Investigation of single-step sintering and performance of planar and wavy single-chamber solid oxide fuel cells

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INVESTIGATION OF SINGLE STEP SINTERING AND PERFORMANCE OF PLANAR AND WAVY SINGLE CHAMBER SOLID OXIDE FUEL CELLS

Yunus Sayan

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University, School of Aeronautical and Automotive, Chemical and Materials Engineering (AACME)

December 2018

Supervisors: Dr Houzheng Wu, Dr Hongtao Zhang, Dr. Jung-Sik Kim

LOUGHBOROUGH UNIVERSITY

UNITED KINGDOM
ABSTRACT

Single step co-sintering is proposed as a method to minimise the time and cost of fabricating solid oxide fuel cells (SOFCs). Such a methodology is attractive but challenging due to the differing sintering behaviours and thermal mismatch of the constituent materials of the anode, cathode and electrolyte in solid oxide fuel cells. As a result it is likely that compromises are made for one layer with respect to optimising another. The single chamber solid oxide fuel cell (SC-SOFC) has not seen widespread adoption due to poor selectivity and fuel utilisation, but relaxed some of the stringent SOFC requirements such as sealing, and the need for a dense electrolyte layer. Thus, to initiate the study into single step co-sintering, the single chamber SOFC is earmarked as the first candidate. The effect of single step co-sintering on cell performance is also an attractive area to investigate. Therefore, in this study, a new co-sintering process (single step co-sintering) was applied to fabricate three different types (in terms of the supporting structure) of planar SC-SOFCs (the anode, cathode and electrolyte supported planar cells) and anode supported wavy types of SC-SOFC in order to reduce fabrication cost and time owing to effective fabrication process. In addition, their performances were tested to establish functionality of the sintered specimens as working electrochemical cells as well as to investigate the maximum performance possible with these cells under single chamber conditions. Moreover, it is also aimed to improve the performance of SC-SOFCs by extending TPB (Triple phase boundary) via wavy type.

This study presents a single step co-sintering manufacturing process of planar and wavy single chamber solid oxide fuel cells with porous multilayer structures, consisting of NiO-CGO, CGO and CGO-LSCF as anode, electrolyte and cathode respectively. Pressure of 2 MPa, with the temperature at 60°C for 5 minutes, was deemed optimal for the hot pressing of these layers. The best result of sintering profile was obtained with heating rate of 1°C min⁻¹ to 500°C, 2°C min⁻¹ to 900°C and 1°C min⁻¹ to 1200°C with 1 hour dwelling; the cooling rate was 3°C min⁻¹. Hence anode supported SC-SOFC (thickness: 200:40:40 μm, thickness ratio: 10:2:2, anode (A): electrolyte (E): cathode (C)) was fabricated via a single co-sintering process, albeit with curvature formation at edges. Its performance was investigated in methane-oxygen mixtures at a temperature of 600°C. Maximum open circuit voltage (OCV) and power density of the anode supported planar cell were obtained as 0.69 V and 2.83 mW cm⁻², respectively, at a fuel-oxygen ratio of 1. Subsequently, anode thickness was increased to 800 μm and electrolyte thickness was reduced 20 μm (thickness ratio of cell 40:1:2) to
obtain curvature-free anode-supported SOFCs with the help of a porous alumina cover plate placed on the top of the cell. The highest power density and OCV obtained from this cell was 30.69 mW cm\(^{-2}\) and 0.71 V, respectively, at the same mix ratio. In addition, the maximum residual stresses between cathode end electrolyte layers of anode supported cells after sintering were investigated using the fluorescence spectroscopy technique. The total mean residual stresses along the x-direction of the final anode supported planar cell after sintering were measured to range from -488.688 MPa to -270.781 MPa.

Determination of optimum thickness and thickness ratio of the cell with the defined ideal hot pressing and sintering conditions for single step co-sintering were carried out for cathode and electrolyte supported planar cells using similar fabrication processes. Their performance changes with thickness ratio were examined. The results show that the cathode and electrolyte supported planar cells can be obtained successfully via single step co-sintering technique with the help of alumina cover plates, as with the anode supported cell. In addition, an anode supported wavy SC-SOFC was fabricated via single step co-sintering and its performance was also investigated. The maximum power density and OCV from the final curvature free cathode supported planar cell (thickness: 60:20:800 µm, thickness ratio: 3:1:20, A:E:C) was measured to be 1.71 mW cm\(^{-2}\) and 0.20 V, respectively, at a fuel-oxygen ratio of 1.6. Likewise, the maximum OCV and power density were found to be 0.55 V and 29.39 mW cm\(^{-2}\), respectively, at a fuel-oxygen ratio of 2.6, for the final electrolyte supported curvature free planar cell (thickness: 60:300:400 µm, thickness ratio: 3:15:2, A:E:C). Furthermore, a maximum OCV of 0.43 V and power density of 29.7 mW cm\(^{-2}\) were found from the final anode supported wavy cell (thickness: 800:20:40 µm, thickness ratio: 40:1:2, A:E:C) at a fuel-oxygen ratio of 1.

In essence, this study can be divided into five chapters. The first chapter addresses the overview of the research background, problem statement, aims and objective of this study as well as that of novelty and impact. In the second chapter, fundamental information is provided regarding SOFCs and SC-SOFCs in terms of working principles, main components including electrodes electrolytes, advantages and disadvantages, types, material used for each cell components, losses in the system, and so forth. Moreover, the second chapter also contains essential sintering information in order to understand how to approach sintering of ceramics or cermet to fabricate SC-SOFCs. The overall methodology of this study is explained in detail in the third chapter while experimental works are described in the chapter 4, chapter 5, chapter 6, chapter 7 and chapter 8. Chapter 5 also contains background for the fluorescence spectroscopy and a modelling technique for residual stress measurement.
between ceramic layers. The results of experiments with discussion session are also in the same chapter. The last chapter presents conclusions and the possible routes for future works of the study.

ACKNOWLEDGE

This report is a result of PhD at Loughborough University at the school of AACME. I would like to express my profound gratitude and deep respect to the people who have helped, supported and contributed to the completion of my first year in PhD.

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PUBLICATIONS

JOURNAL PAPERS


CONFERENCES

Y. Sayan, “Investigation of fabrication and performance of planar and wavy single chamber solid oxide fuel cells” East Midlands Universities Association (EMUA) Postgraduate Research Student Conference, Loughborough, United Kingdom, 1 September 2016 (Poster presentation)

Y. Sayan, H. Wu, J-S. Kim, “Single step fabrication of an anode supported planar single chamber solid oxide fuel cell and its performance”, H2FCSUPERGEN Research Conference, St Andrews, United Kingdom, 11-13 December 2017 (Oral Presentation)
## NOMENCLATURE

<table>
<thead>
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<tr>
<td>Au</td>
<td>Gold</td>
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<td>Ag</td>
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<tr>
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</tr>
<tr>
<td>Al₂O₃</td>
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<tr>
<td>Al₂O₃:Cr³⁺</td>
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<tr>
<td>α</td>
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<td>Gigapascal</td>
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<tr>
<td>H₂</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water vapour</td>
</tr>
<tr>
<td>t</td>
<td>Layer thickness</td>
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</table>
Mean curvature height

Curvature height, from top surface of alumina substrate to the peak point of the top surface of the cell

Kelvin

Kilowatt

Lanthanum

Lanthanum chromite

Lanthanum gallate

Lanthanum and ferrite doped strontium titanate

Lanthanum strontium cobaltite

Lanthanum strontium manganite

Lanthanum strontium ferrite

Lanthanum strontium cobaltite ferrite

Lanthanum nickel trioxide

Magnesium

Magnesium oxide

Micrometre

Millimetre

Millilitre

Manganese

Megapascal

Milliwatt

Nickel

Nickel oxide

Nitric oxide

Nitric dioxide

Nickel hydroxide

Oxygen

Oxygen gas

Palladium

Palladium oxide

Platinum

Partial pressure of hydrogen gas at the anode / electrolyte interface

Partial pressure of hydrogen on the anode surface

Partial pressure of hydrogen vapours at the anode / electrolyte interface

Partial pressure of the H₂O on the anode surface

Partial pressure of oxygen gas at the cathode / electrolyte interface

Partial pressure of the O₂ on the cathode surface

Ideal gas constant
R_i \quad \text{Ohmic resistance}

R_m \quad \text{Fuel-to-oxygen ration}

R1 \quad \text{Fluorescence peak one}

R2 \quad \text{Fluorescence peak two}

S \quad \text{Siemens}

Sc \quad \text{Scandium}

Si \quad \text{Silicon}

SO_2 \quad \text{Sulphur dioxide}

Sr \quad \text{Strontium}

SrO \quad \text{Strontium oxide}

Sc_2O_3 \quad \text{Scandium (III) oxide}

Sm_2O_3 \quad \text{Samarium (III) oxide}

Sm_{0.5}Sr_{0.5}CoO_3 \quad \text{Samarium strontium cobalt (III) oxide}

SrTiO_3 \quad \text{Strontium titanate}

T \quad \text{Temperature}

\nu \quad \text{Poisson ratio}

\nu_o \quad \text{Oxygen vacancy}

W \quad \text{Watt}

Y \quad \text{Yttria}

Y_2O_3 \quad \text{Yttrium (III) oxide}

Zr \quad \text{Zirconium}

ZrO_2 \quad \text{Zirconia}

\Delta \nu \quad \text{Energy change}

\eta_{\text{act}}^a \quad \text{Anode activation polarization}

\eta_{\text{act}}^c \quad \text{Cathode activation polarization}

\eta_{\text{conc}}^a \quad \text{Anode concentration polarization}

\eta_{\text{conc}}^c \quad \text{Cathode concentration polarization}

\Pi \quad \text{Piezo-spectroscopy co-efficient}

\sigma \quad \text{Stress or Residual stress}

\textbf{ABBREVIATIONS}

A \quad \text{Anode}

A:E:C \quad \text{Anode: Electrolyte: Cathode}

AFL \quad \text{Anode functional layer}

ASC \quad \text{Anode supported cell}

ASR \quad \text{Area specific resistance}

BSCF \quad \text{Barium strontium cobalt ferrite}
<table>
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<th>Acronym</th>
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<tr>
<td>BSE SEM</td>
<td>Backscatter electron Scanning electron microscopy</td>
</tr>
<tr>
<td>C</td>
<td>Cathode</td>
</tr>
<tr>
<td>CCL</td>
<td>Current collect layer</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined heat and power system</td>
</tr>
<tr>
<td>CSC</td>
<td>Cathode supported cell</td>
</tr>
<tr>
<td>DC-SOFC</td>
<td>Dual chamber Solid Oxide Fuel Cells</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>E</td>
<td>Electrolyte</td>
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<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<tr>
<td>ES</td>
<td>Electrolyte supported</td>
</tr>
<tr>
<td>ESC</td>
<td>Electrolyte supported cell</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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<tr>
<td>ERZ</td>
<td>Effective reaction zone</td>
</tr>
<tr>
<td>FC</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>FSS</td>
<td>Ferritic-stainless steel</td>
</tr>
<tr>
<td>FT-SOFC</td>
<td>Flat tubular Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>GDC</td>
<td>Gadolinium doped ceria</td>
</tr>
<tr>
<td>HT-SOFCs</td>
<td>High temperature Solid Oxide Fuel Cells</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
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<tr>
<td>IT-SOFC</td>
<td>Intermediate temperature Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
</tr>
<tr>
<td>LSC</td>
<td>Lanthanum strontium cobaltite</td>
</tr>
<tr>
<td>LSCF</td>
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<td>LSF</td>
<td>Lanthanum strontium ferrite</td>
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<tr>
<td>LSGM</td>
<td>Strontium and magnesium doped lanthanum gallate</td>
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<td>LSM</td>
<td>Strontium doped lanthanum manganese</td>
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<td>LST</td>
<td>Lanthanum doped strontium titanate</td>
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<tr>
<td>LT-SOFCs</td>
<td>Low temperature Solid Oxide Fuel Cells</td>
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<td>MIEC</td>
<td>Mixing ionic electronic conduction</td>
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<td>MT-SOFCs</td>
<td>Micro tubular Solid Oxide Fuel Cells</td>
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<td>Ni-GDC</td>
<td>Nickel-Gadolinium doped ceria</td>
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<td>Ni-SeSZ</td>
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<tr>
<td>Ni-SDC</td>
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<td>Ni-YSZ</td>
<td>Nickel-Yttria stabilized zirconia</td>
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<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>PET</td>
<td>Polyester</td>
</tr>
<tr>
<td>R</td>
<td>Fuel to oxygen ratio</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SE SEM</td>
<td>Secondary electron scanning electron microscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>SC-SOFC</td>
<td>Single chamber Solid Oxide Fuel Cell</td>
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<tr>
<td>ScSZ</td>
<td>Scandia stabilized zirconia</td>
</tr>
<tr>
<td>SDC</td>
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<tr>
<td>SIS-SOFC</td>
<td>Segmented in series Solid Oxide Fuel Cell</td>
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<tr>
<td>SOFCs</td>
<td>Solid Oxide Fuel Cells</td>
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<tr>
<td>SSC</td>
<td>Samarium strontium cobalt (III) oxide</td>
</tr>
<tr>
<td>TD</td>
<td>Theoretical density</td>
</tr>
<tr>
<td>CTE</td>
<td>Co-efficient thermal expansion</td>
</tr>
<tr>
<td>TEMs</td>
<td>Thermal expansion mismatches</td>
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<td>TGA</td>
<td>Thermal gravimetric analysis</td>
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<td>TPBs</td>
<td>Three phase boundaries</td>
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<td>V</td>
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<td>W</td>
<td>Width</td>
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<td>YSZ</td>
<td>Yittria stabilized zirconia</td>
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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The worldwide energy demand has been swiftly increasing with increase in the production of high energy requiring devices and the world population. In parallel with this demand, fossil fuel resources have been noticeably diminishing. Additionally, fossil fuels have severe impact on environment and cause greenhouse gases leading to global warming [1–3]. Therefore, alternative fuels and energy systems have been studied so as to meet the world energy demand and diminish greenhouse gases.

Fuel cell (FC) technologies have received great attention among the alternate energy systems owing to the fact that they generate electricity in an effective, efficient and environmentally friendly method [1]. Moreover, fuel cells can be employed for applications with crucial secure energy requirement, for instance distributed systems, uninterruptable power supplies and power generation stations, and are a likely substitute for fossil fuel to meet the energy demand of rural areas where there is no access to the public grid [4]. According to the U.S Department of Energy [5], fuel cells are suitable devices for a variety of applications and markets because of their efficiency, low-to-zero emission, ruggedness, reliability, scalability and fuel flexibility (such as hydrogen, gasoline, methane, propane and so forth). Therefore, Fuel cells are promising alternative energy systems which help to minimize the fossil fuels dependence and greenhouse gas emission into the atmosphere.

Despite the all advantages, fuel cell technologies have some limitations for being used as power generating systems and to compete with the conventional power and heat producing systems. For example, impurities in the gas stream and pulse demands reduce the life span of fuel cell components. Furthermore, less durability, low power density per volume and less accessibility are other difficulties to be overcome for the improvement of fuel cell technologies [4].

Among the variety of fuel cell types, Solid Oxide Fuel Cells have (SOFCs) received great attention for efficient and clean power generation in recent years due to the fact that, (1) they have high efficiency, (2) possess fuel flexibility, (3) employ a solid electrolyte, and (4) have the capability of using a variety of catalysts [1, 6]. However, the high working
temperature of SOFCs gives rise to a number of issues on reliability and long-term stability of these cells [7]. Additionally, fuel and oxidant are sent to the anode and the cathode separately, which requires complex manifolding and gas-tight sealing, thereby leading to complex cell structure and cost [8].

