. In contrast to the unheated sample shown in Fig 9.2.1.3.2(a), there is much lower image contrast (atomic number contrast) across the sample, with no obvious bright layer at the top surface, suggesting the composition is more homogeneous.

This observation is largely confirmed by the EDX results of the individual elements in Figures 9.2.2.2.4(c) and (d), which show the Ba and Sr to be distributed not only on the surface of the cathode but also through the whole thickness of the cathode. The distribution of Ba seems generally more homogeneous across the whole thickness of the cathode whilst the Sr appeared to be more concentrated in upper portion of the cathode.
Fig 9.2.2.4(a). SEM image of cross-section of a two-layer/impregnated oxide cathode after heat treatment of 1100°C.

Fig 9.2.2.4(b). SEM dot mapping showing the distribution of Ni of cross-section of the two-layer/impregnated oxide cathode after heat treatment of 1100°C.
9.2.2.4(c). SEM dot mapping showing the distribution of Ba of cross-section of the two-layer/impregnated oxide cathode after heat treatment of 1100°C.

9.2.2.4(d). SEM dot mapping showing the distribution of Sr of cross-section of the two-layer/impregnated oxide cathode after heat treatment of 1100°C.

9.2.2.3. Macrostructure of the two-layer/impregnated oxide cathode after heat treatment

An SEM image of two-layer/impregnated oxide cathode after heat treatment at 1100°C is shown in Figure 9.2.2.3(a). After heat treatment, the diameter of the whole cathode was 1.4mm, corresponding to a 6.67% shrinkage compared to the cathode before final heat treatment (1.5mm diameter as shown in Figure 9.2.1.2(b)). Both the coating material and the whole cathode remained intact and the coating materials remained adherent across the whole cathode surface. The surface remains flat on a macroscopic scale. In comparison with the unheated sample (Figure 9.2.1.2(b)), the
surface appears somewhat rougher and coarser with an increase in porosity, especially the central area. Some large pores were also obtained.

Figure 9.2.2.2.3(b) is an image showing a conventional oxide cathode after the heat treatment under equivalent conditions (1100°C) to those used for the two-layer/impregnated cathode developed here. The cathode which also has a diameter of 1.4mm, exhibits a highly open, porous structure and macroscopically flat surface with large pores, which is generally similar to that obtained with the two-layer/impregnated cathode.

However, it should be noticed that in contrast with the new cathode design in Figure 9.2.2.3(a), the structure of the conventional oxide cathode is not homogeneous with a reduction in porosity towards the edges of the cathode as shown in Figure 9.2.2.2.3(b). It can also be estimated from this image that the practical diameter of the porous material is about 1.2mm for the conventional cathode.

![Fig 9.2.2.3(a). SEM showing a two-layer/impregnated oxide cathode after heat treatment at 1100°C.](image-url)
Fig 9.2.2.3(b), SEM image of a conventional oxide cathode after heat treatment at 1100°C.

To show more clearly the structure of the edge of the conventional oxide cathode, a higher magnification SEM image of the edge area is shown in Figure 9.2.2.3(c) with the edge area of two-layer/impregnated oxide cathode is shown in Figure 9.2.2.3(d) for comparison. It is apparent that in the conventional cathode, the thickness of the coating decreases substantially with no coating material at the edge of the Ni cap. In comparison, two-layer/impregnated cathode comprises porous emitting material across the entire surface with the emitting material also being strongly adherent to the Ni substrate.
Fig 9.2.2.3(c). SEM showing microstructure of the edge of the conventional oxide cathode after heat treatment at 1100°C.

Fig 9.2.2.3(d). SEM showing microstructure of the edge of the two-layer/impregnated oxide cathode after heat treatment at 1100°C.
Chapter 10

Discussion II-The Two-Layer/Impregnated Oxide Cathode

The two-layer/impregnated oxide cathode developed in this project is thought to provide a promising alternative cathode for the conventional oxide cathode and its manufacturing process. The effects of the various manufacturing steps and the resultant properties of the cathode are discussed in the following sections.

10.1. Effects of manufacturing parameters on the properties of the porous Ni substrate

A porous Ni substrate with satisfactory mechanical, compositional, macrostructural and microstructural properties, is one of the critical components in the two-layer/impregnated oxide cathode. The production process developed for this Ni substrate comprised three main steps, casting, stamping and heat treatment. The resultant products produced from each of these three steps had to satisfy specific requirements to ensure the appropriate properties of the final product.

10.1.1. Effects of the casting process on the as cast Ni/polymer film

As for the integrated oxide cathode described in Chapter 7, casting is used as the primary fabrication process for producing the Ni substrate material in the two-layer/impregnated cathode, and similar requirements for a flat, crack-free, homogeneous as cast film apply. Variations in the casting conditions produced a number of effects on the properties of the as cast Ni/polymer materials.

10.1.1.1. Effects of polymer composition and solid content

As with the integrated oxide cathode, PVA, PEO and PEG were used as processing additives in producing Ni/polymer substrate precursor material. During casting, the compositions of polymers (20wt%PVA/20wt%PEO/10wt%PEG) and the solid content of casting suspension (13.3wt%) of the Ni substrate material were
initially selected to be the same as the optimum conditions determined for the integrated oxide cathode.

The experimental results for the as cast Ni/polymer films (Section 9.1.1) suggested that these conditions of the suspension used previously were also suitable for application in this system allowing the production of good quality, flat and crack free, as cast Ni/polymer films. It is similarly expected that as with the integrated oxide cathode, the polymer composition and its distribution will be the principal factors determining the drying stresses during casting in accordance with the findings by other workers previously discussed in Section 8.2,\textsuperscript{109,115,116} and the development work carried out on the integrated cathode was thus directly relevant to this system.

10.1.1.2. Effects of Ni/polymer composition

10.1.1.2.1. Effect of Ni/polymer composition on the polymer segregation on the Ni film

The reduction in the amount of polymers on the surface of the cast films with decreasing polymer content (Section 9.1.1) can be attributed to the effect of polymer segregation during the drying process. This is similar to the findings of other workers as introduced in Section 4.2.3,\textsuperscript{107-109} which have shown the amount of polymer segregation is essentially decided by the polymer amount and the water content of the suspension.\textsuperscript{107,109} Given that the time of the increasing and constant rate period of each suspension can be assumed to be same because of the same solid and hence water content. In these experiments then the polymer content is presumed to be the cause. The lower the polymer composition in the Ni/polymer suspension, the lower the concentration of polymers in these suspensions (given the same solid content in the suspensions), and thus less polymers migrated to the surface at the same time during the increasing and constant drying period.

The small amount of irregularity of the surface topography after the polymers were thermally removed as observed in the as heated Ni substrate (Figures 9.1.3.2) can be attributed to the effects of removal of the segregated polymer from the surface during heating which is similar as for the integrated oxide cathode. However, because the Ni surface would be covered by BaSr(CO\textsubscript{3})\textsubscript{2} in the later stages, the effects of this
surface irregularity on the properties and performance of the whole cathode would be expected to be relatively insignificant.

10.1.2.2. Effect of Ni/polymer composition on the thickness of the Ni film

The effect of the compositions of Ni and polymer on the thickness of the cast materials as revealed in Table 9.1.1 requires some further explanation.

Given that the total mass of solids is the same in each case, then theoretically, because the density of Ni is higher than that of polymer, the Ni/polymer film with lower Ni content and higher polymer content should have higher thickness. However, the resultant Ni/polymer films showed opposite phenomenon as shown in Table 9.1.1 with the thicknesses of these films increased with increasing Ni content (decreasing polymer content).

The change of thickness with various Ni/polymer compositions and its disagreement with the theoretical trend were thought to be related to the Ni morphology and distribution inside the material. It is supposed that in the substrate material, the Ni filaments did not simply lie in a well packed flat (2D) orientation, but rather that these filaments physically interacted to form a more open three-dimensional distribution. Some evidence of the three-dimensional structure formed by the Ni filaments can be observed in Figures 9.1.2.2(a) to (c). This effect, analogous to a “house of cards” structure, seemed to increase initially with increasing content of Ni, especially from 10wt% to 15wt%.

However, as the Ni content is increased, especially from 20wt% to 25wt%, this effect appears to result in diminishing impact on density and thickness, most probably due to formation of larger and denser Ni agglomerates in the structure. Figures 9.1.2.2(a) to (c) show some evidence of an increase in density of the Ni agglomerates with increasing Ni concentration.