In order to mitigate those issues, a novel type of SOFC, single chamber SOFC (SC-SOFC), which is SOFC with only one gas chamber, has been developed. In this type of SOFCs, there is no need for gas separation and therefore no complex manifolding and gas tight sealing [9].

1.2 PROBLEM STATEMENT

In addition to the challenges of SOFCs mentioned in the literature review in chapter 2, conventional dual-chamber SOFCs also require fuel and oxidant to be provided separately to the respective electrode in order to avoid any mixing of the fuel and oxidant. The necessity of supplying gas separately to the electrodes impose complex gas manifolding, thus complicating stack assembly as well as downsizing of SOFC systems. Furthermore, mechanically strong high temperature gas tight sealing is required to separate the SOFC into leak-proof cathode and anode compartments. The requirement of gas separation and high temperature gas-tight sealing has a severe effect on the thermal and mechanical shock resistance of SOFCs as well as their long-term stability. Moreover, complex cell designs restricts stack build-up and leads to high fabrication cost due to the severe constrains placed on material choice and fabrication cost [1, 6, 8].

Single chamber solid oxide fuel cells (SC-SOFCs), a new configuration of SOFC, were introduced by researchers to eliminate certain problems faced in dual chamber SOFCs (DC-SOFCs), such as gas-tight sealing, complex gas manifolding and flow field structures [8]. Unlike conventional SOFCs, SC-SOFCs consist of only one gas compartment containing a gas mixture of fuel and oxygen [8–11]. This characteristic property of SC-SOFCs enables them to have simplified structures, resulting in better thermal shock resistance and less start-up and shut down time than DC-SOFCs [8, 9, 12]. If their potential is realised, the simplified structure could yield a significant reduction of the total system cost. Furthermore, the electrolyte layer does not have to be dense to stop gas crossover. However, the main issue for single chamber structures is the low power output deriving from low fuel utilisation due to a lack of catalytic selectivity of the electrode materials in a mixed gas condition. One of the other major reasons is the given restriction on fuel mixing ratios, at either very rich or very
lean conditions, in order to avoid auto-ignition of the supplied fuel. Furthermore, SC-SOFCs being a subset of SOFCs, and inherit similar challenges with that of conventional SOFCs regarding sintering, material degradation, redox instability, high operating temperature, coefficient of thermal expansion (CTE) mismatch, low strength and low toughness of the cell, among other issues [8–10, 13, 14]. In addition, high fabrication cost of cells due to precise fabrication methods such as physical vapour deposition (PVD), chemical vapour deposition (CVD), pulsed laser deposition (PLD), spray pyrolysis dip coating etc. and long sintering time is also one of the drawbacks that limit the commercial viability of SC-SOFCs if employed in commercial scale.

1.3 NOVELTY AND IMPACT

In this study, a new co-sintering process was applied to fabricate the anode, cathode and electrolyte supported planar SC-SOFCs and anode supported wavy types of SC-SOFC so as to reduce manufacturing cost and time due to effective manufacturing process. The point of novelty is that green tape layers of all three layers were laminated in thickness ratios before being sintered, in opposition to the majority of works using ink or slurries and co-sintering just two layers. The other novel aspect is the fabrication and examination of a wavy shape SC-SOFC utilising a modified process of the above. Moreover, their performances were tested to establish functionality of the sintered specimens as working electrochemical cells. In addition, it is also aimed to improve the performance of SC-SOFCs by extending TPB (Triple phase boundary) via wavy type. To sum up, it is intended to increase the commercialization of SC-SOFC by mitigating its fabrication cost and time, and improving its performance.

1.4 RESEARCH AIMS AND OBJECTIVES

At present, anode-supported SC-SOFCs are fabricated using at least two sintering steps: co-sintering anode and electrolyte, followed by a separate deposition and sintering of the cathode [6, 15, 16]. The rationale for a two-step sintering is that the materials for anode, electrolyte and cathode require different sintering temperatures to achieve the expected microstructures. Though two-step sintering process decreases possible reactions between electrolyte and cathode [16], there are several reasons why single step co-sintering of SC-SOFCs are desirable, mainly pertaining to simplifying the process along with decreasing the
processing time and input energy [17–19]. These benefits of single step co-sintering of SC-SOFCs reduce further the cost of SC-SOFCs fabrication and thereby improve commercial viability if employed in commercial scale.

The aim of this study to focus on different configurations of SC-SOFCs, including the anode, cathode and electrolyte supported planar SC-SOFCs and anode supported wavy SC-SOFCs and manufactures them by applying the co-sintering method (tape casting-laminating-hot pressing-co-sintering) that a planer or wavy SC-SOFCs can be fabricated via a single production process. The goal of single step co-sintering is to simplify the cell preparation procedure and therefore to achieve a decrease in production time, energy consumption and fabrication cost. The objective of making different supported cells (anode, electrolyte and cathode supported) is to investigate the maximum performance possible with this type of sintering under single chamber condition.

The objective of making a wavy-shaped anode supported cell structure is to increase the performance of SC-SOFC by extending the effective length of TPB for the same planar area. Moreover, the goal of investigating the anode wavy cells is to avoid the issues related to cathode and electrolyte substrate and obtain the maximum performance possible with wavy cell shape under single chamber condition.

The objective of this study can be divided into the following headings:

- To perform a detailed literature review on SOFCs and SC-SOFCs in terms of different cell designs and their operating principles (such as planar design, tubular design, flat tubular design), materials used for each components, stack designs, degradation mechanisms, fuel supply methods, working temperatures, fabrication techniques and so on. In addition, sintering is also studied so as to comprehend and apply single step co-sintering methods to the SC-SOFCs fabrication.
- To prepare different SC-SOFCs (anode, cathode and electrolyte supported planar SC-SOFCs and anode supported wavy SC-SOFC) by applying the tape casting for preparing green layers (anode, cathode and electrolyte layers separately), laminating and hot pressing so as to press those green layers together in order to make them ready for single step co-sintering.
- To sinter those prepared cells at a suitable sintering temperature with heating rates regarding material properties and green tape composition by applying to Thermal gravimetric analysis (TGA), Differential scanning calorimetry (DSC) and in-site shrinkage measurement of the layers.
• To investigate the co-sintering process via in-situ observation of co-sintering process in order to understand the reason of defects occurring during co-sintering such as cracks and delamination.

• Characterisation methods (X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) etc.) are utilised to understand more about fabricated SC-SOFCs.

• To measure residual stress between cathode and electrolyte layer of the sintered anode supported planar SC-SOFCs after sintering using the Fluorescence spectroscopy technique and estimate the magnitude of stress developed during heating (due to the different shrinkage rate of layers) and during cooling (owing to the different thermal expansion co-efficient mismatch) by applying to a modelling technique used for the residual stress measurement due to the CTE misfit between ceramic layers, and deduct these results from the total residual stress in order to find residual stress developed during heating.

• To test the fabricated cells for two aims: to establish functionality of the sintered specimens as working electrochemical cells, and to identify the effects of increasing anode thickness and decreasing electrolyte thickness, which were helpful in obtaining reduced curvature, on the cell performance.
CHAPTER 2

LITERATURE REVIEW

2.1 SOLID OXIDE FUEL CELLS (SOFCs)

A SOFC is essentially described as an electrochemical energy converting device that generates electricity electrochemically by combining an oxidant and a fuel across an ion conductive oxide electrolyte made from a ceramic materials [20, 21]. Furthermore, working temperature of SOFCs ranges from 500°C to 1000°C, thus they are also determined as high temperature fuel cells. A SOFC consists of a dense electrolyte which is sandwiched between a porous anode and cathode, and the structure of anode-electrolyte-cathode sandwich is known as a single cell (see Figure 1 and Figure 2). However, the power output of a single cell is small, and thus several individual cells are connected in electrical series in order to produce high power output and usable voltage (which is known as stack design (see Figure 1)). Moreover, if much more power output is required, for instance for heavy tracks or industrial requirements, then stacks are connected in series, which is known as module.

Figure 1 shows the estimated power output with SOFCs from a single cell to a module and the systematic diagram power requirement according to various applications [7].

Figure 1 Illustration of cell, stack, and module with their mean power output for different applications [7]
2.1.1 Operating Principle of SOFCs

The working principal of a SOFC is relatively simple. Fuel (H₂ or CO etc.) is continuously sent to the fuel channel, and diffuses into the anode electrode where the electrochemical oxidation reaction occurs, and electrons are released to the external circuit. In the meantime, air is sent to the air channels and oxygen molecules in the air stream diffuse into the cathode to react with electrons coming from the external circuit to form the oxide ions. These oxide ions then travel throughout the electrolyte and react with the oxidized fuel at the anode/electrolyte interface. As a result, the direct-current electricity is generated from the electrons flow via the external circuit from the anode to the cathode (see Figure 2) [1, 20, 22, 23].

The summary of electrochemical reactions at the anode and cathode, for a carbon monoxide-fed and hydrogen-fed SOFC are given as follow.

\[
\begin{align*}
\text{CO-fed SOFC} & \\
\text{Anode:} & \quad \text{CO} + \text{O}^2 \rightarrow \text{CO}_2 + 2e^- \quad (1) \\
\text{Cathode:} & \quad \text{O}_2 + 4e^- \rightarrow 2\text{O}^2^- \\
\text{Overall:} & \quad \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \Delta\text{E} \quad (4)
\end{align*}
\]

\[
\begin{align*}
\text{Hydrogen-fed SOFC} & \\
\text{Anode:} & \quad \text{H}_2 + \text{O}^2 \rightarrow \text{H}_2\text{O} + 2e^- \quad (2) \\
\text{Cathode:} & \quad \text{O}_2 + 4e^- \rightarrow 2\text{O}^2^- \\
\text{Overall:} & \quad \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \Delta\text{E} \quad (5)
\end{align*}
\]

Figure 2 (A) SOFC single cell and (B) illustration of its flow diagram [24]
2.1.2 Advantages and Challenges of SOFCs

2.1.2.1 Advantages of SOFCs

SOFCs are a group of fuel cells in which all components are solid and their working temperature ranges from 500°C to 1000°C. Due to high working temperatures, solid-state structure and non-polluting by-products of the reaction, SOFCs offer various advantages over conventional power generating systems, and even over other FCs in terms of their fuel flexibility, efficiency, size flexibility and environmental friendliness [25]. The benefits of SOFCs can be mainly described under the following headings.

**Efficiency:** SOFCs have high chemical to electrical conversion efficiency owing to the absence of the Carnot limitation (approximately 50%). The efficiency can further increase up to 70% when produced heat is utilized in gas turbines and CHP applications, or syngas is burned in a combustion engine [25, 26].

Figure 3 compares SOFCs with different fuel cells and other conventional energy conversion systems in terms of efficiency and system size [27]. It can be clearly seen from the graph that SOFCs have higher efficiency than others.

**Fuel Flexibility:** The main fuels are used in a SOFC are hydrogen and carbon monoxide which are directly and electrochemically oxidized at the anode electrode. Due to high operating temperature (800°C to 1000°C), hydrocarbon based fuels, for instance gasoline, methane, ethanol, etc., can be also utilised in SOFCs. This is because of the fact that

![Figure 3 The efficiency and power size of different energy converting system [27]](image-url)
hydrocarbon based fuels can be directly reformed into hydrogen and carbon monoxide at the anode (called direct internal reforming) or indirect reformed at the anode side by utilizing the released heat present in the system. Therefore, there is no need for a complex and expensive external fuel reformer [6, 26].

**Low emission:** SOFCs have almost zero emissions in terms of SO₂ and NOx (NO, NO₂ etc.) and practically release only water vapour into atmosphere when hydrogen used as fuel [28]. In addition, when hydrocarbon based fuels are preferred to be utilized, they eliminate the dangers of CO in exhaust gases by converting it into CO₂ at high working temperatures [26].

**Modularity:** SOFCs can be used either single cell or stack or module to provide sufficient power outputs and desired voltage for variety of applications from portable devices and transportation applications to distributed and large-scale power production systems in both military and public sectors (see Figure 1) [7]. Furthermore, SOFCs have also decent gravimetric power density owing to availability of being designed as micro-sized with negligible weight (see Figure 4).

![Figure 4 Comparison of different energy conversion systems in terms of specific power and specific energy](image)

Besides the advantages of SOFCs mentioned above, SOFCs have the capability of using a variety of catalyst, and they do not need noble metal electrode catalysts such as Pd, Au, Pt and so forth, which could be issue in price and resource availability in high volume production. In addition, they do not have problems with electrolyte management, for instance, liquid electrolytes which are difficult and corrosive to handle. As a result, the potential
problems owing to the loss of electrolyte and corrosion are eliminated in the absence of any liquids in the cell, [1, 23, 26].

2.1.2.2 Challenges of SOFCs

In theory, SOFCs appear very promising because of their efficiency, versatility and other advantages. However, in reality they are limited with many difficulties. SOFCs have not been employed considerably in domestic and industrial applications, and are not economically competitive with other energy converting systems for the reasons of high material costs, high operating temperatures, complex cell and stack fabrications, concerns regarding handling of gases, safety issues and the cost of routine maintenance [22, 25, 29].

There are significant problems coming from materials of SOFCs themselves, and they can be described under the subheadings as follows: (1) high overpotentials consisting of mainly electrolyte ohmic losses, activation and concentration polarizations, (2) CTE mismatch, (3) sintering, (4) redox instability, (4) chemical incompatibility between each components, (5) chemical changes in material structure, (6) coarsening and/or decomposition of metal and ceramic atoms in each components, (7) high fabrication cost and time owing to the severe constrains exist on material choice and fabrication methods, (8) less strength and less toughness and so forth [1, 30, 31].

In addition, despite the fact that high working temperature of SOFCs leads to performance improvement, it also causes multiple problems on reliability and long-term stability of these cells which includes catalyst poisoning, thermal and chemical instability, high start-up and shutdown during power on and off, thermal (or mechanical) stresses, failure of the gas tight sealing, and so forth, and thereby resulting in restriction of the choice of materials for the electrodes, electrolytes, interconnect and sealants [8, 29, 32]. Additionally, according to Ormerod [23], one of the drawbacks that must be considered for certain SOFC applications is the high required time for heating up and cooling down the system. This is ascribed to utilizing a rather weak, brittle component as substrate material, and problems related to thermal expansion co-efficient mismatches (CTEs) at elevated temperatures. Such issues finally give rise to system failure and limits use of SOFCs to a greater extent. Thus, there have been significant searches on the reduction of SOFC operating temperatures to the low and/or intermediate temperatures (500°C–800°C) in recent years. The benefits of reduced operation temperature include wider choice of materials, improved reliability, reduced cost, shortening start-up and shutdown time, longer cell life and so on [22].
Moreover, a SOFC is composed of multiple components and consequently multiple interfaces, and therefore, physio-chemical phenomenon occurring at the each cell location is very complex. In order to optimize the performance and obtain high efficiency, it is very essential to comprehend prior knowledge of each phenomenon such as detailed investigations on the reaction mechanism and kinetics at anode, cathode, electrolyte, electrodes/electrolyte interfaces, and describing of deterioration mechanism [25].

Furthermore, carbon deposition and sulphur poisoning are series issues in SOFCs when hydrocarbon based fuels are utilised. Carbon deposition on the catalyst surface causes performance degradation and failure of the cell by decreasing catalyst performance and by blocking the fuel and product diffusion paths at the anode side. Similarly, sulphur poisons the catalyst and directly result in degradation of the cell performance [1, 6].

Beside these, sealing is one of the crucial issues in SOFCs. A gas-tight seal is required in SOFCs so as to separate the fuel side from the air side of the cell in order to avoid direct combustion which brings about local overheating (hot spots) and diminishes power generation efficiency [33].

2.1.3 Classification of SOFC Systems

SOFCs can be mainly categorised according to cell and stack design, their operating temperature, fuel reforming type, flow configuration and support type. They will be mentioned briefly under this heading.