This microstructural difference brought by the material composition had significant influence on the choice of the suitable compositions of Ni and polymers for the production of the Ni substrate material. The materials containing 15wt% and 20wt% Ni both provided a microstructure of relatively high porosity (69% and 61%) and larger pores which were expected to result in a highly porous Ni substrate with large pores after heating. This is very important to assist in obtaining the desired “impregnation” feature of this new cathode structure. So, the compositions
15wt%Ni/85wt%polymer and 20wt%Ni/80wt%polymer were chosen as the candidates in this stage for the following investigations.

10.1.2. Effect of the stamping process on the as cut Ni component

The basic requirements for the stamping process are the ability to be able to cut the Ni component with intact shape and smooth edge around it. Ideally a homogeneous material distribution is also required. The success in fabricating the Ni components by this process illustrated in Figure 9.1.2.1 show that the cast material did possess the required mechanical strength. However, the as stamped Ni components revealed some consistent inhomogeneity, comprising higher density region in the edge area when compared to the central areas of the component.

Considering the distribution of these regions, it is believed that this inhomogeneity is produced by the cutting tool during the stamping process. When the cutting tool is pressed into the Ni/polymer material, the materials next to the cutting tool would tend to be compressed at and adjacent to the cutting edge because of the stress generated by the cutting, whilst the central area of the component, far from the area impacted by the cutting tool, would be unaffected. This inhomogeneity in the Ni substrate is thus considered to be inherent to the design and the manufacturing process, although the use of a sharper/thinner walled cutting tool might be expected to greatly reduce the magnitude of this effect.

Although the density difference is rather apparent on the as stamped Ni substrate, it did not appear to be significantly visible after heating as shown in Section 9.1.3.2. This suggested that the material compressed at the edge was mainly the polymers, which would be much easier to move during cutting than the Ni filaments. When the polymers were removed during heating, there was thus little or no significant density difference, which could be observed. So, it can be assumed that this density difference in the as stamped Ni substrate would not be significantly detrimental to the properties of the porous Ni substrate after being heated.
10.1.3. Effect of the heat treatment on the properties of the as heated porous Ni substrate

The initial heat treatment during manufacturing the two-layer/impregnated oxide cathode (as described in Section 6.3.2.1) aimed to produce a porous Ni substrate with adequate mechanical strength, flat and crack free macrostructure, suitable porous microstructure, and appropriate composition.

10.1.3.1. Effects of heat treatment on the composition of the Ni substrate

10.1.3.1.1. Thermal analysis of the Ni/polymer precursor material

10.1.3.1.1.1. Thermal analysis under increasing temperature

The thermal analysis results of Ni/polymer as cast material shown in Section 9.1.3.1.1 under increasing temperature show the expected high similarity to the reactions of the integrated oxide cathode over the same temperature range (Section 7.3.4).

The initial small weight loss (i) from room temperature to 80°C in TGA (Figure 9.1.3.1.1(a)) with its corresponding endothermic peak (A) identified by DTA is thought to be the removal of water.

The next endothermic peak (B) identified by DTA at 120°C with its corresponding constant weight in TGA over the same temperature range can be attributed to the reaction of polymers. Such peak was also found in the integrated oxide cathode at the almost same temperature (peak B in Figure 7.3.4(b)). However, the temperature (120°C) was much higher than the melting temperature of both PEO (70°C as shown in Figure 7.3.1.2(b)) and PEG (40°C as shown in Figure 7.3.1.3(b)). Although no information was found in the literature for the mixed polymer system as introduced in Section 5.4, It is thought that this higher temperature polymer transformation temperature must be caused by some new compound formed by reaction between the three polymer constituents of the PVA, PEO and PEG. Further investigation would be needed to confirm this.

The subsequent weight loss (iii) in TGA from 125°C to 490°C and the various exothermic peaks identified by DTA (C, E~H) are caused by the polymers (PVA, PEO and PEG) decomposition. The temperatures of the exothermic peaks for polymer decomposition in this Ni/polymer material are generally consistent with those in the
integrated cathode material (Section 7.3.4) for the same reactions, indicating the same depolymerisation/combustion mechanisms under the same conditions. However, the exothermic peak F at 320°C identified by DTA in the Ni substrate material did not appear in the DTA of the integrated cathode (Figure 7.3.4(b)). There can be found a slight change of slope in the DTA curve of the integrated cathode material (Figure 7.3.4(b)) after a closer inspection, indicating the possibility of this thermal event. The possible reason for the absence of this peak (F) in the integrated cathode material is that the intensity of this peak is so small because of the lower polymer content in the integrated cathode (50wt%) than in the Ni substrate material (85wt%) that it was hidden by the other peaks with higher intensity.

The most apparent difference of the thermal behaviour between Ni/polymer material and the integrated cathode material over the temperature range (room temperature to 700°C) is the occurrence of an endothermic peak (D) identified by DTA (Figure 9.1.3.1(b)) at 210°C which didn’t appear in the integrated cathode (Figure 7.3.4(b)). According to the thermal analysis of pure PVA (Figures 7.3.1.1(b)), this endothermic peak was most likely to be attributed to the decomposition of PVA (peak A in Figure 7.3.1.1(b)). The apparent absence of this thermal event in the integrated cathode material can again be attributed to the lower amount of PVA (20wt%) in the integrated cathode material than in the Ni substrate material (34wt%), which resulted in lower intensity of this thermal peak with this being masked by the high intensities of the other polymer decomposition reactions.

As in the integrated cathode material, the separate identification of the cause of each sub-stage of the polymer decomposition cannot be ascertained, as many of these degradation reactions occur over similar temperatures for the PVA, PEO and PEG additives.

Polymer decomposition is considered to stop after 500°C because carbon is stable at these temperatures in a reducing (N₂/5%H₂) atmosphere. The small weight increase in TGA (stage III in Figure 9.1.3.1(a)) and the corresponding endothermic peak in DTA (stage I in Figure 9.1.3.1(b)) are therefore both caused by the oxidation of Ni, which also stopped at about 555°C because of lack of oxygen in N₂/5%H₂. In contrast to the integrated cathode material (Figure 7.3.4(a)), the completion temperature of Ni oxidation in this case was very close to that of the pure Ni (Figure 7.3.3(a)). This can be explained as being due to the absence of BaSr(CO₃)₂ in this case which left only Ni in the material after the removal of the polymers during
low temperature heating. The endothermic characteristics of the Ni oxidation process mirror those obtained for the pure Ni material and the integrated cathode discussed in Sections 8.3.1.2 and 8.3.1.4 and no further explanation is given here.

10.1.3.1.2. Thermal analysis under isothermal conditions

The thermal analysis showing the effect of isothermal treatment of substrate sample at 700°C in Figures 9.1.3.1.2(a) and (b) showed that as in the thermal analysis of pure Ni (Figures 7.3.2(a) and (b)), the reduction of NiO did not commence until the temperature reached 700°C and this temperature maintained for about 12 minutes. The reason for the delay of this reduction which has been reported in other studies\(^\text{184,191}\) has been explained in Section 3.2.3 and 8.3.1.3 being associated with the various sub stages of this reaction which involves generation of oxygen vacancies and the adsorption of hydrogen in the NiO which then promote the NiO reduction by hydrogen.\(^\text{184,191}\) The exothermic peak of the NiO reduction is also consistent with the pure Ni materials as reported in Section 7.3.2 and the other researchers as introduced in Section 3.2.3.\(^\text{184}\)

10.1.3.1.2. The composition of the Ni substrate after heat treatment

The final composition of the Ni substrate material after the initial heat treatment can be obtained by the calculation of the corresponding weight loss of the materials. The compositional requirements of this heat treatment of the Ni substrate and the aims of these calculations are thus to establish that: (1), the polymer additives are completely removed during the low temperature heat treatment (500°C); (2), that Ni is present in the form of metal rather than NiO after heating. Again, for simplicity in the following calculations, some assumptions are necessary:

(1), that the distribution of each component in the Ni substrate material is homogeneous, so that the composition of each component in the sample was 15wt%Ni/85wt%polymer.

(2), that the oxidation reaction of Ni filaments in the Ni substrate material is the same as pure Ni as in Figures 7.3.2(a) and (b).