2.1.3.1 Categorization According to Operating Temperature

SOFCs might be described as low-temperature SOFCs (LT-SOFCs, 400°C–650°C), intermediate temperature SOFCs (IT-SOFCs, 650°C–800°C) and high temperature SOFCs (HT-SOFCs, 800°C–1000°C). Increasing the working temperature of an SOFC enhances the electrode kinetics and mitigates the cell resistivity, and consequently results in an increase in the cell performance. Furthermore, high operating temperatures lead to a better thermal integration with other energy systems such as gas turbine, CHP, and thus result in improved thermal efficiency. Nevertheless, high operating temperatures of SOFCs brings about some substantial issues, which are mentioned briefly in section “Challenges of SOFC” such as material degradation [1, 7, 29, 31].
2.1.3.2 Categorization According to Support Type

In order to increase the performance and the mechanical strength of SOFCs, researchers have studied and manufactured different type of cells which are defined as self-supported configuration (anode-supported, cathode-supported, electrolyte-supported and external-supporting configuration (porous-substrate supported and interconnect-supported (see Figure 5) [1]. Self-supported configuration can be generally summarised as follow;

**Anode Supported:** This cell differs from the normal single SOFC by its anode thickness. The thickness of the anode is relatively high in comparison to that of the cathode and electrolyte, and the anode is mainly composed of anode functional layer (fine structure) and support layer (coarse structure which has good electron conductivity). The main advantages of this configuration are that the anode is highly conductive and lower operating temperature via utilizing of thin electrolyte. However, potential anode oxidation and the limitation of mass transport because of the thick anode is its main drawbacks [20, 34].

**Cathode Supported:** The thickness of the cathode is higher than that of the anode and electrolyte. There is no substantial oxidation issue but potential cathode reduction. In addition, the working temperature is reduced owing to use of the thin electrolyte. Nonetheless, lower conductivity as well as lack of mass transport due to the thick cathode is crucial issues that must be taken into consideration.

**Electrolyte Supported:** A relatively robust structural support from a dense electrolyte is utilised. This configuration is less susceptible to failure due to cathode reduction and anode reoxidation, but it has high resistivity owing to low electrolyte conductivity and thus requires higher operating temperature so as to mitigate electrolyte ohmic losses (ibid).

![Classification of SOFC single cell](image)

*Figure 5  Classification of SOFC single cell [20]*
2.1.3.3 Categorization According to Flow Configuration

The flow in a SOFC can be determined as co-flow, cross-flow and counter-flow (see Figure 6). The type of flow affects the temperature distribution and therefore the performance and durability of SOFCs [35, 36]. Figure 6 shows the temperature distribution of different flow arrangements. According to a study done by Zhang et al. [36] the counter-flow and co-flow configurations have better performance than that of the cross flow at the same experimental conditions. They also define that the co-flow configuration has lowest temperature in the anode and cathode inlets and increases along the flow direction as the heat is produced owing to electrochemical reactions. The maximum temperature for the co-flow is seen in the area close to the air and fuel channel outlets. They also determine that the maximum temperature attained in the counter-flow configuration is 25°C is higher than that of the cross-flow and 10°C lower than that of the co-flow at the same experimental conditions. In other words, the co-flow categorization has higher temperature than that of others. This is because of the facts that (1) the cooling effect of inlet air on the outlet temperature of the cell in the co-flow configuration is reduced along the cell by the heat produced in the three phase boundaries (TPBs), (2) the air at the inlet of cathode in the counter-flow configuration has higher cooling effect on reducing the higher cell temperature which is expected to be seen at the outlet of the anode or inlet of cathode [36]. As a result of Zhang et al. study, the highest temperature gradient is seen at the co-flow configuration. However, Recknagle et al. claims that the most uniform temperature distribution and the lowest thermal gradients can be obtained when the co-flow configuration is used for average cell temperature and similar fuel utilization [35].

Figure 6 Temperature distribution in a cell for: (A) co-flow, (B) counter-flow and (C) cross-flow arrangements [36]
21.3.4 Categorization According to Fuel Reforming Types

Hydrocarbon based fuels are reformed into CO and/or hydrogen gases in order to be used in SOFCs. This reforming process may be inside the stack of a SOFC (which is defined as internal reforming) or outside of the stack (which is described as external reforming). The internal reforming is also classified for a SOFC as direct internal reforming SOFC (DIR-SOFC), where the reforming occurs directly at the anode catalyst, and indirect internal reforming SOFC (IIR-SOFC, where the reformer section is separated from the other components inside the cell [6]. Reforming is mainly endothermic and thus brings about cooling of the stack. Therefore, an external reforming can be utilized in order to provide uniform stack temperature. However, it makes the stack more complicated and expensive. In an IR-SOFC, the reformer is in near thermal contact with the anode section. Although an IIR-SOFC is an effective method to mitigate carbon deposition issues in a SOFC, it is challenging to prevent uniform temperature distribution in the stack. Additionally, the DIR-SOFC is an promising method to make the stack of a SOFC more simpler and reduce the cost, but the carbon deposition at the anode electrode is the main problem that must be taken into account [37, 38].

2.1.3.5 Categorization According to Cell and Stack Designs

SOFCs are mainly categorized as planar and tubular according to their cell and stack designs [6]. Recently, flat-tubular types of SOFC have been studied in order to combine both advantages of the planar and the tubular SOFCs [22, 39]. Some of these types of SOFCs designs are mentioned as follow:

2.1.3.5.1 Planar SOFCs

In this design, an anode, electrolyte, cathode and interconnect are sandwiched as flat plates (see Figure 7), and the electrical connectivity is attained as series. In this configuration, interconnect separates the anode and cathode in the stack and provide electronic conductivity as well as gas channels. Fuel and air flow through channels and diffuse into the anode and cathode respectively. In addition, a sealant material is utilized so as to prevent the mixing of fuel and oxidant. Common shapes of planar SOFCs are square, rectangular and circular, and
all categories of support types (external-supporting and self-supporting) have been studied for this design [20, 25].

Figure 7 Illustration of (A) planar SOFC cell and (B) its stack [40]

Figure 8 depicts an example of planar standard cell current voltage curve and power density measured at a temperature of 700°C, 750°C and 800°C with air and humidified hydrogen (3% H₂O) as oxidant and fuel respectively. It can be clearly seen that the performance of the cell increase with increasing temperature owing to improved catalytic activity, decreased ohmic losses and so forth [41].

Figure 8 I-V curves and power densities of a standard SOFC cell made by Yoon at different operating temperatures with oxygen and humidified hydrogen as oxidant and fuel [41]

Planar SOFCs have better current density and theoretical performance than that of tubular designs owing to decreased in-plane ohmic resistance which is as a result of simpler
electrical connection between cells provided by bipolar plates. In addition, they are more compact than tubular designs as cells can be stacked with fewer voids, and consequently have better volumetric power density than that of tubular SOFCs [1]. The production cost of a planar design is also fewer than that of a tubular type since the tape casting, screen printing and other mass production methods such as plasma-spraying can be simply applied for the manufacturing of planar SOFCs [34, 42]. However, planar SOFCs have certain drawbacks including larger spaces which need high temperature for gas sealing, as well as inherently less thermal stability [34]. They are also fragile and unable to withstand rapid heating and cooling for applications which their stacks are required to reach their working temperature as soon as possible. In addition, the planar design concept requires interconnects in the stack of a SOFC to be much thicker and have channels for gas distribution while the tubular design concept has thin and stable interconnects. The thick interconnect creates sealing and thermo-mechanical stress issues due to the partial pressure gradient of oxygen across the thick plate as well as higher cell weight. Therefore, it is difficult to fabricate moderately complex and dense interconnects within precision tolerances [43]. In addition to all difficulties mentioned in this part, there are also several issues that are not mentioned here such as chromium poisoning due to metallic interconnect, chemical reaction between components, oxidation/reduction of nickel based on anode, material degradation and so forth. Some of them will be mentioned in the material section but others can be found in literature.

2.1.3.5.2 Tubular SOFCs

The cell in this design is formed as a hollow tube, and a stack is composed of a package of single cell tubes (see Figure 9) [20]. In this design, fuel is supplied on the outside of the bundle of tubes which is attached a gas manifold while air is sent on the inside of the tubes [26].
Figure 9 Illustration of different tubular cells and a stack of tubular SOFC [40, 44]

Figure 10 Electrical connect of tubular cells in a bundle of stack [45, 46]

Figure 9 depicts different design of tubular cells and an example of tubular SOFC stack. In addition, Figure 10 shows the electrical connection of tubular cells in a bundle of stack. Many methods for tubular SOFC production have been studied in recent times such as extrusion, dip-coating, iso-pressing and slurry casting. The basic fabrication of a tubular SOFC is that firstly the support component of the cell (anode, cathode or electrolyte) is extruded, and then other main components are coated on the surface of support component by dip coating or by other suitable deposition techniques. Electrical contact in a stack of tubular SOFC is throughout interconnectors located between adjacent hollow tubes. In order to
increase current and voltage, tubular cells are connected both in parallel and series, respectively [45, 46].

Figure 11 depict the power density and OCV of an anode supported tubular cell as an example. According to Duan et al. the cell performance increases with temperature increment [47].

![Figure 11](image)

*Figure 11 The performance of anode supported tubular SOFCs without (A) and with (B) PdO infiltration at different temperatures [47]*

It has been considered that tubular SOFC designs have many desirable advantages over planar designs. The main benefits are: (1) Sealing in a tubular design is less of an issue than in a planar design because there is less space (circumference) to seal it ; (2) due to the tubular/concentric structure, the cell can withstand high thermal stress caused by rapid heating up to the working temperature and therefore less start-up and shutdown time. Thus, small-scale tubular designs are expected to be commercialized in transportation and commercial applications [48]. However, the higher production cost due to complex manufacturing methods, difficulty to provide uniformly the air and fuel gas to each single cell, the penalties to area-specific and volumetric power densities owing to more voids in the stack, and long path distances for electrons to flow from anode to the cathode sides are crucial technical barriers that must be taken into consideration [49].

The diameter of tubular SOFCs can be varied from a small diameter (< 5 mm) to a large diameter (> 15 mm). The former is known as micro tubular SOFCs (MT-SOFCs) [50].
Micro Tubular SOFC

MT-SOFC was first invented by Kendall in the early 1990s for the purpose of improving the performance of tubular SOFC by the decreasing the cell diameter into micron scales [34]. Reduction of the tubular cell size is demonstrated to have potential for remarkable benefits. For example, it offers higher volumetric power output density attributed to large active area to volume ratio, better tolerance to thermal shock, quicker start-up capability due to thermal shock resistance and capability to be utilized in small scale portable applications in comparison to planar and tubular SOFCs. According to Kendall [6], a diameter of 2 mm MT-SOFCs could provide 10 times more power per stack volume than that of a diameter of 20 mm diameter tubes. MT-SOFCs are considered to be used in the small scale applications which are in the order of W to kW, stationary power production and indeed mobile power facilities [35, 51]. However, complex manufacturing processes of MT-SOFCs, which limit mass-scale production, and the difficulties of collecting current in a MT-SOFC efficiently and economically from anode and cathode as a consequence of very small diameter tube are main drawbacks that must be solved for the marketplace potential of MT-SOFCs [28].

![Diagram of Micro Tubular Anode Supported SOFC](image)

*Figure 12 Systematic illustration of a micro tubular anode supported SOFC with the stack configurations of the MT-SOFCs [27]*
Figure 12 shows an example of a MT-SOFC cell and its use in a stack. Similar to tubular SOFCs, one of the MT-SOFC components is required to support other cell components which are coated on the surface of the support tube. It can be cathode, electrolyte and anode. At present, the support tube is generally fabricated by extrusion technique and other components are coated on it [34].

Figure 13 also shows one of the gas supply system of MT-SOFC invented by Lee et al. In this design, the red conductive inlet pipe and orange wires are utilized to provide fuel and collect current from the anode.

Figure 13 The illustration of the gas supply system and current collection from the anode [52]

Figure 14 The performance of one of MT-SOFC fabricated by National Institute of Advanced Industrial Science and Technology [27]
Figure 14 illustrates the performance of a MT-SOFC made of GDC electrolyte), Ni/GDC anode and (La, Sr) (Co, Fe)-GDC cathode with a diameter of 1.6 mm. It can be seen from the graph that moderate power density was obtained at low temperature [27].

### 2.1.3.5.3 Flat Tubular SOFC Design (FT-SOFC)

Flat tubular design is the combination of planar and tubular SOFCs. Therefore it contains the both advantages of tubular and planar designs, for instance, a minimized sealing area, improved volumetric power density, high resistance to thermal cycling and so forth [22]. A flat tubular SOFC possesses the same components that of a tubular SOFC. It basically consists of an electrolyte, a cathode and an anode in a flat-tube structure (see Figure 15). It has similar methods of the fuel and air delivery with a tubular SOFC. Furthermore, it has also multiple ribs in the anode side (for anode supported flat-tubular cell) and fuel flow area is divided into several chambers by these ribs. The ribs are conductive and provide short routes for inner electron conducting circuit, and thus reduce ohmic losses and consequently improve the power density of the cells [52].

![Illustration of an example of (A) flat-tubular SOFC and (B) its stack](image)

*Figure 15 Illustration of an example of (A) flat-tubular SOFC and (B) its stack [40]*

FT-SOFs are fabricated in terms of ceramic structure but metallic support can be utilized in order to decrease the material cost and improve the feasibility of mass production [53].
2.1.4 SOFC Materials

2.1.4.1 General Requirements for the SOFC Components

As mentioned in the previous sections, a SOFC consists of three main components (an anode, electrolyte, cathode) with interconnect when more than one cell is connected to form a stack. These components are required to possess certain properties and more than one function. The components of a SOFC must have good chemical stability (undergo no chemical change) and physical stability (have sufficient dimensional and morphological stability in order to prevent the phase transition and mechanical damage of the cell) in the oxidation and reduction atmospheres at the wide range of operating temperatures. Additionally, they must possess adequate conductivity (less ohmic losses) and similar CTEs so as to avoid delamination or cracking during production and operation. Furthermore, SOFC components must also be compatible chemically with each other, and chemical interaction and elemental diffusion between each component must be minimized. They should also endure to high thermal and mechanical shock at high operating temperature, and possess a life span of ranging from 40000 hours to 80000 hours. In addition to them, high strength and toughness, easy to fabricate and low cost are other desirable requirements for these components [1, 6, 23].

2.1.4.2 Electrolyte

The electrolytes for SOFCs must possess sufficient ionic conductivity with minimum electronic conductivity in addition to required properties for the SOFC components mentioned above at cell working temperature. They must also be dense (non-porous) to prevent the mixing of the fuel and oxidant gases [6].

The Yttria stabilized zirconia (YSZ) is the most common electrolyte material employed in the HT-SOFC systems due to its favourable oxygen ion conductivity, being unreactive towards other components and good stability in both reducing and oxidising atmosphere. In addition, it has relatively low cost [6, 54].

The YSZ has fluorite structure, which is the face-centred cubic arrangement of cations with anions placing all the tetrahedral sites. This arrangement of fluorite structure leads to a large number of octahedral interstitial voids (vacancies) which provide paths for oxygen ions’ diffusion from the cathode to the anode site [6, 55]. The pure zirconia (ZrO$_2$) is in the
monoclinic structure at room temperature, and not stable with increment of the temperature. Its monolithic structure turns into tetragonal structure above 1170°C and finally become the cubic fluorite symmetry structure when the temperature is above 2300°C. Thus, some amount of dopants is doped in the pure zirconia structure in order to make it stable. Yttria ($\text{Y}_2\text{O}_3$), among other aliovalent oxides ($\text{Sc}_2\text{O}_3$, $\text{CaO}$, $\text{MgO}$), possess great solubility in zirconia in the structure of the cubic fluorite at a temperature range from room temperature to its melting point (2680°C). It also contributes to increase of the oxygen vacancies by charge compensation, and consequently enhance the oxygen ion diffusion (see Figure 16). The concentration of dopants is important to define the maximum ion conductivity of the doped zirconia electrolyte [54]. It can be determined as the lowest level of dopant oxide needed to fully stabilize the cubic fluorite phase. The ionic conductivity decreases with the increase of dopants level after the cubic fluorite structure is fully stabilised. This is attributed to vacancy clustering or electrostatic interaction. The highest ionic conductivity of zirconia was obtained with 8 mol% $\text{Y}_2\text{O}_3$ dopant at 1000°C (approximately 0.1 S cm$^{-1}$) and its CTE was measured as $10 \times 10^{-6}$ K$^{-1}$ [6].

![Figure 16 Cubic fluorite YSZ structure](image)

The solution of yttria into ZrO$_2$ fluorite phase is given by the following defect equation:

$$\text{Y}_2\text{O}_3 (\text{ZrO}_2) \rightarrow 2\text{Y}^{+3}_{\text{Zr}} + 2\text{O}^{+} + \text{V}_o$$

(6)
Where $V_o$ is the oxygen anion vacancy, $O^{x_o}$ is the normal anion in an oxide with zero effective charge and an yttrium atom occupied in the place of zirconium atom [29, 30].

The YSZ electrolyte based SOFCs generally work at an operating temperature above 850°C for high performance (note that operating temperature is defined by the temperature desired to achieve adequate ionic conductivity in the electrolyte). This high working temperature causes severe damages on materials utilized, which were mentioned in the previous sections. Thus, there are significant interests in reducing the SOFCs operating temperatures to under 700°C so as to enable the utilization of cheaper materials, and diminish fabrication cost, though providing high power outputs [23]. There are two general methods to mitigate the operating temperature of a SOFC. The first is to decrease the YSZ electrolyte thickness, and the second is to use different electrolyte materials with higher ionic conductivities (ibid). Therefore, bismuth oxide (Bi$_2$O$_3$) composition, scandia stabilized zirconia (ScSZ), doped ceria (CeO$_2$) based electrolyte, lanthanum gallate (LaGaO$_3$) and so forth were investigated and have been improved. Figure 17 compares some selected electrolyte materials in terms of their ionic conductivity according to temperature dependence.

Among these common SOFC electrolytes, stabilized Bi$_2$O$_3$ has the highest ionic conductivity (2.3 S cm$^{-1}$ at 800°C) but it is only stable at temperatures between 730°C to the its melting point 804°C, and easily reduced and decomposed into bismuth metal at the low oxygen partial pressure. Therefore, bismuth based electrolytes are still questionable for SOFCs [55, 56].

Scandia stabilized zirconia shows superior ionic conductivity at intermediated temperature and it is attributed to facts that the ion radius of Sc$^{+3}$ is close to that of host ion, Zr$^{+4}$ and the low association enthalpy of the defective reaction [6, 57, 58]. According to Zhao and his co-workers, the ionic conductivity of ScSZ at 780°C is comparable to that of YSZ at 1000°C, which ZrO$_2$ with doped 11 mol% Sc$_2$O$_3$ has a ionic conductivity of 0.3 S cm$^{-1}$ with a CTE of $10 \times 10^{-6}$ K$^{-1}$ at 1000°C [1]. Furthermore, it has also sufficient set of mechanical properties as the YSZ however the high cost of scandium is the severe issue for further commercialization of the ScSZ.

Ceria based electrolytes such as gadolinia (Gd$_2$O$_3$) doped ceria (GDC) and samaria (Sm$_2$O$_3$) doped ceria (SDC) have been reported as alternative electrolyte materials for LT–SOFCs at high oxygen partial pressure [49, 59]. The conductivity of the SDC and GDC at 750°C was measured as $6.1 \times 10^{-2}$ S cm$^{-1}$ and $6.7 \times 10^{-2}$ S cm$^{-1}$ respectively, and the conductivity of the GDC below 600°C is much greater than that of the SCSZ and YSZ (see
Figure 17). They have also similar CTEs with other cell components. In addition, the conductivities of the GDC and SDC were found to be as high as $3.8 \times 10^{-3}$ S cm$^{-1}$, $5.0 \times 10^{-3}$ S cm$^{-1}$ at 500°C, respectively [1]. However, the SDC and GDC electrolytes are partially reduced (Ce$^{4+}$ to Ce$^{3+}$) either at low oxygen partial pressure (especially on the anode side of SOFCs) or at high operating temperatures (above 600°C). This phenomenon of the ceria based electrolytes leads to the electrolyte can also conduct current, which would decrease the OCV of the cell, and consequently general cell efficiency. In order to minimize this problem, an ultra-thin interfacial electrolyte layer such as an YSZ to prevent electronic transfer can be coated between the anode and electrolyte layers. However, inter-diffusion between the YSZ and ceria could be an issue. Furthermore, the ceria-based electrolytes require sintering aid such as CuO, CoO due to their lack of sinterability [1, 60].

![Figure 17 Temperature dependence of electrical conductivity for selected oxide ion conductors][6]

Recently, magnesium (Mg) and strontium (Sr) doped LaGaO$_3$ (LSGM) has received great attention due to its low electronic and high ionic conductivity even at low partial pressure of oxygen. Though it has slightly lower ionic conductivity than that of GDC at
500°C (see Figure 17), it is more suitable to utilize this electrode at operating temperature higher than 600°C when reduction of Ce⁴⁺ to Ce³⁺ in the GDC become so important [1, 61–64]. Nonetheless, the LSGM can react with NiO and form LaNiO₃ which is ionically non-conductive layer between the anode and electrolyte through fabrication process. This issue can be avoided by coating a thin GDC layer between the anode and electrolyte [1].

2.1.4.3 Anode

In addition to general requirements for SOFC components, the anode of a SOFC must also have proper catalytic properties towards the electrochemical oxidation of the desired fuel and towards chemical reformation of hydrocarbon based fuels. Unlike the electrolyte, it must have sufficient porosity (> 30 vol%) to provide gas diffusion to the triple phase boundaries. Moreover, it should also provide good electronic and ionic conductivity (required ionic conductivity should be greater than 0.1 S cm⁻¹ and electronic conductivity could range from 1 S cm⁻¹ to 100 S cm⁻¹ with the higher conductivity needed for anode-supported cells). Furthermore, it should show tolerance to contaminants such as tars and sulphur, and carbon resistance when hydrocarbon based fuels are utilized. In addition to them, the anode should possess good redox stability during start up and shut down [1, 65].

The function of the anode is to oxidise the fuel (see equation 2) and provide sufficient transport of electrons from the reaction sites to the current collector as well as oxygen ions’ transport from the electrolyte sites to the deep inside of the anode when cermet anodes are used [25, 29]. Moreover, it also provides fuel gas diffusion to the TPBs, where the electron conducting phase, oxygen ion conductor, and the gas phase (pore) meet all together, and reaction products away from them. The location of the TPB depends on the material used. If the anode offers only catalytic and electronic conduction properties such as NiO anode (metal), the TPBs of the anode are restricted to the dual phase boundary between the anode and the electrolyte (see Figure 18A) [25]. Conversely, if the anode made of electronic-ionic composite anodes (see Figure 18C), then the TPBs increase markedly inside the anode. The aims of making composite anode are not only to enhance the TPBs, but also (1) to prevent the Ni anode agglomeration at high operating temperature, (2) to match the CTE of the anode to that of the ceramic electrolyte and (3) provide good adhesion between the anode and electrolyte which results in reduction of contact resistance [65]. Thus, high densities of the TPB are preferred. In addition to them, a mixed ionic electronic conductor anode was also reported, and it substantially improves the effective reaction zone (ERZ) through the whole
the anode-gas interfacial area, and consequently increases the performance of SOFCs (see Figure 18B) [25, 29].

![Figure 18 The illustration of the TPB for (A) the pure electronic conductor, (B) the MIEC and (C) the composite anode [25]](image)

A graded anode structure for an anode supported SOFC has been reported by Virkar et al. so as to decrease both the activation and concentration polarizations [66]. The anode functional layer (AFL) (with a thickness of 10 µm–50 µm) has finer microstructure than that of the anode support layer (outer layer, around 1 mm) in terms of pore size, volume present porosity and pore distribution. The fine microstructure of the AFL is considered to increase the TPB areas by achieving high surface area so that activation polarization can be minimized. The anode support layer with a coarse microstructure offers mechanical strength to the cell, and facilitate rapid fuel gas transport into and reactant gas removal out of the anode so that concentration polarization can be minimised [67, 68].

Although a number of different types of anodes have been reported as a potential SOFC anode, the Ni-YSZ anode has been considered as the best anode due to (1) its high electrical conductivity (1000 S cm\(^{-1}\): 30 vol% and 1200 S cm\(^{-1}\): 60 wt% at 1000°C [1]), (2) sufficient electro catalytic property and (3) acceptable CTE (around 12 × 10\(^{-6}\) K\(^{-1}\) for 43 vol% Ni [1]) matching with other SOFC components [1, 69]. The CTE of the Ni-YSZ reduces with Ni content reduction, but to the detriment of the other properties useful to cermet anode. Moreover, a power density up to 1.2 W cm\(^{-2}\) was obtained in a Ni-YSZ anode supported SOFC in hydrogen gas at 800°C. In addition, the Ni-GDC, Ni-SsSZ etc composite anode can also be utilised according to operating temperature of SOFCs. However, the main limitation
of the nickel-ceramic based anode is reduction and re-oxidation (Redox) cycle instability, especially for anode supported cell, which lead to volume change and thereby damaging the cell (see Figure 19) [65, 70–72].

Figure 19 The illustration of NiO-YSZ (A) as sintered state and (B) first re-oxidation state [65]

Lanthanum doped SrTiO$_3$ (LST) perovskite anode has also gained great attention as an alternative replacement to the Ni-YSZ anode owing to its dimensional and chemical stability upon redox cycling, and good resistance to carbon coking, despite higher over-potentials and lower performance than that of the Ni-YSZ cermet. The LST perovskite anode has favourable electronic conductivity in reducing atmosphere but has poor electro-catalytic performance [1, 73, 74].

2.1.4.4 Cathode

The cathode is one of the main components of SOFCs where the oxygen molecules from the air flow and adsorbed onto the porous cathode surface, and were reduced to oxygen ions by electrons coming from to the anode via current collector. Depending on the nature of the SOFC cathode, oxygen reduction reaction can occur either in the vicinity of electrolyte/electrode/gas interface or on the gas/electrode interfacial areas. The partially or fully reduced oxide ions are thereafter transferred throughout the surface pathways or bulk to the electrode/electrolyte/gas interface, and subsequently to the anode via the dense electrolyte by diffusion (see Figure 20) [29].
The cathode is considered to possess good electro-catalytic properties towards oxygen reduction and facilitate good transportation of electrons (preferred electronic conductivity more than 100 S cm\(^{-1}\)) from the interconnector to the reaction site. It is also expected that to have adequate oxygen gas diffusion and oxygen ion conductivity. Moreover, the cathode must also have good properties mentioned in the “General Requirements for the SOFC Components” [23, 45, 49, 75].

The cathode also has porous structure so as to deliver oxygen gas to the TPBs. Similar to the anode, the cathode can be made as the composite or MIEC structure and be graded in case of cathode supported cell for the same benefits mentioned for the anode [75–77].

Among the variety of the cathode materials exist in the literature such as noble metals and electronic conducting oxides, the lanthanum-based perovskite materials have gained great attention due to their sufficient specific properties for the SOFC cathode. The most well-known perovskite cathodes are: (1) Lanthanum strontium cobaltite (LSC), (LaSr)CoO\(_3\), (2) Lanthanum strontium manganite (LSM), LaSrMnO\(_3\), (3) Lanthanum strontium ferrite (LSF), (LaSr)(Fe)O\(_3\), and (4) Lanthanum strontium cobaltite ferrite (LSCF), (LaSr)(CoFe)O\(_3\) [26, 76].

Among them, the LSM is the most studied and utilized electron-conducting cathode material because of its good CTE (11 \(\times\) 10\(^{-6}\) K\(^{-1}\)–12 \(\times\) 10\(^{-6}\) K\(^{-1}\)), excellent electrical conductivity (around 300 S cm\(^{-1}\)), excellent stability, manageable interaction with ceramic interconnect, and relatively less interaction with the YSZ electrolyte at high operating temperature (1000°C). However it has negligible ionic conductivity (about 5.76 \(\times\) 10\(^{-6}\) S cm\(^{-1}\) at 1000°C) which is performed by oxygen vacancies [1, 6, 45]. This limits the LSM cathode to be used at decreased temperature. LSM-YSZ composite cathode can be used at
intermediated temperature due to the improved ionic conductivity as well as better thermal expansion match with the YSZ electrolyte. [23, 75, 78–80].

The LSC and LSF (MIECs) have also studied extensively for an alternative cathode at intermediate temperatures because of their good oxygen ion conductivity [81]. The peak electrical and ionic conductivities of the LSC were measured as 600 S cm\(^{-1}\) at 800°C and 2.0 \(\times 10^{-5}\) S cm\(^{-1}\) at 680°C respectively. However, its high CTE (\(26 \times 10^{-6} K^{-1}\)), which is almost twice that of the YSZ and ceria based electrolytes, is a greater challenge that limits it to be utilized as cathode material [1, 82]. In contrast, the LSF has acceptable CTE (between 12 \(\times 10^{-6} K^{-1}\) to 18 \(\times 10^{-6} K^{-1}\)) as well as a good electrical conductivity of 352 S cm\(^{-1}\) at 550°C. However, both the LSC and LSF cathodes react with the YSZ electrolyte and form the insulating SrZrO\(_3\), SrFe\(_{12}\)O\(_{19}\) and La\(_2\)Zr\(_2\)O\(_7\) layers which decrease the performance of the SOFCs. This problem, but, is not a concern with ceria based electrolytes in SOFCs [81, 83, 84].

LSCF (MIEC) is also an attractive cathode material for IT-SOFCs owing to the fact that it has better catalytic activity as well as electronic and ionic conductivities than that of the conventional LSM cathode. It has an electrical conductivity of around 340 S cm\(^{-1}\) at 550°C and an ionic conductivity of about \(10^{-2}\) S cm\(^{-1}\) [1]. Therefore, the polarization losses of the LSCF cathode are much less than that of the LSM, as a result, has better performance. Similar to the LSC and LSF cathodes, the LSCF reacts with YSZ electrolyte to form insulating layers. Similarly, it can be used with GDC or YSZ as composite cathode material for the same benefits mentioned above for other cathode materials [76, 84–87].

In order to prevent the reaction of the cathodes (LSM, LSC, LSF and LSCF) with the YSZ and LSGM electrolytes at intermediate operating temperatures, a protective ceria based electrolyte (such as GDC) layer could be used as interlayer between the cathode and electrolytes [82–84, 87].

2.1.4.5 Interconnect

In a SOFC, one individual cell may not provide sufficient voltage and power output for a system. Hence, several individual cells are connected in series to form a stack so as to achieve required cell voltage and power output. In the stack, these series connection are provided by employing interconnects. An interconnect not only offers an electrical connection between the anode of one individual cell to the cathode of the adjacent cell in a
stack, but also provides a physical barrier to prevent oxygen gas and fuel flow from oxidizing atmosphere to the reducing atmosphere, and from the reducing atmosphere to the oxidizing atmosphere, respectively (see Figure 21) [88, 89].

![Figure 21 The illustration of an interconnect in (A) a counter-flow and (B) cross-flow in a planar SOFC stack](image)

Therefore, an interconnect must exhibit (1) excellent electrical conductivity (greater than 1 S cm⁻¹), (2) good corrosion resistance, (3) be dense enough to prevent the direct combination of the fuel and oxidant (combustion), (4) possess moderate stability in terms of microstructure, chemistry, dimension and phase at high operating temperature in both oxidising and reducing atmosphere as well as required properties mentioned in the section of “General Requirements for the SOFC Components” [89, 91, 92].