On this basis, the loss of the polymer and the final composition of Ni substrate can be calculated as following:
(i). Step (i)

First, from the TGA graph of the material (Figure 9.1.3.1(b)), it can be estimated that the as cast Ni/polymer material comprised 98wt% solid constituent with the remaining 2wt% being water which was removed on heating below 80°C. Given the assumption that the proportions of the solid components were 15wt%Ni/85wt%polymer, the overall composition of all the components in the as cast Ni substrate material can thus be assumed to be: 14.7wt% Ni, 83.3wt%polymer and 2wt%water.

(ii). Step (ii)

The net weight loss between 125°C and 500°C was 82wt%, comprising weight loss due to polymer decomposition and weight increase of Ni oxidisation.

It can be calculated from Figure 7.3.2(a) that by 500°C, the weight increase due to oxidation of the pure Ni material was 14wt% assuming that the Ni oxidation behaviour in the composite was the same as for the individual Ni. On this basis, the expected increase due to oxidation of the 14.7wt% Ni in the substrate material is thus:

\[
\Delta W_{Ni} = \frac{14\text{wt%}}{100\text{wt%}} \times 14.7\text{wt%} = 2.058\text{wt%}
\]

Compensating for the additional mass due to oxidation of the Ni, then the calculated weight loss due to removal of the polymers in the Ni substrate material by 500°C is:

\[
\Delta W_{polymer} = 82\text{wt%} + 2.058\text{wt%} = 84\text{wt%}
\]

This calculated weight loss is higher than the total weight of the polymers in the sample (83.3wt%), indicating that all the polymers in the Ni substrate should be able to be removed by the heat treatment at 500°C in air. The discrepancy between the calculated and the theoretical mass loss probably come from the experimental error of the measurements and the assumptions made, in particular that the compositions sampled are homogeneous and representative.

As with the results obtained from Section 8.3.1.4, there is no strong or clear evidence for the catalytic effect of Ni on the decomposition of the polymers as mentioned in Section 4.3.1.2.\textsuperscript{108,112-114} by comparison between the decomposition of the individual polymers (PVA and PEO) and with the behaviour of the Ni containing mixtures under the same conditions.
(iii). Isothermal heating

As for the composition of Ni substrate after heating, the final weight of the sample after holding at 700°C in N₂/5%H₂ for 30 minutes (Figure 9.1.3.1.2(a)) is equivalent to as the theoretical Ni weight (14.7wt%) in the substrate material before heating, it can thus be reasonably assumed that all the NiO formed has been reduced back to Ni, and that only Ni remains in the substrate material after the complete heating process.

10.1.3.1.3. Effect of the thermal analysis results on the selection of the heat treatment conditions

As with the integrated oxide cathode discussed in Section 8.3.2, the thermal analysis results were used to help deciding the heat treatment for the Ni substrate material.

The purpose of the first stage heating and thus the selection of the heating conditions were same as for those of the integrated oxide cathode as discussed in Section 8.3.2. As a result, 500°C was chosen as the temperature and air chosen as the atmosphere from the TGA results which indicated that the polymers could be almost completely decomposed under these conditions.

One of the compositional requirements for the as heated Ni substrate is the retention of a conductive Ni phase, not NiO, in the as heated Ni substrate. The second stage heating aimed to achieve this. According to the thermal analysis of the Ni substrate material under isothermal conditions, it was decided that a further 30 minutes dwell time was required holding the sample at the high temperature during the second stage heating with the protective/reducing atmosphere, N₂/5%H₂, determined to be a suitable medium allowing any oxidation of the Ni at lower temperatures to be reversed. However, the temperature of the high heating stage will be finally decided by both macrostructure and microstructure of the as heated cathode material in addition to the chemical composition, with this being discussed in the next section.
10.1.3.2. Effect of high temperature heat treatment on the Ni substrate material

10.1.3.2.1. Effects of Ni composition on the microstructure of the Ni substrate after heat treatment

Despite the similar microstructures (porosity and pore area distribution) of the Ni substrate material containing 15wt% Ni and 20wt% Ni before heating, as reported in Figures 9.1.2.2(a) and (b), there were much more apparent differences between these two materials after heat treatment as shown in Figures 9.1.3.1(a) and (b). The different behaviour can be attributed to the effect mentioned in Section 4.3.2 that any inhomogeneity within or differences between materials can be enlarged during sintering.\(^{[81]}\)

The higher Ni content in 20wt% Ni material resulted in more Ni agglomerates before heat treatment as shown in Figure 9.1.2.2(b). This increase in the agglomeration of the Ni has also been mentioned in Section 10.1.1.2.2 which also resulted in the diminishing effect of Ni addition on the thickness. After heat treatment, these Ni agglomerates became larger and less disperse because of the coarsening and densification processes occurring during heating, leading to the formulation of large pores between these large agglomerates. By contrast, the formulation with lower (15wt%) Ni content resulted in a more homogenous distribution of the Ni filaments before heating due to the low Ni density and thus a more homogeneous microstructure after heating.

10.1.3.2.2. Effects of sintering temperature on the microstructure of the Ni substrate

Apart from the compositional requirement as discussed in Section 10.1.3.1.3, the second heating step of the cathode manufacturing process is also required to obtain the following effects: (1), sintering of the Ni filament to provide an interconnected structure of Ni filaments which can provide both mechanical support(strength) and electron conductivity pathway; and (2), to generate large pores and high porosity in the Ni substrate material to facilitate BaSr(CO\(_3\))\(_2\) penetration impregnation in the later process stage.
Comparing the microstructure of the Ni substrate material before (Section 9.1.2.2) and after heating (Section 9.1.3.2.2), necks were shown to be formed between the Ni particles in the as heated materials, with their sizes and number increased with increasing temperatures. This is generally in agreement with the predicted behaviours as introduced in Sections 4.3.2.3.1.1-4.3.2.3.1.3 for all the possible governing mechanisms. The formation of these necks was critical to provide the mechanical strength to the as heated Ni substrate and resulted in intact Ni substrate as shown in Figure 9.1.3.2. This also explained the failure of the Ni substrate when heated to temperatures below 700°C (as mentioned in Section 9.1.3.2), as a result of the lack of neck formation because of the low sintering temperature and thus lack of mechanical strength.

According to the small size and amount of necks in the Ni substrate after heating at 700°C, it can be assumed that the initial stage of sintering took place when the temperature approached 700°C according to the microstructural changes listed in Table 4.3.2.3. The main reaction mechanism at this temperature was coarsening as evidenced by the relatively high residual porosity (59%) after heating compared to that in the Ni substrate before heat treatment (69%). However, both coarsening and densification was shown to take place with increasing temperature evidenced by the apparent increasing in the diameters of the Ni filaments (from 0.5-0.6µm to 2µm), decreasing in pore sizes and porosity in the material (59% to 31%). The tendency of the pores to change from being mostly open and round in shape at 700°C to more closed and cylindrical shape at 900°C also indicated the commencement of the intermediate sintering stage as normally defined.

It should be recalled that the aim of this process was to promote sintering and possibly coarsening, but to avoid densification which would reduce the size and extent of desirable porosity present and thus a sintering temperature of 900°C (intermediate sintering) can thus be considered to be excessive for the purpose of this application.
10.1.3.3. Summary-determination of the heating conditions and the candidate material

On the basis of the previously described results, the composition of the Ni substrate material and the conditions of the heat treatment were thus chosen as follows so that the optimum properties could be obtained.

For the initial heat treatment, 500°C was determined as the maximum temperature and air was chosen as the atmosphere, with the results indicating that the polymer additives could be removed completely under these conditions as discussed in Section 10.1.3.1.1.

For the higher temperature stage, aiming for the reduction of Ni, and the generation of mechanical strength and porosity, 700°C was chosen as the maximum temperature and N₂/5%H₂ was used as the atmosphere with the maximum temperature being maintained for a period of 30 minutes. These heating conditions were shown to result in a Ni substrate with proper composition (only Ni present after heating), satisfactory mechanical strength and microstructure, including high porosity and large pores.