Sr doped lanthanum chromite (LaCrO₃) is the most common used perovskite type ceramic interconnect at high operating temperature due to its acceptable conductivity (about 1 S cm⁻¹ at 1000°C), stability in low oxygen partial pressure (even at 10⁻¹⁶ atm) in reducing atmosphere, and relatively less CTE (9.5 × 10⁻⁶ K⁻¹) mismatch with other cell components. Conversely, it has poor sinterability in air, which is ascribed to the vaporization of gaseous Cr-O species and the migration of transient liquid phases such as SrCrO₄ into the porous substrate during sintering. Moreover, Cr containing interconnects can bring about formation of the volatile CrO₃ and CrO₂(OH)₂ during operation, which then diffuse into the cathode and then increase the polarization resistance. The electrical conductivity of this interconnect decreases with temperature as other cell components, thus it is not convenient for IT-SOFCs and LT-SOFCs [29, 45, 88, 92].
Metallic alloys, thus, have been investigated in recent times as alternatives to the ceramic interconnect materials as a result of decreased operating temperatures of SOFCs below 800°C. Among the metallic interconnects, ferritic-stainless steels (FSS) (e.g. Crofer 22 APU) are commonly utilised due to the fact that (1) they possess good resistance to oxidation, (2) low manufacturing cost, (3) good machinability, (4) can be used at temperatures between 600°C and 800°C and (4) possess close CTE to the anode and cathode [94]. However, metallic interconnects generally have two main challenges: first, the precipitation of Cr$_2$O$_3$(s) phase, and second the formation of the volatile CrO$_3$ or CrO$_2$(OH)$_2$ due to the reaction of the oxide layer (Cr$_2$O$_3$) with the gaseous H$_2$O, which blocks the electrodes (mainly cathode)/electrolyte interface or TPBs (see Figure 22). These issues result in fast area specific resistance (ASR) of SOFCs [93, 95]. In order to avoid or minimize these problems, protective coatings between interconnect and electrodes are in general utilized. Ceramics with a spinel structure such as (Mn, Co)$_3$O$_4$, (Mn, Co, Fe)$_3$O$_4$ are the most common ceramics to be employed as protective coatings, as they have sufficient electrical conductivity, similar CTE behaviour with the other fuel cell components, and capability to form more stable Cr-containing spinels [95–97].

2.1.4.6 Sealant

Sealant is required (especially in the planer SOFC designs) to avoid any leakages of either air or fuel from their respective chambers, (separate tightly fuel and air from each other) and thereby preventing direct chemical combustion which causes cell voltage decrease and reduces power generation efficiency [29].
The required properties for sealant materials can be generalized as follow:

- No gas leakage
- Similar CTE with other cell components
- Strong enough against thermal cycling and thermal shock
- Chemical compatibility with the adjoin SOFC components
- Chemical stability under oxidising and reducing condition
- Sufficient bond strength to avoid leakage
- Long lifetime, more than 40000 hours, low cost and so forth [29, 98, 99].

However, none of the current sealing materials can satisfy all above requirements at the same time for SOFC sealing in spite of the fact that many advantages have been achieved.

The sealant can be categorised under the two main different headings as follow:

**Compressive Seals (non-bonding seals):** A compliant material such as mica-based or metallic sealant is placed between two sealing surfaces, and compressed by an external loading between the components so as to achieve an air tight hermetic sealing (see Figure 23). They are free to expand during thermal cycling which results in not dependence on CTE. Metallic compressive seals such as platinum, gold and silver are not commonly required for sealing due to their susceptibility to oxide scale formation upon exposure to oxygen at high working temperature and properties to conduct electricity. Therefore mica-based sealants are generally preferred as compressive seals.

*Figure 23 Systematic illustration of a SOFC stack with detail of compressive sealing and unit cell [29]*
**Glass and Glass-ceramic sealants:** they are in the group of rigid sealing which refers to the fact that SOFC components are rigidly bonded together by sealants, and cannot be separated from each other after sealing (see Figure 24). In addition, they are most commonly utilized sealant materials because their properties can be easily modified by changing glass compositions, and they are simple to be processed as well as cost effective [98–100].

![Illustration of the sealing in a planar SOFC from different two views](image)

*Figure 24 The illustration of the sealing in a planar SOFC from different two views [100]*

### 2.1.5 Fabrication Technique for SOFCs

A wide variety of ceramic manufacturing techniques have been used to fabricate SOFCs. In general, cell fabrication techniques can be divided into two extensive groups: the deposition method and the particulate method. The deposition method involves the formation of the cell components on a substrate by a physical or chemical process, for instance, physical vapour deposition (PVD), chemical vapour deposition (CVD), pulsed laser deposition (PLD), spin coating, spray pyrolysis, plasma spraying, dip coating, screen printing, slip casting and so forth whereas the particulate method involves the consolidation of ceramic powders into cell components such as tape casting, tape calendaring [6, 20]. Among this technique, some of them are only utilised for the fabrication of the planar SOFCs up to now, others can be changed in order to be used for the fabrication of the tubular or flat tubular SOFCs such as dip coating, thermal spraying, PVD and CVD [50]. In addition to them, the extrusion technique is one of the another methods utilised for the fabrication of a tubular [34] and flat tubular cells [22, 39]. Furthermore, a gel-casting method is also used for the planar and tubular cells’ fabrications.
It is important to choose an appropriate fabrication technique in order to obtain fully dense thin electrolyte layers [49]. Advance fabrication techniques, for instance, CVD, gel casting, PVD etc. can be applied to achieve this requirements, however, either high fabrication cost or limited continuous mass production of the cell layers are main drawback for the applicability of these techniques[42, 101]. therefore it is more reasonable to use cheap mass production technique such as tape casting, screen printing and so on for the planar SC-SOFCs fabrication where small cracks or crack like defects in the electrolyte layer is tolerated [9, 34, 69, 101].

2.1.6 Polarization Losses in a SOFC

The operational cell voltage is always lower than the voltage of the ideal cell by the reason of the presence of the ohmic polarization, activation polarization, and concentration polarization [89]. The ohmic losses are largely associated to (1) the resistance to the ions’ flow in the electrolyte, which is the main ohmic losses in the system, (2) the resistance to the flow of electrons in the electrodes as well as interconnect, and (3) resistance through contact areas of the cell components. In addition, the concentration polarization is mainly due to the limitation of the fuel or air transport through the porous electrodes. The concentration polarization at the cathode is negligible for an anode supported SOFC owing to thin electrodes while it becomes series issue at the thick anode. The losses related to activation polarization result from the sluggish reactions at the electrodes or electrodes/electrolytes interface, and include a number of series steps which can be defined as gas adsorption, dissociation, electron transfer and transfer of ionic species into or out of electrode/electrolyte interface [102–104]. The voltage of an operating cell can be described as

\[
V(i) = E_o - iR_i - \eta_{act}^a - \eta_{act}^c - \eta_{conc}^a - \eta_{conc}^c
\]  

(7)

Where, \(E_o\) is the open circuit voltage, \(i\) is the current density, \(R_i\) is the ohmic resistance (Ωcm\(^2\)); \(iR_i\) is the ohmic loss), and \(\eta_{act}^a, \eta_{act}^c, \eta_{conc}^a, \) and \(\eta_{conc}^c\) are respectively the anode activation, cathode activation, anode concentration, and cathode concentration polarizations [102, 105]. The equation 7 can be rearranged in detail as follow:
\[ V(i) = E_\circ - iR_1 - a - b\ln i + \frac{RT}{2F} \ln \left( \frac{P^0_{H_2}(i) P^0_{H_2O}}{P^0_{H_2} P^0_{H_2O}(i)} \right) + \frac{RT}{4F} \ln \left( \frac{P^0_{O_2}(i)}{P^0_{O_2}} \right) \]  

(8)

Where \( a \) and \( b \) are the Tafel coefficient, \( R \) is the ideal gas constant, \( F \) is the Faraday constant, \( T \) is the operating temperature in K, \( P^0_{H_2}(i) \) is the partial pressure of hydrogen gas at the anode / electrolyte interface, \( P^0_{H_2O}(i) \) is the partial pressure of hydrogen on the anode surface, \( P^0_{H_2O} \) is the partial pressure of the H\(_2\)O on the anode surface, \( P^0_{O_2}(i) \) is the partial pressure of oxygen gas at the cathode/electrolyte interface, and \( P^0_{O_2} \) is the partial pressure of the O\(_2\) on the cathode surface (see Figure 25) [106]. Figure 25 also shows that the partial pressure changes of the H\(_2\) and O\(_2\) through both the anode and cathode electrodes, respectively.

![Figure 25](image)

*Figure 25 The illustration of the partial pressure of H\(_2\), H\(_2\)O and O\(_2\) through the anode supported cell structure [106]*

The schematic representation of operating cell voltage of a typical SOFC is shown in Figure 26. The common mechanisms of losses differ depending on the current density level. It can be clearly seen from the Figure 26 that the activation polarization is dominant at low current density due to the sluggish reaction kinetics of the electrodes. Despite the concentration polarization occurs over an entire range of the current density, it, however, becomes dominant at high current density because of difficulty to deliver enough reactants flow to the cell reaction areas. In addition, the ohmic polarization is directly proportional to the current due to the constant cell resistance [89].
Figure 26 A schematic illustration of a SOFC operating cell voltage with respect to current density and the region of the potential losses [105]

It is generally accepted that the highest performance is obtained in an anode supported SOFC because it has quite thin electrolyte and cathode, which in turn result in low ohmic and concentration losses comparing to thin electrolyte and cathode containing cells. However, the thick anode causes high anode concentration polarization in the cell. Furthermore, the sluggish reaction of the conventional cathodes such as the LSM and LSCF makes the cathode the main contributor of polarization losses in an anode supported SOFC at a sufficient operating temperature, in other words, the cathode activation polarization is higher than the anode concentration and activation losses [1, 6, 41, 107].

Besides these, the operating temperature has significant effects on these three main concentration losses. The cell performance increases generally with the increment of the operating temperature (see Figure 8, Figure 11 and Figure 14). This is ascribed to the improvement in ionic conductivity especially in the electrolyte, and catalytic activity in both anode and cathode electrodes. In contrast, the concentration polarization either at the anode or cathode remains almost constant or is slightly decreased with temperature reduction [104, 108, 109].

2.2 SINGLE CHAMBER SOLID OXIDE FUEL CELL (SC-SOFC)

This configuration of SOFC allows cathode and anode to be in the same gas chamber where both the cathode and anode are exposed to the same fuel-oxidant gas mixture (see Figure 27) [14]
The operating principle of a SC-SOFC differs from a conventional or DC-SOFC by catalytic selectivity properties of the anode and the cathode against fuel-air gas mixture [110]. In other words, the anode must ideally be active for partial oxidation of hydrocarbon based fuels to form syngas (CO, H\textsubscript{2}) as well as electrochemical oxidation of these products but be tolerant to the oxygen reduction whereas the cathode must be active to oxygen reduction and tolerant to fuel oxidation [14, 110, 111]. In a SC-SOFC, hydrogen is avoided to be used directly as fuel due to its high reactivity with oxygen, which can cause an explosion. Therefore, hydrocarbons such as methane, propane and so forth are mainly preferred to be utilized as fuel in SC-SOFCs, which hydrogen can be formed through partial oxidation of hydrocarbons [112]. Equation 9 gives the general partial oxidation reaction of hydrocarbons at the anode, and Figure 27 show the systematic illustration of a SC-SOFC as well as expected chemical and electrochemical reaction at both anode and cathode electrodes when methane is used as fuel [113]. Equation 10, 11 and 12 can also occur at anodes after the formation of CO, H\textsubscript{2} gases [6].

\[
\text{CnHm + n/2O}_2 \rightarrow n\text{CO} + m/2\text{H}_2 \tag{9}
\]

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \text{(Steam reforming)} \tag{10}
\]

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \text{(Dry reforming)} \tag{11}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad \text{(Water gas shift reaction)} \tag{12}
\]

Similar to the conventional SOFCs, the OCV of SC-SOFCs depend on partial pressure gradient of oxygen across the cathode and anode electrodes, which can be determined by the Nerst equation (see Equation 13) [114]. Depletion of oxygen at the anode and maximum oxygen concentration at the cathode results in an oxygen partial pressure gradient between the anode and cathode when no current is drawn. This phenomenon creates the OCV of the SC-SOFCs [112].

\[
E = \frac{\Delta G}{nF} = \frac{RT}{4F} \ln \left( \frac{P_{\text{O}_2}^\text{c}}{P_{\text{O}_2}^\text{A}} \right) \tag{13}
\]
Where T is the absolute temperature, ΔG is the Gibbs free energy at any moment, R is the gas constant, n is the electron equivalent of oxygen (n = 4), F is the faraday constant, $P_{O_2}$ is the oxygen partial pressure at on the cathode side and $P_{O_2}^A$ is the oxygen partial pressure on the anode side.

Figure 27 Systematic illustration of a SC-SOFC which is made of Ni-GDC composite anode/GDC porous electrolyte/BSCF-GDC composite cathode with expected reaction at both anode and cathode electrodes[113]

### 2.2.1 Advantages and Challenges of SC-SOFCs

SC-SOFCs are the type of SOFCs, and therefore they inherit generally the benefits and challenges of SOFCs. Nevertheless, SC-SOFCs have also certain advantages and disadvantages over conventional SOFCs. First of all, they do not require complex manifolding and high temperature gas-tight sealing between the anode and cathode electrodes due to operation of SC-SOFCs in a diluted fuel-air gas mixture in a single chamber with comparing to the conventional SOFCs. These characteristic properties of SC-SOFCs enable them to have simplified structures (compact from not requiring complex gas manifolding and flow field structures), thereby resulting in more shock resistance both thermally and mechanically, less start-up and shutdown issues, and easier stack assembly than that of conventional SOFCs [8, 12, 14, 115]. This simplified structure also results in a reduction of the total system cost. Furthermore, SC-SOFCs have additional benefits such as: (1) the
temperature of the cell being effectually raised owing to exothermic fuel oxidation reaction, thus improving ionic conductivity as well as catalytic activity of the electrodes; (2) the solid electrolyte can be made of porous microstructure or very thin electrolyte, whilst cracks and defects (in case of dense electrolyte) can be tolerated in the system as no need to avoid mixing the air and fuel gases, which consequently leads to (3) utilization of less expensive manufacturing methods of the electrolyte, thus resulting in reduction of production costs and finally (4) there is less carbon coking at the anode due to the existence of the oxygen gas on the anode side, which reacts with the C to form CO or CO$_2$ gases [8, 9, 13].

In contrast, the efficiency (approximately 1% for an anode supported cell) and power output (see Table 1) of the SC-SOFCs are quite low compared to conventional SOFCs due to (1) very low fuel utilization (around 1.5%), (2) parasitic reactions on both the anode and cathode sides such as fuel partial oxidation at the cathode and oxygen reduction at the anode, (3) cross-diffusion of products (CO, H$_2$) at the anode throughout the cathode side, and so forth. The low fuel utilization is attributed to the lack of selectivity of both the anode and cathode electrodes towards fuel oxidation and oxygen reduction respectively, and elevated flow rates. Besides these, they have explosion risk for fuel-air mixture at high operating temperature [1, 116].