The composition 15wt%Ni/85wt%polymer was chosen as the composition of the Ni substrate precursor material which resulted in an interconnected Ni network with the optimum microstructure (highest porosity, most homogeneous distribution) compared with the other compositions after the same processing steps.
10.2. Effects of manufacturing parameters on the properties of the two-layer/impregnated oxide cathode

The following sections (10.2.1 and 10.2.2 and their sub-sections) are concerned with the processes occurring during the final stages of the manufacturing of the two-layer/impregnated cathode as reported in Section 9.2.

10.2.1. Effects of BaSr(CO$_3$)$_2$ suspension preparation conditions on the properties of the two-layer/impregnated cathode

The impregnation step in the manufacturing process for the two-layer/impregnated cathode entails the application of BaSr(CO$_3$)$_2$ to the Ni substrate as described in Sections 6.2.2.2 and 6.2.2.3. Experiments showed that the conditions of the BaSr(CO$_3$)$_2$ suspension preparation step had significant influence on the microstructure of the cathode coating material and also on the structure of the whole cathode and these effects are discussed in the following sections.

10.2.1.1. Effect of the suspension preparation conditions on the BaSr(CO$_3$)$_2$ morphology in suspension

The effects of the dispersant (Darvan821A) and ultrasonic treatment on the morphologies and sizes of BaSr(CO$_3$)$_2$ in the suspension were reported in Sections 9.2.1.1.1 and 9.2.1.1.2.

The large number and size of the BaSr(CO$_3$)$_2$ agglomerates from the suspension without ultrasonic treatment and dispersant (Figure 9.2.1.1.1(a)) were attributed to the attractive surface forces between the particles, which were too great to allow the agglomerates to be broken up simply by magnetic stirring. Similarly the essentially unchanged morphology and size for these BaSr(CO$_3$)$_2$ agglomerates after ultrasonic treatment (Figure 9.2.1.1.2(a)) is further evidence of the strong attractive force within the agglomerates, which prevented them being broken even under this higher energy treatment$^{[92,93]}$ or possibly led to the reforming rapidly once the treatment process was complete.

By contrast, the substantial change in the morphology of the BaSr(CO$_3$)$_2$ agglomerates, especially after ultrasonic treatment, shown in Figure 9.2.1.1.2(b) after...
the addition of dispersant (Darvan821A) indicated a significant reduction in the bonding forces responsible for agglomerates formation. This change was due to the imposition of the electrosteric repulsive force from the Darvan molecules adsorbed on them as described in Section 5.5. The net attractive force was thus lower than the energy input during ultrasonic treatment and enabled the particles to be broken into small and unagglomerated particles by this method, although magnetic stirring was still not effective. The repulsive forces generated between the particles by the adsorbed dispersant also protected them from re-agglomerating.

A particularly attractive feature of this dispersant is that it was found to be effective without the need for any further pH modifying additives, which are often required for dispersants as described in Section 5.5. It is highly preferable not to add pH value-adjusting additives in manufacturing the oxide cathode in order to avoid their potential effect as impurities in the resultant cathode material. As with the polymer additives (PVA, PEO and PEG) and the dispersant used, any additive added into the cathode material is required to be subsequently removed prior to use as such contaminations are very likely to damage the cathode performance if left in the material after it is sealed in the electron gun. The dispersant is also readily removed by heat treatment as described in Section 9.2.2.1.1 and the choice of this dispersant thus simplified the whole manufacturing process and avoided the risk of introducing impurities to the final cathode.

10.2.1.2. The microstructure of the two-layer/impregnated cathode coating material and its comparison to that of the conventional cathode material

The small and discrete particles in the microstructure of the two-layer/impregnated cathode coating material as shown in Figures 9.2.1.4(a) and (b) provided clear evidence of the effectiveness of the dispersant and ultrasonic treatment in breaking down the BaSr(CO3)2 agglomerates.

However, although the coating material was produced directly from the BaSr(CO3)2 suspension, the difference in morphologies of the BaSr(CO3)2 particles observed between the particles when analysed from the original suspension which apparently comprised both rod-like and cubic-shape particles (Figure 9.2.1.1.2(b)) and
the structure of the particles after application to the Ni substrate in the cathode material which apparently comprised only discrete cubic-shape particles (Figures 9.2.1.4 (a) and (b)) requires further explanation.

This difference is considered to be generated by two possible reasons. During the application of the suspension to the Ni substrate in the impregnation process (Section 6.2.2.3), liquid could be imagined to flow downwards into the pore structure of the substrate carrying the \( \text{BaSr(CO}_3\text{)}_2 \) particles with the fluid flow causing them to align vertically in the material. Another possibility came from the manufacturing process. After finishing the ultrasonic treatment, the \( \text{BaSr(CO}_3\text{)}_2 \) suspension was still kept under magnetic stirring to prevent the deposition of the \( \text{BaSr(CO}_3\text{)}_2 \) particles before impregnation step. The remaining rod-like particles and/or the agglomerates may have continued to be broken by the magnetic stirring because the attractive forces between them had already been decreased by the addition of the dispersant. In practice a combination of both effects may be responsible.

Some evidence to support these hypothesis is provided by the microstructure of cathode on a sloping surface as shown in Figure 9.2.1.4(c) in which some rod-like agglomerates/particles can be observed to settle vertically while the number and sizes of these agglomerates were much smaller than those directly from the suspension (Figure 9.2.1.1.2(b)).

The inhomogeneity between different areas of the cathode in terms of their flatness and the pores as shown in Figures 9.2.1.4(a) and (c) is thought to be caused by a combination of the surface topography of the Ni substrate and the impregnation process. As discussed in Section 10.1.1.2.1, polymer segregation at the top surface of the cast Ni substrate material would be expected to lead to surface roughness of the Ni substrate after heating when the surface-accumulated polymer has been removed. After the \( \text{BaSr(CO}_3\text{)}_2 \) containing suspension was applied on the Ni substrate, the \( \text{BaSr(CO}_3\text{)}_2 \) particles would be expected to accumulate in those areas where there were surface hollows subsequently leading to solid rich and solid poor regions in the coating.

The breaking down of the \( \text{BaSr(CO}_3\text{)}_2 \) agglomerates also made the microstructure of the two-layer/impregnated cathode (as shown in Section 9.2.1.4) significantly different from that of the conventional cathode (as shown in Figure 7.2.2(e)), with the former material generally comprising much smaller particles, pores,
and lower porosity. This is a negative consequence of the process, and testing will be required to determine how this translates into the emission performance.

As introduced in Section 2.3, little treatment is carried out to break down the initial agglomerates resulting in the presence of large rod-like particles and agglomerates in the conventional cathode material. These particles/agglomerates are harder to pack compactly and homogeneously compared with the small, cubic-like BaSr(CO₃)₂ particles in the two-layer/impregnated cathode material, and thus generate a more porous microstructure and larger pores. Although there were also agglomerates in the two-layer/impregnated cathode material, because of their smaller sizes, lower amount, and vertical alignment inside the material, the pores in the new cathode material, especially those on the flat surface, were much smaller than those in the conventional cathode.

10.2.1.3. Effect of the suspension preparation on the structure of the cathode

The preparation conditions of the BaSr(CO₃)₂ suspension also changed the structure of the two-layer/impregnated cathode precursor, noticeably from a the “two-layer” (Section 9.2.1.3.1) structure obtained when prepared from the suspension without the ultrasonic treatment to a “impregnated” structure (Section 9.2.1.3.2) when prepared from the suspension with the ultrasonic treatment.

The separate distribution of BaSr(CO₃)₂ and Ni in the “two-layer” structure resulted apparently came from the larger size and the columnar shape of the BaSr(CO₃)₂ particles/agglomerates leading to these being too big to penetrate through the pores in the Ni substrate material leaving the BaSr(CO₃)₂ as a coating layer on top of the Ni substrate. By comparison, for the cathode produced from the suspension with both ultrasonic treatment and the dispersant, the particles/agglomerates were significantly broken up and thus were able to penetrate into the pores of the Ni substrate, resulting in an “impregnated” structure.
10.2.1.4. Summary

The preparation conditions used for the suspension provide a number of options for the development of this cathode design-ultrasonic treatment combined with the use of appropriate surfactant allowed the production of a pre-impregnated porous Ni structure directly from the casting process at the expense of desirable porosity. Dispensing with the treatments leads to a layer-type structure at this stage, with enhanced porosity/surface area but inferior homogeneity. In this project, the BaSr(CO₃)₂ suspension with both dispersant and the ultrasonic treatment is investigated initially because of its impregnated structure. However, further investigation was also considered worthwhile to investigate the two-layer/impregnated oxide cathode produced from the BaSr(CO₃)₂ suspension with dispersant but without the ultrasonic treatment.