<table>
<thead>
<tr>
<th>Year</th>
<th>Electrolyte</th>
<th>Electrolyte thickness(µm)</th>
<th>Anode</th>
<th>Cathode</th>
<th>Gas Mixture($R_m$)</th>
<th>$T_{furnace}$ (˚C)</th>
<th>OCV (V)</th>
<th>$P_{max}$ mWcm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>SDC</td>
<td>150</td>
<td>Ni-SDC</td>
<td>SSC</td>
<td>CH$_4$-air $R_m$=1</td>
<td>550</td>
<td>0.82</td>
<td>644</td>
</tr>
<tr>
<td>2004</td>
<td>YSZ</td>
<td>10</td>
<td>Ni-YSZ</td>
<td>LSM</td>
<td>CH$_4$-air $R_m=0.88$</td>
<td>800</td>
<td>0.84</td>
<td>360</td>
</tr>
<tr>
<td>2004</td>
<td>YSZ</td>
<td>10</td>
<td>Ni-YSZ</td>
<td>LSCF-GDC</td>
<td>C$_3$H$_8$-air $R_m=0.6$</td>
<td>750</td>
<td>1.00</td>
<td>360</td>
</tr>
<tr>
<td>2006</td>
<td>SDC</td>
<td>15</td>
<td>Ni-SDC</td>
<td>BSCF-SDC</td>
<td>CH$_4$-air $R_m=1.16$</td>
<td>650</td>
<td>0.7</td>
<td>760</td>
</tr>
<tr>
<td>2009</td>
<td>ScSZ</td>
<td>25</td>
<td>Ni-ScSZ</td>
<td>LSM</td>
<td>CH$_4$-air $R_m=1.3$</td>
<td>850</td>
<td>0.95</td>
<td>275</td>
</tr>
<tr>
<td>2009</td>
<td>YSZ</td>
<td>500</td>
<td>Ni-YSZ</td>
<td>LSM</td>
<td>CH$_4$-air $R_m=1$</td>
<td>700</td>
<td>0.92</td>
<td>114</td>
</tr>
<tr>
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<td>200</td>
<td>Ni-SDC</td>
<td>LSC-SDC</td>
<td>CH$_4$-air $R_m=1.4$</td>
<td>800</td>
<td>0.9</td>
<td>215</td>
</tr>
</tbody>
</table>

2.2.2 Parameters Affecting the Performance of SC-SOFCs

The performance of a SC-SOFC depends strongly on the selectivity of the anode and the cathode, electrolyte performance and operating conditions for example the flow rate, the
temperature and the fuel-oxygen ration. These parameters can be generalized under different headings as follow:

2.2.2.1 Materials

Anode: Anode materials employed in SC-SOFCs are similar to the anode materials utilized in the conventional SOFCs such as Ni-YSZ, Ni-ScSZ Ni-SDC, Ni-GDC, and so on. The choice of these materials is dependent on operating temperatures of SC-SOFCs; for instance the Ni-SDC is employed at temperature range 300°C to 600°C due to similar reasons for conventional SOFCs (see section 2.1.4). The anodes in SC-SOFCs must have dual functions. They must have not only high catalytic properties for partial oxidation of hydrocarbons but also electro-catalytic properties for oxidation of CO and H₂ [11, 14, 114, 118].

Cathode: It is expected from the cathode to possess good electro-catalytic properties towards oxygen reduction and less chemical oxidation of fuel. Cathodes employed in the conventional SOFCs are also preferred to be utilized in SC-SOFCs for instance LSM, LSF, LSCF or their compositions with electrolytes. Additionally, some cathode materials for SC-SOFCs were also developed by scientists as Sm₀.₅Sr₀.₅CoO₃ (SSC) and Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃ (BSCF) [8, 21]. Viricelle et al studied to compare the LSM, SSC and BSCF in terms of electrical conductivity catalytic properties under similar experimental conditions. They found that the SSC has the highest electrical conductivity of 650 S cm⁻¹ at 600°C. They also reported that the LSM and BSCF have the electrical conductivity about 130 S cm⁻¹ and 10 S cm⁻¹ at 600°C, respectively. Additionally, according to Viricelle et al. the BSCF has the lowest catalytic activity towards fuel oxidation [111]. However, they found that the long term stability of the SCC and BSCF cathode materials are questionable in air-propane mixture. Moreover, according to Yin et al, the LSM is not convenient cathode material because it has already been utilized for methane combustion catalyst [115]. Therefore, the LSM is not suitable to be used at high operating temperature. Yin also reported that the SSC and BSCF cathodes are susceptible to CO₂ poisoning even with relatively small quantities. Besides these, temperature has significant effect upon the cathode properties. The catalytic activity of the cathode electrodes towards fuel oxidation increases with temperature increment, which is not desirable, although their electrical conductivities are enhanced. Therefore, SC-SOFCs are preferred to operate at temperature between 300°C to 600°C so as to obtain not just better performance from the cathode materials but also achieve some benefits mentioned in the previous sections by the reduction of operating temperatures [8, 13, 119, 120].
**Electrolyte:** Generally, YSZ, ScSZ, GDC and SDC are also utilized in SC-SOFCs according to required operating temperature as the conventional SOFCs. LSGM can also be used as electrolyte material at intermediate temperature with the GDC or SDC buffer layers between the Ni based anodes and LSGM electrolyte. These buffer layer prevent the interfacial reactions between the anode and electrolyte [117, 121]. In an SC-SOFC, the electrolyte can be made of porous structure owing to not needing gas-tight sealing. It allows thin electrolytes with cracks and defects to still be employed in the cell. Therefore, less expensive manufacturing methods can be used to fabricate electrolytes, thereby reducing cost [8, 9]. In addition, the porous electrolyte leads to an increase in the ionic conductivity due to the surface ionic conduction through the pores. Moreover, the tolerance for thin electrolytes also results in reduction of ohmic losses, but care should be taken to avoid the anode and cathode short circuiting through the pores in the electrolyte [116].

In addition, SC-SOFCs utilising a porous electrolyte have lower OCVs than that of the same SC-SOFCs which use a dense electrolyte under the same experimental conditions due to the flow of the H₂ and CO from the anode side to the cathode side, which react oxygen and leads to a decrease in oxygen partial pressure on the cathode side. In order to enhance the OCV of SC-SOFCs which use a porous electrolyte, thick porous electrolytes can be employed such as an electrolyte supported SC-SOFC so as to minimize the cross mixing of reactants/products from one electrode to the other electrode, although the ohmic losses are increased. Alternatively, the thin electrolyte with less porosity is can be employed for simultaneously minimising both the cross-mixing effects and the ohmic losses [8, 9, 112, 117, 122].

**2.2.2.2 Gas Concentration and Flow Rate**

Methane-air mixtures are the common fuel-oxidant gas mixture utilized in SC-SOFCs. Determining a sufficient fuel-oxidant gas mixture can result in better cell performance. Therefore, a term known fuel-to-oxygen ratio, $R_m$, is used by the SC-SOFC community for better clarification and evaluation of the fuel-oxygen gas mixture [8]. In order to avoid carbon deposition, $R_m$ is preferred to be less than 2. In addition, $R_m$ is not required to be less than 0.85 because the gas mixture then becomes explosive. Beside them, if the gas mixture is less than 0.5, then Ni might be re-oxidised. Therefore, $R_m$ is generally required to be between 0.85 and 2. In general, higher power output is obtained when $R_m$ is greater than 1.2 in dry gas condition. Additionally, $R_m$ is chosen to be approximately 2 for sufficient partial oxidation of
methane. However, carbon coking and less fuel utilization are serious issues for fuel-rich gas mixtures (such as $R_m = 2$). In order to mitigate carbon deposition and trigger steam reforming and water gas shift reactions (see Equation 9 and 11), humidified fuel-air is used in a SC-SOFC [123]. The highest fuel efficiency (25%) for methane-air mixture was found by Demin and his co-workers when $R_m = 1$. The fuel efficiency for $R_m = 2$ is quite low though the power density was enhanced. Therefore, a post-treatment should be required so as to increase fuel efficiency such as unreacted fuel gases from the exhaust gas can be either used in another cell or can be directed to the fuel cell inlet [113, 124].

Similarly, the flow rate of gas mixture has strong influence on the performance of SC-SOFCs, while having less effect on the OCV according to many researchers [9, 11]. In almost all cases, the cell performance increases with increasing gas flow rate due to decreased the overpotential associated to the gas diffusion at both anode and cathode electrodes. The decrease of the overpotential is because of the increased diffusion of the gas mixture, which results in enhanced gas exchange at the electrodes. The performance improvement can also be associated to the increased cell temperature because the heat generation by CH$_4$-O$_2$ partial oxidation at the anode electrode is proportional to gas flow rate at a constant temperature of furnace, and the cell temperature increases almost linearly with increasing gas flow rate [125]. However, the fuel efficiency significantly decreases by increasing the gas flow rate owing to large amounts of unreacted fuel passing through/by the cell [9]. In addition, the gas flow is required to be kept constant for a continuous operation [116].

### 2.2.2.3 Temperature

The influences of temperature on SC-SOFCs is the same with that of conventional SOFCs, therefore it will not be repeated here [8, 113, 119]. However, for SC-SOFCs, one should also bear in mind that, cathode materials could be active for fuel oxidation with temperature increase such as SSC and LSM cathode become more active for fuel oxidation at temperature above 600°C, and consequently leads to decrease in power density [111, 116]. In general, SC-SOFCs are, therefore, required to be operated at temperatures ranging from 500°C to 600°C.
2.2.3 Different Type of SC-SOFC Designs

SC-SOFCs possess broader design classifications than that of conventional SOFCs due to no need for fuel and gas separation. SC-SOFCs can be categorized in terms of design types as Conventional Planar SC-SOFC, Supported SC-SOFCs, Co-Planar or Side by Side SC-SOFCs, Tubular and Micro-tubular SC-SOFCs. However, in this study, the tubular and micro tubular SC-SOFCs will not be considered.

2.2.3.1 Conventional Planar SC-SOFCs

These SC-SOFCs are similar to conventional planar SOFCs, where the anode and the cathode are placed on the opposite side of an electrolyte. They can also be made of anode, cathode, or electrolyte supported. They differ from the conventional SOFCs by capability to use porous electrolytes and by employing just one gas chamber for both fuel and oxidant due to the unique operating principal of SC-SOFCs [8].

In the conventional planar SC-SOFC systems, fuel-air mixture can be sent to the cell with three different ways: (1) the gas mixture is firstly supplied over the cathode, and afterwards is passed over the anode (see Figure 28A), (2) fuel-air mixture is simultaneously delivered to both the cathode and anode (flow-by configuration, see Figure 28B), (3) the gas mixture are supplied perpendicularly to the cathode (flow through configuration, see Figure 28C) [9–11, 126]. Additionally, for all flow regimes, the cell performance is substantially influenced by the flow rate, and increases with an increase of the gas mixture flow rate.

The aim of the design A is to ensure that maximum oxygen can be delivered to the cathode in order to provide large amount oxygen ions for electrochemical oxidation of fuel species. The gas mixture is not supplied first to the anode because it is highly likely that the most of the oxygen gas would be consumed by the anode for partial or full oxidation of the fuel, which leads to oxygen deficient mixture on the cathode side. In this design, an injector and a closed end gas-chamber tube are employed. The former is for directing the gas mixture firstly to the cathode and the latter is in order for directing to the flow back to the anode electrode. Besides these, a thin electrolyte is preferred in this design for less ohmic resistance [126].
**Figure 28 Flow configuration in a conventional planar SC-SOFCs**, (A) flow subsequently through the cathode and the anode electrodes, (B) flow simultaneously divided to both the electrodes and (C) flow perpendicular to the cathode and passes through the porous the electrolyte to the anode [113]

In flow design B of the SC-SOFC, the fuel-oxidant mixture is simultaneously sent to the both electrodes. This design leads to simplicity in gas flow management though back flow issues can arise owing to the open end of the gas-chamber tube. The problem of the back flow can be dealt with by either utilizing a back-flow preventing valve or decreasing the outlet diameter [126].

In order to enhance mass transport to the electrodes for better cell performance, the flow through the cell (perpendicular to the cell, see Figure 28C) was suggested by Priestnal et all. [127]. In this flow configuration, the gas fuel-oxidant mixture has to pass through the cathode and the electrolyte so as to reach the anode, hence this design requires a porous electrolyte.

### 2.2.3.2 Co-Planar or Side by Side SC-SOFCs

In this design, the anode and cathode are coated on the same surface of the electrolyte (see Figure 29) [119]. The electrodes are placed side by side on the same electrolyte surface as electrode strips, and can be connected in either series or parallel [116]. The oxygen ions generated at the cathode transfer in the longitudinal direction of the electrolyte to the anode rather than through thickness of the electrolyte. Furthermore, this design firstly tested as sensor, thereafter as a FC [126].
The advantage of the co-planar configuration over the conventional planar configuration is the potentiality to utilize a thick and mechanically robust electrolyte. Conventional planar designs need quite thin electrolyte so as to decrease the ohmic losses, however those thin films are delicate and require expensive manufacturing methods. In the case of the co-planar SC-SOFCs, the ohmic losses are defined by the gap distance between two neighbouring electrodes, and thus reduced by lessening the inter electrode distance whilst facilitating the use of a thick electrolyte substrate. This leads to better mechanical and thermo-mechanical cell stability as well as improved integration compatibility in order for packaging and stack assembly [8, 119]. However, the power densities of this configuration are much lower in comparison to conventional planar SC-SOFCs. Hibino et al. reported a power density of a co-planar SC-SOFC as 143 mW cm\(^{-2}\) (369 mV at 360 mA cm\(^{-2}\)) at 0.5 mm gap distance between the anode and the cathode. He also discovered that the wide of the electrodes has significant effect of the ohmic losses in co-planar SC-SOFCs, and the conduction paths of ions increases with the electrodes width. Therefore, he and his co-workers developed a comb-shape or interdigitated co-planar SC-SOFC (see Figure 30), in which electrodes face each other in close proximity, in order to decrease effectively the width of the electrode while maintaining a large electrode area, and thereby enhance the cell performance [118, 119].

![Figure 29 Systematic illustration of a co-planar SC-SOFC](image)

![Figure 30 The systematic illustration of the comb-like SC-SOFCs [8]](image)
Besides these, the flow rate in this design is required to be low, in contrast to conventional planar configurations, for better cell performance [8, 128].

Additionally, the Ceramic Society of Japan and the Korean ceramic Society introduced a novel concentric electrodes as a co-planer SC-SOFCs, in which the cathode was made of circular shape on the electrolyte and surrounded by ring-shaped outer anode (see Figure 31A) [118]. They compared this configuration with a conventional co-planer SC-SOFC which consist of only one layer anode and cathode (see Figure 31B) under the same experimental conditions, and they found that the cell power density of this novel concentric cell configuration was much better than that of the conventional co-planer SC-SOFC due to the better flow management (see reference [118] for more information).

![Figure 31 Illustration of a novel concentric co-planar SC-SOFCs. Note: electrolyte is not shown][118]

2.3 SINTERING

Sintering is one of the crucial processes for the fabrication of the ceramic SOFC components. It can be defined as the heat treatment in which material powders are formed to a useful solid with desired microstructure by which the particles of crystalline powder reduce their free surface energy, derived from the elimination of the internal surface area [129]. The decrease in the total surface energy and grain boundary by the movement of atoms, ions, or other charged species leads to densification and shrinkage of the body, which can be defined as matter transport from inside the grains to the pores, and matter rearrangement between different parts of pore surfaces without leading to a reduction in the pore volume, respectively [130]. Sintering can also be utilised to enhance the performance of materials such as strength, conductivity, etc. The sintering temperature of a green body is generally in the range of 50% to 75% of the melting temperature [129]. Moreover, sinterability and the microstructure are mainly affected by material properties (such as chemical composition,
shape, size, size distribution of powders and degree of powder agglomeration) and variables for the heat treatment process (for instance, temperature, pressure, holding time, heating and cooling rates) [131, 132]. All these parameters influencing the sinterability and the microstructure make difficult to predict the ceramic powder kinetics and behaviour during sintering. Therefore, manufacturers generally utilise trial and error method to define the effect of sintering and find appropriate composition and heating routes for the manufacturing of the required materials [130].

2.3.1 Sintering Categories

Sintering can generally be classified into solid-state sintering and liquid phase sintering categories. In addition to these sintering types, transient phase sintering and viscous flow sintering can be used [131]. However, in this study, solid-state sintering will be primarily focus.

2.3.1.1 Solid-State Sintering

No liquid is present and sintering temperature typically ranges from 50% to 90% of the melting temperature. It is the simplest method of sintering [129]. The driving force for sintering is the factor that gives rise to the powder compacting to sinter, which leads to the decrease in free energy. The reduction of free energy is associated with the elimination of the internal surface area of the powder compact. This can occur by an increase in the average size of the particles, which leads to coarsening (see Figure 32B), and/or the elimination of solid/vapour interfaces and the formation of grain boundary area followed by grain growth, leading to densification (see Figure 32A) [133, 134].
Figure 32 Representation of two possible routes by which a collection of particles can lower its energy. (A) densification followed by grain growth and (B) coarsening where the large grains growth at the expense of the smaller once [133]

The sintering stages can be described as follows:

- Preparing the green body which is composed of identifiable particles in contact with porosity between them,
- Sintering start, which lead to the formation of the necks (the particles merge at the contact point) owing to the transport of matter to the necks by diffusion, thus the body strength grows.
- The increment in the neck diameter and smoothing of the surfaces of the pore by further sintering.
- The shrinkage and a decrease in porosity. If the sintering is proceeded from this stage, then, eventually, continuous pore network begins to break into individual and isolated pores.
- Continuous reduction in porosity at a slow rate until the green body reaches its maximum densification [129, 135, 136].

During the sintering process, the grains continue to grow in contrast to reduction in porosity and the growth become faster in the latest stages of densification. The faster growth of grains can cause the pores become isolated, following which it is almost impossible to remove these pores with further heating.

In order to assist the sintering process in many ceramics, a small amount of liquid is used in the solid mixture at the sintering temperature, which is usually a few percent of the original solid mixture [137]. This process of sintering is known as liquid-phase sintering and will not mentioned in this study.
2.3.1.1 Sintering Mechanism

There are mainly six sintering mechanisms of polycrystalline materials: surface diffusion, lattice diffusion from the surface, vapour transport (evaporation/condensation), grain boundary diffusion, lattice diffusion from the grain boundary and plastic flow (by dislocation motion) (see Figure 33). However, the densification or shrinkage is led by only some mechanisms. The mechanisms 1, 2 and 3 lead to neck growth without causing densification or shrinkage because such a mechanism does not allow particle centres to move closer together and are defined as non-densifying mechanisms. They lead to concomitant increase in a compact strength, a change in the shape of the pores and a growth in the neck by size. Conversely, mechanisms 4 and 5 are the most significant densifying mechanisms which materials are removed from the grain boundary region leading to densification as well as neck growth [129, 131, 132, 135, 138].

![Systematic representation of sintering mechanisms in polycrystalline materials](image)

1. Surface diffusion: Diffusion of atoms along the surface of a particle
2. Lattice diffusion (from the surface): Atoms from the surface diffuse through lattice
3. Vapour transport: Evaporation of atoms which condense on a different surface
4. Grain boundary diffusion: Atoms diffuse along grain boundary
5. Lattice diffusion (from the grain boundary): Atoms from grain boundary diffuses through lattice
6. Plastic flow: Dislocation motion causes flow of matter

The non-densifying mechanism cannot simply be overlooked. They cause coarsening of the microstructure, where little particles dissolve at the expense of the big one, thus decreasing driving force for the densifying mechanisms. Therefore, sintering can be defined to involve a competition between coarsening and densification [129]. The production of ceramics with highly porous body would be favoured when the coarsening mechanisms are dominant, while high density would require choosing sintering conditions under which the coarsening mechanisms are not very active [129, 133].
2.3.1.2 Grain Growth and Coarsening

Grain growth refers to an increase in the average grain size of a polycrystalline material at high temperature (see Figure 34). According to conservation of matter law, the sum of the individual grain size must remain constant, thus the average grain size growth is accompanied by the disappearance of some grains, generally the smaller ones. Furthermore, the grain boundary is the complex area where two grains are in contact [140]. The atoms placed in the grain boundary region have greater energy than those in the bulk of the grains. Therefore, the reduction in the grain boundary results in reduction of energy associated with grain boundaries. This provides the driving force for grain growth.

![Grain Growth Illustration](image)

*Figure 34 Illustration of grain growth: (A) initial stage and (B) later stage of sintering [141]*

In addition, in ceramics, grain growth is usually categorized under two sections: (1) normal grain growth and (2) discontinuous or abnormal grain growth. In the first one, the mean grain size increases with time but the grain size distribution remains almost invariant in time (see Figure 35A). However, in the second type of grain growth, some large grains grow fast at the expense of smaller grains, resulting in a bimodal grain size distribution (see Figure 35B) [134].
A) Normal Grain Growth       B) Abnormal Grain Growth

Figure 35 Microstructure illustration: (A) normal grain size distribution in an alumina ceramic and (B) initiation of abnormal grain growth in an alumina ceramic [142]

The coarsening term is usually utilised to determine porous ceramic processes. Coarsening happens by the growth of larger particles at the expense of smaller particles (see Figure 36) [143]. Moreover, the total surface area per unit volume decreases with coarsening. The rise in mean grain size is accompanied by an increase in the mean pore size. In other words, coarsening causes a production of porous structure [139]. It also leads to a reduction in the driving force for sintering. In addition, the diffusion distance for matter transport increases with coarsening, thus decreasing the rate of sintering. In porous ceramic, the pores are ruptured from the boundaries due to abnormal or exaggerated grain growth [140, 144].

A)  

R₀  

Rᵢ > R₀

B)  

C)

Figure 36 Schematic diagrams (A) illustrating stages of coalescence, (B) initial stage of sintering and (C) coarsening at elevated temperature [143, 145]

2.3.1.1.3 Stages of Sintering

Sintering is usually composed of stages regarding the sequence in physical alterations that occur as the particles link together and the porosity disappears. Table 2 shows the summary of the physical phenomenon of a material during different sintering stages [144].
The initial stage (first stage) is composed of neck contact between particles by rearrangement of particles consisting of slight movement or rotation of adjacent. At this stage, differences of surface curvature between particles are eliminated and neck growth for the densification mechanism is accompanied by the small amount of shrinkage. It is generally accepted that liner shrinkage of around 3% or 5% happens for a powder system with around 50% to 60% initial density of the theoretical density (TD). At the intermediate (second stage) of sintering, the pores reach their equilibrium and are interconnected with each other. At this stage neck growth continues and total porosity reduces. In addition, average pore size increases because migration of boundaries results in coalescence of pores. Moreover, densification mainly occurs at this stage with dramatic grain growth, thus the intermediate stage is the main part of the sintering process. In addition, it is generally assumed that densification occurs through the pores simply shrinking. At this stage, density of a compact reaches a value of around 90% TD. The final stage starts when the continuity disappears and become isolated at the grain corners. Pores shrink continuously and may disappear altogether. [137, 139, 140, 146–148].

Table 2 Stages of sintering and physical phenomenon occurrence at these stages [144]

<table>
<thead>
<tr>
<th>Stages of Sintering</th>
<th>1st Stage (Initial)</th>
<th>2nd Stage (Intermediate)</th>
<th>3rd Stage (Final)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1. Rearrangement of particles consisting of slight movement or rotation of adjacent.</td>
<td>1. Neck growth and at the same time porosity reduces</td>
<td>1. Much grain growth</td>
</tr>
<tr>
<td></td>
<td>2. Initial Neck formation at the contact point between each particle.</td>
<td>2. Grain growth</td>
<td>2. Discontinuous pore phase</td>
</tr>
<tr>
<td></td>
<td>3. High shrinkage</td>
<td>3. High shrinkage</td>
<td>3. Grain boundary pores eliminated by vacancy diffusion along grain boundaries</td>
</tr>
<tr>
<td></td>
<td>4. Pore phase continuous</td>
<td>4. Pore phase continuous</td>
<td></td>
</tr>
</tbody>
</table>

2.3.2 Sintering Influential Parameters

In order to optimize sintering and obtain required properties from powder compacts after sintering, the main parameters that affect sintering must be controlled. These parameters are generally divided under two sections: External factors such as sintering temperature, heating rate, dwell time, structure configuration, atmosphere, and dimensional ratio: internal factors, for instance, particle size, particle size distribution, shape structure and packaging as well as pore distribution and a ratio of additives such as surfactants, binders, solvent, and so forth [129, 139, 149, 150]. Some of these parameters are explained below.
2.3.2.1 Temperature

Sintering temperature is the dominant factor in the ceramic fabrication process, and affects the phase stability, densification behaviour and the microstructure of sintering material, which are subject to viscosity and activation energy for matter transport. It can significantly influence electrical and mechanical properties of materials. Therefore, it is of great importance to obtain the optimum sintering temperature for required mechanical and electrical properties of materials [139, 149, 151–154]. It is essential to achieve moderately high temperatures so as to make diffusion occur, throughout different routes. Moreover, the temperature results in grain growth and pore removal, as a result, ceramic structures can be more dense during sintering [155]. Viscosity, which has a great influence on microstructural deformation, is eventually dominated by temperature. It initially diminishes with temperature and increases at the later stage of densification [139]. Ceramic materials generally have different sintering temperature ranges and even the same ceramic materials may have different sintering temperature ranges due to variables, for instance, solid content, particle size in the slurry etc. In a co-sintering or single step co-sintering of several materials, it is significantly important to define the active sintering temperature range, since structures which are composed of several different layers have different sintering behaviours and they have to be treated by a single heating cycle.

2.3.2.2 Particle and Green Compact Characteristics

In order to optimize sintering key parameters must be controlled. The particle size and particle packing of the green body are important parameter, however structure of particle, shape and size distribution can also exert a crucial effect [129].

Particle size has significant effect on ceramic powder sinterability. Because the driving force for densification is a decrease in particle surface area, the bigger the surface area, the larger the driving forces [133]. Reduction in particle size increases the number of contact points per unit volume [156]. Therefore, the particle size reduction helps sinterability of ceramic compacts and speed up sintering [129, 144, 157–159]. According to Rahaman [135] large reductions in sintering temperature can be achieved by utilising nanoscale particles (less than 50 nm to 100 nm in size). For instance, CeO₂ with 10 nm particle size can be sintered at a temperature of less than 1150°C, compared to around 1600°C for 1µm particles. This implies that it is possible to modify particle size in green body in order to
make sintering temperature of different materials during co-sintering, and thereby reducing the mismatch of sintering behaviour between different layers at a specific temperature. However, in practice, very fine particles cause serious issues. Finer particles are more prone to agglomeration. It is because electrostatic (and other) surface forces increase due to an increase in the surface/volume ratio. The agglomerates have propensity to sinter together into larger particles upon heating. This phenomenon not only dissipates driving force for densification but also forms large pores between partially sintered agglomerates [133, 144].

In solid state sintering, it is usually assumed that, particles are monodispersed: however a particle size distribution may have important influences on sintering. Generally, differential densification between finer and coarser phases coupled with interaction between the particles in the coarser phase can seriously impede densification. The use of a wide range of particle size can leads to an increase in the packing density. It is because the fine particles can filter into the gaps between the larger particles. As a consequence of that, the shrinkage required for complete densification is reduced[140].

In addition, green density of ceramic powder also influences sintering. There is a correlation between the green density and final density. Higher green density leads to a decrease in the shrinkage required to obtain a given density. In addition, less pore volume is eliminated when green density is higher. Furthermore, the green density should be high and particles must be homogeneously packed so as to improve sintering rate and obtain high density as well as prevent agglomeration and differential densification in the material, thereby obtaining desired properties of material after sintering [133].

2.3.2.3 Impurities

The role of impurities cannot be ignored in ceramic sintering. They could: (1) be utilised as sintering aid, which are purposefully added into green body to enhance sintering kinetics and thus decrease sintering temperature; (2) suppress coarsening by reducing evaporation rate and diminishing surface diffusion; (3) suppress grain growth and reduce grain boundary mobility; (4) improve diffusion rate [133, 146].

2.3.2.4 Additives in Green Body

The green body microstructure has significant effects on the microstructural evolution of the material during sintering. For the tape casting and screen printing techniques, it is
important to bear in mind the state of slurry and casting direction so as to define the initial state of microstructure prior to sintering. Additives in green tapes of ceramics such as plasticiser, surfactants, binder, solvent and so forth have been studied in order to investigate their influence on densification behaviour and stress distribution during sintering. These additives do not participate directly in the sintering process, mainly evaporated before main shrinkage occurs during sintering. However, they influence the ceramic slurry properties followed by changing the initial position of particle distribution. In addition, it is possible for additive to break the connection of particles or increase pore size during their evaporation at low temperature of sintering [139, 160–164].

2.3.2.5 Pores

Densification during sintering can also be defined as the pore removal process. Because sintering of ceramics generally begins with a porous compact of an aggregation of particles. Therefore, it is important to have a proper understanding of pore evolution during sintering [139, 165]. Honda et al. also states that detailed understanding of the pore formation during sintering is essential to comprehend and control microstructure development during sintering, and thus control the mechanical and reliability of a sintered ceramic [166]. In general, the proportion of finer pores diminishes significantly during sintering due to densification, however, the amount of coarse pores increases. This can be ascribed to pore coalescence taking place in the latest stage of sintering [167]. In addition, if the pores’ size or the amount of pores is high at the initial stage of sintering, the densification will be difficult because the distance between particles become higher. Moreover, if there is anisometric pore distribution or inhomogeneous pore distribution in the ceramic compact, it leads to anisometric shrinkage, and thereby a different resultant microstructure. Furthermore, the shape and distribution of pores may bring about a reduction in the sliding or rotation on grain boundary, and thus contributing to energy mitigation during sintering [168]. In co-sintering, one should take into consideration that the different densification behaviours between layers influences the properties related to pores along the thickness direction, therefore resulting in a microstructural gradient and thereby leading to the generation of a stress gradient at the same layer during sintering [139].
2.3.3 Heating Schedules

Heating schedule generally consists of six stages and can be illustrated as in Figure 37:

![Figure 37 An example of heating schedule for the solid-state sintering process [129]](image)

- **Stage 1**: Removal of volatiles (water, etc.), binder burnout, and conversion of additives such as polymers occur in this stage. The heat-up rate must be controlled carefully in order to avoid specimen bloating or even breakage which can be caused by boiling and evaporation of organic additives due to the rapid heating.
- **Stage 2**: Reaction of powder components,
- **Stage 3**: Heating up to the isothermal sintering stage
- **Stage 4**: Isothermal sintering stage, which the majority of densification and development of microstructure occur.
- **Stage 5**: Additional holding before final stage of cooling for mitigating the internal stress or allow for precipitation.
- **Stage 6**: Final cool down stage [129, 135].

The heating schedule can be categorized as isothermal sintering, constant heating rate sintering, multistage sintering, rate controlled sintering, fast sintering, microwave sintering, and plasma-assisted sintering. Among these, the isothermal sintering and constant heating rate sintering will be briefly examined.
2.3.3.1 Isothermal Sintering

This is the most common type of heating schedule, which the temperature is monotonically increased to a sintering hold temperature, and thereafter decreased to room temperature. The heat-up times are short in comparison to holding times and are limited by the furnace thermal characteristics and by the sample size. Moreover, in order to prevent the formation of an outer dense layer on an incompletely densified core, as well as cracking due to the temperature gradients, heat-up time for large bodies are keep high. Isothermal sintering is usually preferred to obtain a desired final density within the reasonable time. Besides these, higher sintering temperature results in faster densification. However, higher sintering temperature also leads to an increase of the grain growth rate. Abnormal grain growth might occur if the sintering temperature is too high, thereby limiting the final density [129].

2.3.3.2 Constant Heating-Rate sintering

The sample in this case is heated to a defined temperature at a controlled heating ratio, and cooled immediately to room temperature. The sample size also limits the constant heating rate. In addition, the finer grain size can be obtained at higher heating rates [130].