10.2.2. Effect of the heat treatment on the cathode coating material and the properties of the as heated two-layer/impregnated oxide cathode

As in the manufacturing of the integrated cathode, the final heat treatment of the two-layer/impregnated cathode (Section 6.3.2.2) is critical to achieving many of the requirements for the properties of the cathode material, including the desired composition, and microstructure, which would determine the performance of the two-layer/impregnated cathode during operation.

The effects of this final stage of heat treatment on the properties of the two-layer/impregnated oxide cathode are discussed in the following sections.

10.2.2.1. Effects of the heat treatment on the composition of the as heated two-layer/impregnated oxide cathode

10.2.2.1.1. Thermal analysis of the dispersant

It is important for the development of the two-layer/impregnated cathode material that the dispersant used as process aid can be removed completely during heat treatment prior to sealing in the CRT assembly where they might contaminate the...
device during operation. The thermal decomposition of Darvan821A was reported in Section 9.2.2.1.1 which showed a very simple and quick weight loss which stopped at 115°C with the material being decomposed completely.

There is little information in the literature about the decomposition of Darvan821A. In the Material Safety Data Sheet for the material,\textsuperscript{170} it states that the products of combustion are carbon oxides (CO, CO\textsubscript{2}) and ammonia, and it has been assumed that the various sub-stages of the DTA/TGA data result from these decompositions, although these cannot be assigned with certainty. However, the details of the decomposition process are not the main concern of this study.

10.2.2.1.2. Thermal analysis of BaSr(CO\textsubscript{3})\textsubscript{2}/dispersant mixture

The aim of the thermal decomposition studies of the BaSr(CO\textsubscript{3})\textsubscript{2}/dispersant mixture reported in Section 9.2.2.1.2 was to determine how the thermal degradation process occurred during heating, allowing the temperature for the removal of the process aid and the onset and completion temperature for the conversion reaction of BaSr(CO\textsubscript{3})\textsubscript{2} in the mixture to be identified and used to determine the optimum conditions for the following investigations and final heat treatment.

The first weight loss stage in TGA (Stage I) and the three endothermic peaks identified by DTA (A–C) are thought to comprise the decomposition of both Darvan821A and water. Despite the appearance of several weight loss steps and thermal peaks in the decomposition of pure Darvan821A between room temperature and 120°C (Figures 9.2.2.1.1(a) and (b)), only a few thermal peaks and a single continuous weight loss could be identified for the (BaSrCO\textsubscript{3})\textsubscript{2}/dispersant material over the same temperature range (Figures 9.2.2.1.2(a) and (b)). Most probably the absence of the corresponding thermal peaks is because of the very low amount of Darvan821 present in the mixture (1wt%), resulting in very low intensities of the thermal and TG peaks below the detection limits of these systems.

As with the results discussed for the integrated cathode design (Section 8.3.1.3), the endothermic peaks identified by DTA at 800°C, 930°C and 960°C (D, E and F) can be attributed to the phase transformation of BaCO\textsubscript{3} from orthorhombic to hexagonal (D), of SrCO\textsubscript{3} (E) and of BaCO\textsubscript{3} from hexagonal to cubic (F) respectively, as discussed for the thermal analysis of BaSr(CO\textsubscript{3})\textsubscript{2} (Section 8.3.1.3).
The weight loss between 760°C and 1130°C (Stage III) in TGA and the corresponding endothermic peak (G) identified by DTA at 1045°C were both due to the conversion of BaSr(CO₃)₂ to BaSrO₂, according to the thermal analysis results obtained for pure BaSr(CO₃)₂. The conversion reaction stopped at 1130°C and no reaction happened after that. These results mirror those obtained for the carbonate components of the integrated cathode discussed in Section 8.3.1.3 and no further explanation is given here.

### 10.2.2.1.3. Effect of heat treatment on the composition of the as heated two-layer/impregnated oxide cathode

As with the previously discussed systems, the thermal analysis data primarily provide information on the composition of the cathode material after heat treatment. The compositional requirement for this final heating process for the two-layer/impregnated cathode material include: (1), complete removal of the dispersant (Darvan821A) during the lower temperature stage sintering; (2), that BaSr(CO₃)₂ can be converted completely to BaSrO₂ under the heat treatment conditions of the second stage.

Again, for simplicity in the following calculations, it is assumed that the distribution of every component is homogeneous, with the initial compositions of the materials in the suspension being 99wt%BaSr(CO₃)₂ and 1wt% Darvan821A.

The composition of the (BaSrCO₃)₂/Darvan821A mixture after heat treatment can be calculated as following:

(i). Stage I.

For the decomposition of Darvan821A in the BaSr(CO₃)₂/dispersant mixture, the thermal analysis didn’t show clearly the completion temperature of the Darvan821A decomposition because the removal of water in the material happens at these temperatures as well. However, it is still reasonable to assume that the dispersant (Darvan821A) could be removed completely by 150°C (first stage temperature used) with no residue being left in the material according to the following reason: (1), the quick decomposition process of pure Darvan821A and the low completion temperature (Figures 9.2.2.1.1(a) and (b)); (2), the small composition of Dravan821A in the mixture; and (3), the similar water removal temperature in pure BaSr(CO₃)₂ as shown in Figure 7.3.3(a).
According to this assumption, it was decided that the atmosphere switch temperature for this heating process would be 150°C. Water can still be removed by 560°C according to the thermal analysis (Figure 9.2.2.1.2(a)).

(ii). Stage III.

The practical composition of BaSr(CO₃)₂ in the sample was 97wt% with the remaining 3wt% being water and Darvan821A which were removed on heating below 560°C.

The theoretical decomposition percentage for 97wt% BaSr(CO₃)₂ can be calculated as:

\[ \Delta W_T \% = 97 \times 28 \text{wt}\% = 27.16 \text{wt}\% \] 10.2.2.1.2(i)

where 28wt% is the theoretical weight loss of a 100wt% BaSr(CO₃)₂ sample as calculated previous in Section 8.2.1.3.

By 1130°C, the actual weight loss due to conversion of BaSr(CO₃)₂ was 25wt% by weight, which is only 92% of the theoretical weight loss according to the following calculation:

\[ \Delta W \% = \frac{25 \text{wt}\%}{27.16 \text{wt}\%} \times 100 \text{wt}\% = 92.05 \text{wt}\% \] 10.2.2.1.2(ii)

The slightly lower percentage completion of the conversion reaction at these temperatures (1130°C) compared to the behaviour of the integrated cathode at 1170°C discussed in Section 8.3.1.3 is consistent with the temperature dependence of the reaction 3.1.2 as discussed in Section 3.1.2 on the basis of the literature reported in that section. Such a temperature is expected to be adequate to allow complete conversion under higher vacuum conditions.

According to the thermal analysis results, 1110°C and 1150°C were chosen as the highest temperature of the second sintering stage to investigated the other properties of the as heated two-layer/impregnated oxide cathode.
10.2.2.2. Effects of high temperature heat treatment process

10.2.2.2.1. Effect of high temperature heat treatment process on the microstructure of the surface of the two-layer/impregnated oxide cathode

The aim of the heat treatment process was to achieve the conversion of the BaSrCO₃ to the oxide form and to obtain adequate mechanical strength whilst still retaining suitable porosity. Sintering of the solid materials can be observed in the as heated cathode coating material reported in Figures 9.2.2.2.1(a) to (e), indicating the occurrence of the material transportation at the temperatures used, as predicted by sintering theory as described in Section 4.3.2. During this process necks were formed by material at the convex surface transporting to the contact points between particles, causing these particles to connect into aggregates and also apparently smoothing the surface.

The principal process occurring during this heat treatment appears to be coarsening rather than densification evidenced by the relatively high porosity in the as heated material, especially for the cathode material sintered at 1100°C which had a porosity (58%) which was apparently higher than that of the cathode material before heat treatment (50%) with increased number and size of large pores. This is beneficial as coarsening rather than densification is not detrimental on the retention of the necessary pore structure in the material. The porosity was thought to be strongly influenced by morphologies of the solid phase in the cathode coating material before heating. Although the amount of the agglomerates in the coating material before heating is relatively low, they would be expected to be still an important source for the pores. According to other published studies, on heating these have a tendency to sinter together into larger aggregates and create large pores between the sintered aggregates which are subsequently difficult to eliminate. It is also known that the presence of agglomerates in the green body dissipates the driving force for densification during heating. Moreover, the presence of both cubic-like and rod-like shaped particles in the green body as shown in Figure 9.2.1.4(c) also led to low packing densities and thus also promoted the formation of porosity. The generation of pores in the cathode coating material should not be regarded as a disadvantage of the cathode manufacturing process. The thermal analysis result in
Sections 9.2.2.1.2 and 10.2.2.1.3 confirm that the complete decomposition of $\text{BaSr(CO}_3\text{)}_2$ to $\text{BaSrO}_2$ occurred during sintering. The decomposition of $\text{BaSr(CO}_3\text{)}_2$ was expected to decrease the volume of the particles during heating.

Although it is not possible to determine the exact sintering mechanism during sintering of the material from the results in this investigation, it is possible to make some reasonable assumptions: given that the material investigated ($\text{BaSr(CO}_3\text{)}_2$ and $\text{BaSrO}_2$) would be expected to have low vapour pressure at these temperatures and on the evidence of the coarsening rather densification which primarily occurred during heating, it can reasonably be assumed that it was mainly surface diffusion that governed the sintering process, especially for the heating process at 1100°C.

However, some evidence of densification was observed, especially in the material heated to slightly (50°C) higher temperature. The reduction of porosity from 58% (1100°C) to 56% (1150°C) and more significantly, the tendency for the pores to change from round-shape to cylindrical shape are both indicative of the enhancement of mass transportation with higher temperature, indicating a transition to intermediate stage sintering as discussed in Section 4.3.2.3.2.\textsuperscript{51,95,135}

10.2.2.2. Comparison to the microstructure of the coating material of the conventional oxide cathode

Despite the apparent difference in the microstructures between the two-layer/impregnated cathode and conventional cathode before heat treatment, the difference between these two materials after heat treatment was not so apparent, as shown in Sections 9.2.2.2.1 and 9.2.2.2.2. This can largely be attributed to the effect of the heat treatment which tended to result in the formation of aggregates even where these were not initially present.

However, the different microstructures before heating still resulted in some differences between the materials after heating. The much smaller particles/agglomerates and much reduced number of large agglomerates in the two-layer/impregnated cathode material compared to the conventional cathode material before heating resulted in smaller sized and fewer aggregates in the former material for the same sintering temperature and time. Similarly, the lower amount of large pores in the two-layer/impregnated cathode than in the conventional cathode after heating as revealed by the image analysis (Figures 9.2.2.2.1(g) and 9.2.2.2.2(b))
can be ascribed to the lower porosity of the former material before heating as discussed in Section 10.2.1.2.

As for the much increased amount of cracking in the conventional cathode after heating than the two-layer cathode, it is believed that these cracks are probably be generated in the same way as those in the integrated cathode material after heating (Figure 7.4.2). When the converted cathode was left in the ambient atmosphere after it was taken out from the furnace and before it was sealed in to the vacuum chamber for SEM, $\text{BaSrO}_2$ can react with $\text{CO}_2$ and moisture as introduced in Section 3.1.5 generating volume changes associated with these reactions leading to cracks similarly to the integrated cathode material discussed in Section 8.4.1. It appears that the use of a more porous substrate provided the opportunity for the materials in the two-layer/impregnated cathode to accommodate these volume changes with generally less stress in the oxide/carbonate material as the reactions with the atmosphere occur. This would appear to be an additional potential benefit of this process, which might ultimately allow initial processing to be carried out in air (at much lower cost) rather than in vacuum as currently used for the conversion reactions and binder removal.

10.2.2.2.3. Effect of sintering on the microstructure of the interfacial layer of the two-layer/impregnated oxide cathode

The sintering of $\text{BaSrO}_2$ and Ni at the interface of the two-layer/impregnated cathode, as revealed in Figure 9.2.2.2.2.3(a) and (b), indicated very strong bonding between the Ni substrate and coating layer, which is thought to be crucial in keeping the integrity of the cathode during operation.

Some evidence of partial fusion (liquid phase sintering) could be found in both the conventional oxide cathode (Figure 9.2.2.2.2) and the interfacial layer of the two-layer/impregnated cathode (Figures 9.2.2.2.3(a) and (b)), but no evidence of fusion can be found on the surface layer of the two-layer/impregnated cathode. Due to the absence of fusion in the surface material and also considering the melting temperature of barium strontium oxide in comparison to the temperature used in the experiments (1100°C), it can be assumed that direct melting as a result of excessive temperature is not the reason for this fusion phenomena and this effect is rather problematic to explain. One possibility is that this effect is associated with a reaction between nickel and the $\text{BaSrO}_2$ to form a lower melting temperature phase.
although this could not be confirmed from literature and requires further investigation to fully explain.

10.2.2.3. Effect of heat treatment on the penetration of Ba and Sr

The effect of the higher temperature heat treatment stage on the distribution of Ba, Sr in the two-layer/impregnated cathode can be shown clearly by comparing the distribution before heating (Section 9.2.1.3.2) and after heating (Section 9.2.3.3), which showed the promotion of Ba, Sr penetration through Ni substrate during heating.

The driving force for the penetration of Ba, Sr into the Ni substrate was the concentration gradient of Ba and Sr through the Ni substrate thickness both before and after heating, resulting in diffusion of Ba and Sr. During sintering, this diffusion reaction is promoted because of the increase in the diffusion coefficient, according to the Arrhenian relation as described in equation 4.4(ii)\(^{77,194}\) (Section 4.4).

Theoretically, the diffusion should progress until there is no concentration differences between different areas and from the evidence of the EDX maps in Figures 9.2.2.2.4(c) and (d), and evidence that this was achieved as least in the case of Ba is given by the intensity and distribution of Ba, Sr in SEM dot maps across the whole thickness of Ni substrate after heating.

However, it was interesting to find that despite the smaller radius of Sr\(^{2+}\) than Ba\(^{2+}\), which might be expected to result in higher diffusivity,\(^{241}\) the diffusion rate of the Ba was apparently higher in this system, as evidenced by the EDX mapping after heat treatment which showed that distribution of Sr was more concentrated in the upper layer of the cathode (Figures 9.2.2.2.4(c) and (d)). As mentioned in Section 4.4, the diffusion of Ba and Sr have been investigated as trace elements in various studies.\(^{171-174}\) However, it is difficult to infer too much from these studies which were all based on geological systems which are very different in scale and conditions. No information could be identified in the literature for the diffusion of these elements in conventional cathodes.
10.2.2.4. The final determination of the heat treatment conditions

10.2.2.4.1. Effect of the sintering process on the composition of the as heated two-layer/impregnated oxide cathode

Apart from the thermal analysis, the composition of the cathode material after the final heat treatment can be finally identified by the assistance of EDX analysis of the resultant material.

It has been assumed in Section 10.2.2.1.3 that the dispersant (Darvan821A) can be decomposed completely before 150°C in air and initial heat treatment up to this temperature was carried out in air before switching to N₂/H₂ atmosphere for higher temperatures. The EDX analysis (Figures 9.2.2.2.1(c) and 9.2.2.2.1(f)) of the cathode materials after heating at both 1100°C and 1150°C appears to confirm this supposition and no element could be found in the as heated cathode material related to the dispersant (carbon and nitrogen). However, it should be noted that there might be small amount of dispersant (trace levels) left below the detection limit of the EDX equipment.

As for the barium and strontium carbonates and oxides, the EDX analysis (Figure 9.2.2.2.1(c) and 9.2.2.2.1(f)) showed no evidence of carbon left in the as heated material after heating at 1100°C or 1150°C. This appears to contradict slightly the result of the thermal analysis results reported in Section 9.2.2.1.2 which showed a temperature of 1130°C was required to complete the BaSr(CO₃)₂ to BaSrO₂ conversion process. Most probably this discrepancy can be attributed to the longer (30 minutes) heat treatment time used compared with the thermal analysis results obtained under a 5°C/min heating rate with this providing enough time for the decomposition reaction to finish. Another possibility is that the remaining 2wt% BaSr(CO₃)₂ (according to the TGA results in Figure 9.2.2.1.2(a)) did not decompose. The remaining 2wt% BaSr(CO₃)₂ equates to only 0.2wt% carbon left in the sample, which is again too low to be detected by the EDX. It should be noted that there is not an exact value for the detection limit of EDX as it will depend on what other elements are present (the limit will be higher for heavier elements) and the spread of the trace element.

However, it has been determined that actually carbon is not a problematic impurity for the oxide cathode, as long as it is kept at a low concentration. During
operation carbon is commonly used as one of the activators for the oxide cathode.\textsuperscript{[40]} Thus it can be considered that even in the worst case, the residual approximately 0.2wt% of carbon left in the oxide cathode would not be expected to affect the performance of the cathode.

10.2.2.4.2. \textit{Final determination of the optimum heat treatment conditions}

The optimum heat treatment conditions can be finally decided from both the composition and the microstructure of the as heated cathode material.

For the heat treatment of the two-layer/impregnated cathode, the objective of the low temperature stage heating is to completely remove the dispersant, whilst depressing the undesirable oxidation of the Ni component as much as possible. Air was again chosen as the atmosphere for the initial heat treatment to allow the most effective removal of the dispersant. The value of 150°C chosen as the maximum temperature for the low temperature heating process was based firstly on the fact that the dispersant could be fully decomposed below 150°C in air according to both the thermal analysis and the EDX analysis, and secondly from the fact that this temperature was also sufficiently low to prevent the oxidation of Ni in the Ni substrate, simplifying the subsequent investigation and process, in that no concern is needed for the reduction of NiO in the higher temperature heating process, which might be expected to result in significant structural changes, shrinkage and possible loss of integrity of the structure.

The high temperature heat treatment stage required for complete BaSr(CO\textsubscript{3})\textsubscript{2} conversion required the use of a protective/reducing gas environment as in the integrated cathode material, to avoid oxidation of the Ni and reversal of the calcination reactions. The protective/reducing atmosphere, N\textsubscript{2}/5%H\textsubscript{2}, as used in the integrated oxide cathode material, is a suitable medium allowing the conversion reaction to take place. From the experimental results, 1100°C was determined to be the maximum temperature which allowed the production of a suitable cathode material with complete BaSr(CO\textsubscript{3})\textsubscript{2} conversion, a porous microstructure of the coating material, strong bonding of the coating material and Ni substrate by sintering of BaSrO\textsubscript{2} and Ni and most importantly, very similar porosity (58%) to that of the conventional oxide cathode material (60%), which is one of the ultimate objectives in this project.
10.3. Characteristics of the two-layer/impregnated oxide cathode

From the various results regarding the properties of the two-layer/impregnated cathode and the discussions above, the principal characteristics of the impregnated cathode and its manufacturing process can be concluded. In the following sections these characteristics are reviewed.

10.3.1. Features of the two-layer/impregnated oxide cathode

The design concept of the two-layer/impregnated oxide cathode is largely a development of the concept of the integrated oxide cathode, as described in Section 8.1.1. In the case of the two-layer/impregnated design, the advantages outlined for the integrated oxide cathode over the conventional cathode design are further enhanced as discussed below.

(1). Improvement to the electron conductivity.

As mentioned in Sections 2.1.2 and 8.1.1, the emission property of the oxide cathode is largely dependent on the conductivity of electrons inside the coating layer. However, as discussed in Section 8.4, in the case of the integrated cathode materials, the poor distribution of the Ni filaments and the effective coating of these Ni filaments by BaSrO₂ after heating inhibits them from effectively forming a continuous network.

However, for the two-layer/impregnated cathode, an effectively interconnected Ni network was formed within the Ni substrate as shown by the experimental results. This percolating Ni network throughout the whole cathode is therefore anticipated to improve the electron conductivity of the two-layer/impregnated cathode, and subsequently result in enhanced electron emission property in comparison to both the conventional oxide cathode and the integrated oxide cathode.

(2). Improvement to the reactions between activators and BaO.

As mentioned in Section 8.1.1 the distribution of the activating elements, which are normally present in the form of alloying additives within the Ni metal, also plays an important role in the initial activation and long-term operation of the oxide cathode. A shorter diffusion path length for them to reach the BaO leads to quicker activation according to the reactions described in Section 2.4.2 for the electron emission of
the oxide cathode. As discussed in Section 8.4.2, one likely effect of the poor distribution of Ni in the integrated cathode is that the resultant poor distribution of the activators would affect the performance of the cathode by increasing diffusion path length and thus activation time.

However, for the two-layer/impregnated oxide cathode, the Ni substrate of the two-layer/impregnated cathode with its homogeneous microstructure provides the potential for much improved and homogeneous distribution of the activators, than the integrated cathode and thus should result in easier and better reactions between activators and BaO.

(3). Reduction of the formation of continuous interfacial layer and its subsequent damage to the cathode.

As discussed in Section 8.1.1, the more homogeneous distribution of the activator inside the cathode material is advantageous to avoid the formation of a continuous high resisting layer at the substrate/coating interface which is detrimental to the performance of the conventional oxide cathode. In comparison to the integrated cathode where this effect might also occur in the regions of high nickel/activator content as shown in Figure 7.4.3(b) this possibility can be decreased significantly by the homogeneous distribution of the Ni in the two-layer/impregnated cathode, and hence of the activators which will be alloyed with them.

The two-layer/impregnated oxide cathode also allows the biggest disadvantage of the integrated cathode, poor mechanical strength (as discussed in Section 8.4) to be overcome. The pre-formed Ni substrate of the two-layer/impregnated cathode, providing mechanical support as a result of the early stage sintering and neck formation between the Ni particles which occurred during heating as discussed in Section 10.1.3.2.

In addition, there are a number of other advantages that this design can offer over the conventional cathode.

(4). Larger emitting area of the two-layer/impregnated oxide cathode than the conventional oxide cathode.

The absence of emitting material at the edge of the conventional cathode as shown in Figure 9.2.2.3(b) contrasts with the cathode surface of the two-layer/impregnated cathode as shown in Figure 9.2.2.3(a) in which the entire
surface is capable to contribute to emission, with the practical diameter of emitting surface of the two cathodes being 1.2mm and 1.4mm respectively, providing the two-layer/impregnated cathode an increase of 36% in emission area compared to a conventional oxide cathode of the same nominal size as calculated as follows:

$$\Delta S\% = \left( \frac{S_{\text{impregnated}} - S_{\text{conventional}}}{S_{\text{conventional}}} \right) \times 100\% = \frac{\pi \times 1.4^2}{4} - \frac{\pi \times 1.2^2}{4} \times 36\%$$  

The absence of BaSrO$_2$ at the edge of the conventional cathode responsible for the effective reduction in emitting surface area inherently results from the spraying process, during which, as introduced in Section 2.3 a mask is used on the Ni cap when BaSr(CO$_3$)$_2$ is sprayed on it, which then prevent the deposition of BaSr(CO$_3$)$_2$ at the edge of the Ni cap. Such an effect is avoided by the alternative cathode design developed here.

(5). Better adherence between the BaSrO$_2$ and Ni.

The structure of the conventional oxide cathode makes it inherently susceptible to poor adhesion between the BaSrO$_2$ layer and the Ni alloy substrate. In service this may arise as a result of the formation of the interface layer as has been described in Section 2.5. The effect may also arise from the conversion from BaSr(CO$_3$)$_2$ to BaSrO$_2$ which will cause volume change while there is no volume change in the Ni cap underneath and this can then cause the debonding of the two materials.

The bonding of the coating material and the Ni substrate in the two-layer/impregnated cathode is considered to be inherently stronger as a result of both the penetration of BaSrO$_2$ into the porous Ni substrate (Section 9.2.2.2.4) which provides mechanical interlocking and more importantly, the sintering of BaSrO$_2$ and Ni filaments as shown from the SEM images (Figures 2.2.2.3(a) and (b)) after heat treatment, which can be supposed to provide very strong bonding between these two materials.
10.3.2. Main features of the new manufacturing process

As with the manufacturing process developed for the integrated cathode design, the main benefit of the manufacturing process for the two-layer/impregnated cathode over conventional oxide cathode was the improvement in material wastage/efficiency and the associated reduced environmental impact. The manufacturing process of the two-layer/impregnated cathode is also very similar to that of the integrated cathode material being based around on the use of casting processes. Generally, it has the following features compared with the integrated cathode and the conventional cathode.

(i). The simplicity of the manufacturing process.

Due to the structure designed for the two-layer/impregnated cathode, the manufacturing process comprised two parts, the preparation of a porous Ni substrate and then the complete cathode structure as described in Section 6.2.2. Although this manufacturing process is not as simple as that of the integrated cathode material in terms of the number of the process operations, when compared to that of the conventional cathode, there is no additional complexity as concluded in Figure 10.3.2 (final page). It can be concluded that the manufacturing complexity of the two-layer/impregnated cathode is likely to be broadly comparable to that of the conventional oxide cathode, excluding the cost benefits of substantially reduced wastage and environmental impact.

(ii). Lower wastage

Probably the most significant feature and advantage of the manufacturing of two-layer/impregnated oxide cathode is the much improved usage of the active BaSr(CO₃)₂ components compared to the currently used spray deposition process. In the case of the cathode produced by the process as described in Section 6.2.2.3, the wastage of material can be reduced to negligible levels. This decrease in BaSr(CO₃)₂ wastage from over 90% in conventional cathode and 55% wastage in integrated cathode (calculated in Section 8.1.2) to almost 0% waste can greatly improve the cost of the oxide cathode and also decrease the environmental impact of the manufacturing process.
(iii). Less environmental impact.

The highly efficient usage of BaSr(CO$_3$)$_2$ in the new manufacturing process inherently results in significantly decreased environmental impact compared to the process used in the production of the conventional cathode. As discussed in Section 8.1.2 for the integrated cathode, the aqueous system developed for the process also provides substantial benefits in terms of environmental impact and lower price compared to the current organic solvent based systems.
10.4. Summary-Viability of the two-layer/impregnated oxide cathode

In conclusion, the viability of the two-layer/impregnated oxide cathode and its manufacturing process can be summarised based on all the properties discussed previously.

As for the structure of the two-layer/impregnated oxide cathode, it can provide a cathode of (1), satisfactory mechanical strength for handling during the whole process; (2), satisfactory microstructure with very close porosity to that of the conventional oxide cathode after heating under the same conditions; (3), strong bonding between the emitting material (BaO) and the Ni substrate.

As for the manufacturing process developed for this cathode, the most apparent advantage of it is the almost zero wastage of BaSr(CO₃)₂ during the process, significantly decreasing materials costs during manufacture and resulting in much lower environmental impact than the conventional spray deposition process. Moreover, the new manufacturing process is comparable to the conventional manufacturing process in terms of the complexity.

This alternative design and manufacturing process can be concluded to offer an attractive option for future manufacture of the two-layer/impregnated oxide cathode which appears to meet all the requirements for the new oxide cathode and is considered to be a promising alternative new cathode to the conventional oxide cathode.
Fig 10.3.2. Manufacturing process of (a). Conventional oxide cathode; and (b). Two-layer/impregnated oxide cathode.
Part Six

Conclusions and Future Work
Chapter 11

Conclusions

11.1. The integrated oxide cathode and its manufacture process

(1). The integrated oxide cathode is essentially in the form of a porous pellet with the material being a mixture of BaSrO₂ and Ni. The manufacturing process developed for it comprises casting to obtain the precursor material (BaSr(CO₃)₂/Ni) followed by a heating process for additives removing, BaSr(CO₃)₂ conversion and partial sintering. The experiments showed that it is a simple manufacturing process which comprises fewer process steps and lower wastage of BaSr(CO₃)₂ (55%) than that of the conventional manufacturing process for the oxide cathode (90%). (See Section 8.1)

(2). The optimum composition of the casting suspension for obtaining precursor material with appropriate properties is 50wt%(BaSr(CO₃)₂/Ni), 50wt%polymer mixture, which contains 20wt%PVA/20wt%PEO/10wt%PEG, and a solid content of 13.3wt%. (See Section 8.2.1 and 8.2.2)

(3). The heat treatment process determined for the integrated cathode includes an initial heating stage from room temperature to 500°C in air and a dwelling time of 30 minutes to remove the processing additives and a second heating stage from 500°C to 1100°C in N₂/5%H₂ and a dwelling time of 30 minutes for BaSr(CO₃)₂ conversion and partial sintering. Satisfactory porous microstructure with porosities of 50% could be obtained in the as heated integrated cathode. (See Section 8.3)

(4). The main disadvantage of the integrated oxide cathode is the low mechanical strength of the as heated cathode and the lack of interconnection of the Ni filaments inside the cathode. It is considered that this cathode structure is not a suitable candidate to replace the currently used oxide cathode. The two-layer/impregnated design was thus developed as an alternative. (See Section 8.4&8.5)
11.2. The two-layer/impregnated oxide cathode and its manufacture process

(1). The two-layer/impregnated oxide cathode comprises a porous, sintered Ni substrate with BaSrO₂ distributing both on it as a coating layer and impregnating in it. The manufacturing process of this cathode includes the preparation of the porous Ni substrate followed by the application of BaSr(CO₃)₂ particles onto the Ni substrate to form the whole cathode. The most important advantage of this manufacturing process is its remarkably low (potentially zero) material wastage of BaSr(CO₃)₂. (See Section 10.3)

(2). The preparation of the porous Ni substrate comprises casting to obtain a Ni/polymer precursor material and the subsequent heating step to remove the polymers and produce pores. The results showed that the optimum composition of the casting suspension for obtaining a Ni precursor film with appropriate properties was 15wt%Ni, 85wt%polymer mixture, which contains 34wt%PVA, 34wt%PEO, 17wt%PEG and a solid content of 13.3wt%. (See Section 10.1.1)

(3). A two-steps heating process: a low temperature heating stage from room temperature to 500°C in air and a dwelling time of 30 minutes and a high temperature heating stage from 500°C to 700°C in N₂/10%H₂ and a dwelling time of 30 minutes, is proven to be the proper heating conditions to obtain the appropriate composition, macrostructure and microstructure for the porous Ni substrate. The resultant Ni substrate has a highly porous (59%) percolating conductive Ni framework. (See Section 10.1.3)

(4). The two-layer/impregnated oxide cathode is produced by applying BaSr(CO₃)₂ containing suspension onto the Ni substrate using a hypodermic syringe. The BaSr(CO₃)₂ suspension contains 13.04wt%BaSr(CO₃)₂, 0.13wt% Darvan 821A as dispersant and water as liquid, which results in a cathode with a semi-impregnated structure with a coating layer consisting of small particles (1-2μm) and a porosity of 50%. (See Section 10.2.1)
(5). The heat treatment of the two-layer/impregnated cathode includes an initial heating stage from room temperature to 150°C in air plus a dwelling time of 30 minutes and a second heating stage from 150°C to 1100°C in Nz/10%H₂ plus a dwelling time of 30 minutes. The resultant cathode has a multilayer structure in which the emitting BaSrO₂ compound is incorporated onto and into the porous Ni substrate. A porous microstructure can be obtained both in the coating layer with a porosity of 58% and inside the cathode with a porosity of 61% at the interface. (See Section 10.2.2)

(6). On the basis of these observations, the two-layer/impregnated oxide cathode appears to be a very promising alternative that can potentially be used to replace the currently used oxide cathode. (See Section 10.3&10.4)
Chapter 12

Future Work

The characteristics of the newly developed two-layer/impregnated oxide cathode produced in this work allow the promising emission performance of this new cathode structure to be expected. However, there are a number of areas in this work from which further investigations is required.

(1). The BaSr(CO₃)$_2$ suspension with both dispersant and ultrasonic treatment was investigated after heat treatment in this project. However, we think that the suspension with only the dispersant is also worth investigating because the morphologies of the BaSr(CO₃)$_2$ particles and agglomerates were quite similar to those in the conventional oxide cathode.

(2). The cathode systems developed in this work could not be tested for emission. In order to produce a functional cathode, a viable process is required in which the activator elements can be alloyed into the Ni powder or otherwise suitably added to the system. This is the next logical step in the development of the process.

(3). Although comparable emission performance of the new cathode to that of the currently used oxide cathode is expected due to the similar microstructure of these two cathodes, the emission characteristics of the new cathode have not been determined in this project. A full study of the emission properties of the new oxide cathode is thus needed once the issue of activator addition has been resolved.
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