2.3.4 Sintering Types

2.3.4.1 Free Sintering

Free sintering is a well-established technique for the production of monolithic ceramic bodies from a porous powder compact [169]. In this type of sintering, sintering of a material can be performed at its sintering temperature without application of any external constrains which may affects natural shrinkage behaviour. Therefore, a uniform shrinkage rate can be achieved in all directions if other influential parameters on sintering do not distort uniform densification [139, 170, 171]. Figure 38 depicts a schematic illustration of dimensional change of free-standing sintering ceramic material undergoing isotropic shrinkage. In this case, the overall volumetric changes can be obtained by only monitoring one dimensional change.
2.3.4.2 Constrained Sintering

Constrained sintering of ceramic materials has become a widespread ceramic processing technology utilized to fabricate many products such as protective coating, solid oxide fuel cells and so on. Single or several layers of powder materials are deposited on a substrate utilising a suitable deposition technique such as tape casting, inkjet printing, dip coating, etc. Thereafter, they are exposed to high temperature in order to consolidate. During heating, these porous layers shrink owing to (1) drying and (2) sintering. However, the shrinkage is constrained by the substrates and adjacent layers, thereby densification is retarded in comparison to an unconstrained case, and leads to in-plane tensile stress which may cause crack-like defects, delamination from the substrate and porous channels in the constrained film [171–174]. Figure 39 shows a schematic illustration of a constrained sintering process. Amaral et al.[172] emphasise that the substrate material plays a significant role during sintering, which is usually underestimated. It is possible to control the degree of constraint in the system by changing mechanical properties such as elastic constant and ability to deform at high temperature. In addition, the substrate materials are generally considered to be a rigid inclusion. As a result, the shrinkage of ceramic during sintering is completely constrained along the substrate plane due to constrained neck growth, tensile stress effects and substrate viscous drag. However, the direction perpendicular to the substrate is considered free from the constraint [23, 169, 171, 175–177]. According to Martin et al. the viscous drag, more distinct closer to substrate, leads to the contact loss between certain particles in the sintering ceramic due to the substrate drags forces resisting normal densifying sintering forces. This contact disruption results in: (1) pores which are directed perpendicular to the substrate open, and (2) a decrease on the constraint of the particles
contacts because of some contacts being absent causing contact growth with neighbouring particle where the contact still remains intact. As a consequence of these sintering mechanisms, isotropic green microstructure becomes anisotropic during sintering [178]. Additionally, in real film-substrate system, the degree of constraint is subject to the film adhesion to the substrate. Well-bonded interfaces are expected to hinder the lateral shrinkage, whereas insufficient bonded films may delaminate or slip during sintering, giving rise to non-zero lateral shrinkage [177].

![Figure 39 Schematic illustration of the shrinkage of a film constrained on a substrate undergoing constrained sintering](image)

**2.3.4.3 Co-Sintering**

The co-sintering process is a cost-effective method for fabrication of large scale ceramic substrates and multi-layered structures [179–181]. The co-sintering method helps a reduction in repeated sintering process for fabrication of multilayer structure [139]. However, sintering multilayer ceramic with different materials leads to stress arising due to different shrinkage behaviour and CTEs of adjacent layers [182]. In addition, a very large amount of shrinkage occurs during the sintering of green tapes. Therefore, the shrinkage mismatch between layers brings about stress and thereby results in curvature formation and non-uniform shrinkage, or even more serious issues such as delamination and cracks. In order to avoid these undesired issues during sintering, sintering kinetics of each layer should be analysed well. Thus, induced stress level can be controlled within the acceptable range [139]. Figure 40 shows the schematic illustration of a co-sintered bi-layer structure.
At present, anode-supported SC-SOFCs are fabricated using at least two sintering steps: co-sintering anode and electrolyte, followed by a separate deposition and sintering of the cathode [6, 15, 16]. The co-sintering of anode and electrolyte causes a constraint on the sintering of each layer and thus resulting in distortion and stress during the sintering process [183]. Nevertheless, some common shrinkage occurs in plane of the bilayer composites during sintering and this leads to relax the constraint slightly. In addition, when the cathode is sintered on a rigid anode-electrolyte substrate, it is also exposed to constraints (basically constrained sintering). The rationale for a two-step sintering is that the materials for anode, electrolyte and cathode require different sintering temperatures to achieve the expected microstructures. Furthermore, a two-step sintering process decreases possible reactions between electrolyte and cathode [16]. In recent times, single step co-sintering of SOFCs has been studied in order to pertain to simplifying the process along with decreasing the processing time and input energy [17–19]. These benefits of single step co-sintering of SC-SOFCs reduce further the cost of SC-SOFCs fabrication and thereby improve commercial viability if employed in commercial scale.

In this study, a single step co-sintering process is applied to fabricate anode-supported planar SC-SOFCs. Sintering the anode, cathode and electrolyte in one step is difficult because each component has different sintering behaviours and microstructures [17, 179, 184, 185]. Therefore, each component of the cell must match in shrinkage behaviour to avoid or minimize strain mismatches. Otherwise, there exists a high possibility to form crack or crack-like defects in the cell as a result of the mismatch stress. Furthermore, thermal expansion coefficient (CTE) mismatch between each layer becomes a dominant factor when materials have higher viscosity i.e. during cooling process [186]. Therefore, in order to achieve the single step co-sintering of an anode supported SC-SOFC, the sintering temperature should be
decreased to obtain a preferable cathode microstructure, while still densifying the electrolyte [16, 187, 188]. Lowering sintering temperature is also helpful in reducing the CTE mismatch between each component and thereby mitigating possible cracking or delamination in the cell during sintering [186]. Furthermore, possible reactions between electrolyte and electrodes are reduced owing to decreased sintering temperature [184, 189]. However, lowering the sintering temperature of the electrolyte results in the electrolyte not being fully densified, which is unacceptable for DC-SOFCs since the fuel and oxidant have to be separated from each other. However, one of the benefits of using SOFC in a single chamber condition is the available tolerance for a porous electrolyte structure [8, 9]. Therefore, the porous structure of electrolyte at low sintering temperature can be ignored, although the cell performance is decreased due to lower open circuit voltage (OCV) and higher electrolyte resistance [184, 190, 191]. In addition, heating rate and cooling rate should also carefully be defined to prevent any cracking, delamination and curvature formation due to the different shrinkage rates and CTEs of anode, cathode and electrolyte [181, 186, 192].
CHAPTER 3

RESEARCH METHODOLOGY

3.1 MATERIAL SELECTION

In order to make SC-SOFCs with better performance and reliability, it is important to use suitable materials for the anode, cathode and electrolyte. Thus, a comprehensive study has been carried out by many researchers, to date, so as to find appropriate materials of these cell components. It is reported that the Ni-ceria based composite anodes such as Ni-SDC and Ni-GDC have acceptable performance at low operating temperature conditions [1, 8, 126]. For example, the Ni-GDC has acceptable ionic conductivity, good catalytic properties towards partial oxidation of hydrocarbons and electro-catalytic properties for the oxidation of the CO and H₂ under single chamber condition at low operating temperature. In contrast, the Ni-YSZ and Ni-ScSZ, which are the most common used anode materials at temperature above 800˚C, have less performance at low operating temperatures due to decreased ionic conductivity [1, 67].

In case of cathode, the LSM is not convenient cathode material at low operating temperature due to its high polarization resistance and it is also limited to be used at high operating temperature owing to its catalytic activity towards fuel oxidation [21, 120]. Additionally, though the SSC cathode high electrical conductivity and the BSCF cathode possess less catalytic activity towards fuel oxidation, both cathode materials are susceptible to CO₂ poisoning even with relatively small quantities [111]. However, the LSCF has appropriate conductivity and stability under methane-air mixture [8].

For electrolyte material, the YSZ and ScSZ possess low ionic conductivity at low working temperature and the LSGM has serious chemical reaction problems with electrodes. However, the GDC electrolyte has good ionic conductivity and acceptable stability at low operating temperature [1, 8].

Therefore, the Ni-GDC, GDC and LSCF (and/or GDC-LSCF) were utilized as the anode, electrolyte and cathode materials, respectively, for SC-SOFCs.
In order to support SC-SOFCs in the furnace during free sintering as well as to limit the densification of cathode to a certain degree, the commercial porous alumina sheet, which is in the size of 50 mm × 50 mm with 1 mm thickness and has a 40% porosity (purchased from ESL ELECTRO-SCIENCE [193]), were utilized as a substrate. In addition, similar porous alumina was utilized as cover plate so as to suppress curvature formation during the initial firing of the cells, while retaining gas permeability during organic burn out. The porous alumina used as cover plates are in dimensions of 50 mm × 50 mm and 75 mm × 75 mm with the same thickness and porosity of the porous substrate. The required size and number of porous cover plates on the top of the cells for suppression of curvature formation of different SC-SOFCs were defined according to trial and error method. Furthermore, dense alumina rods which have a diameter of 2.7 mm and 3.4 mm were used during co-sintering so as to make a wavy anode supported SC-SOFC. Likewise, the weight of rods required to make wavy cell was also determined by trial and error method.

3.2 CELL PREPARATION

3.2.1 Green Tape Preparation of Electrodes and Electrolyte of Cells

The anode, cathode and electrolyte green layers, which are made by Maryland tape-casting company via tape-casting method [194] (see Figure 41), were utilized to make required thickness and thickness ratio of the electrodes and electrolyte for the anode, cathode and electrolyte supported planar and wavy SC-SOFCs. The sintering temperature of the LSCF cathode is generally less than that of the anode and electrolyte [60, 195]. Therefore, in order to retard the sintering behaviour of the LSCF and thereby balancing the final density of materials during the process of co-sintering, the LSCF particle size was chosen to be larger than that of the anode and cathode. Table 3 shows the composition and grain size of those materials. Furthermore, the green tape preparation of the anode, electrolyte and cathode were explained in details as follow:
Table 3 Green tape slurry composition and particle size of main constituent

<table>
<thead>
<tr>
<th>Green Tape Layer</th>
<th>Composition</th>
<th>Particle size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Green Tape</td>
<td>63.3 wt% Nickel Oxide (NiO) – Gadolinium doped ceria (20% Gd)(Ce₀.₈Gd₀.₂O₂₋δ) (GDC)(60 wt% NiO–40 wt% GDC); 14.22 wt% Xylenes; 14.22 wt% Ethyl Alcohol (95%); 4.11 wt% Polyvinyl Butyral B-98; 1.44 wt% Triethyleneglycol bis(2-ethyl hexanoate); 1.44 wt% Polyalkylene Glycol; 1.27 wt% Hypermer KD 1</td>
<td>0.3</td>
</tr>
<tr>
<td>Electrolyte Green Tape</td>
<td>62.13 wt% GDC (20%Gd); 14.61 wt% Xylenes; 14.61 wt% Ethyl Alcohol (95%); 4.35 wt% Polyvinyl Butyral B-98; 1.53 wt% Triethyleneglycol bis (2-ethyl hexanoate); 1.53 wt% Polyalkylene Glycol; 1.24 wt% Hypermer KD-1</td>
<td>0.3</td>
</tr>
<tr>
<td>Cathode Green Tape</td>
<td>62.13 wt% LSCF (La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ) (LSCF)-GDC (20% Gd) 50 wt% LSCF–50 wt% GDC); 14.62 wt% Xylenes; 14.62 wt% Ethyl Alcohol (95%); 4.35 wt% Polyvinyl Butyral B-98; 1.52 wt% Triethyleneglycol bis (2-ethyl hexanoate); 1.52 wt% Polyalkylene Glycol; 1.24 wt% Hypermer KD-1</td>
<td>1</td>
</tr>
</tbody>
</table>

NiO-CGO (20% Gd) anode green tape preparation procedure:

- Add 10 grams KD-1, 112.3 grams xylenes and 112.3 grams ethyl alcohol to a 1 liter HDPE jar with 500 grams of 1/2" cylindrical magnesia-stabilized zirconia grinding media.
- Roll for 60 minutes on jar rollers (speed~40 RPM) to dissolve fully.
- Weigh and add 500 grams NIO-CGO (60/40 wt%) powders to the jar.
- Dispersion mill for 18 hours–24 hours on jar rollers.
- Add 11.4 grams Triethyleneglycol bis (2-ethyl hexanoate) and 11.4 grams Polyalkylene Glycol plasticisers to jar.
- Add 32.5 grams Polyvinyl Butyral, B-98 binder to mill jar, stirring by hand to wet and mix binder.
- Mix for an additional 18 hours–24 hours.
- Pour slurry into 32 oz. HDPE container.
- Vacuum de-air container for 8 minutes at 25 “Hg.
- Measure viscosity (RV 4 spindle @ 20 RPM) and the temperature of the slip.
- Cast:
  - Blade gap: 0.0034–0.0040” with a 6.5” width single doctor blade assembly
- Carrier (base) film: 75 micron thick silicone coated PET × 12 inch width
- Casting speed: 20 inches per minute
- Air flow on lowest setting, SP:80°C (actual temperature 93–114 °F)
- Four underbed heating zones set at 40–50–60–70°C

The anode green tape had a measured thickness of 0.00085” at the lead end of the cast, 0.0008” on samples measured during the cast and 0.0007–0.0008” on samples measured at the trial end of the cast. In addition, the green bulk density of the anode was measured to be between 2.75 g/cc–3.15 g/cc and the green oxide only density ranged from 2.41 g/cc–2.76 g/cc.

**CGO electrolyte green tape preparation procedure:**

- Add 8 grams KD-1, 94.1 grams xylenes and 94.1 grams ethyl alcohol to a 1 liter HDPE jar with 500 grams of 1/2” cylindrical magnesia-stabilized zirconia grinding media.
- Roll for 60 minutes on jar rollers (speed~40 RPM) to dissolve fully.
- Weigh and add 400 grams CGO powders to the jar.
- Dispersion mill for 18 hours–24 hours on jar rollers.
- Add 12.3 grams Triethylene glycol bis (2-ethyl hexanoate) and 12.3 grams Polyalkylene Glycol plasticisers to jar.
- Add 35 grams Polyvinyl Butyral, B-98 binder to mill jar, stirring by hand to wet and mix binder.
- Mix for an additional 18 hours–24 hours.
- Pour slurry into 32 oz. HDPE container.
- Vacuum de-air container for 8 minutes at 25 “Hg.
- Measure viscosity (RV 4 spindle @ 20 RPM) and the temperature of the slip.
- Cast: Casting is the same with that of NIO-CGO, except that blade gap is 0.0041–0.0045”

The electrolyte green tape had a measured thickness of 0.0008” at the lead end of the cast, 0.0007–0.0008” on samples measured during the cast and 0.0007” at the trial end of the cast. Furthermore, the electrolyte green bulk density was measured to be between 3.63 g/cc–3.82 g/cc and the green oxide only density ranged from 3.19 g/cc–3.36 g/cc.
CGO-LSCF cathode green tape preparation procedure:

- Add 8 grams KD-1, 94.1 grams xylenes and 94.1 grams ethyl alcohol to a 1 liter HDPE jar with 500 grams of 1/2” cylindrical magnesia-stabilized zirconia grinding media.
- Roll for 60 minutes on jar rollers (speed~40 RPM) to dissolve fully.
- Weigh and add 200 grams CGO and 200 grams LSCF powders to the jar.
- Dispersion mill for 18–24 hours on jar rollers.
- Add 9.8 grams Triethyleneglycol bis (2-ethyl hexanoate) and 9.8 grams Polyalkylene Glycol plasticisers to jar.
- Add 28 grams Polyvinyl Butryl, B-98 binder to mill jar, stirring by hand to wet and mix binder.
- Mix for an additional 18 hours–24 hours.
- Pour slurry into 32 oz. HDPE container.
- Vacuum de-air container for 8 minutes at 25 “Hg.
- Measure viscosity (RV 4 spindle @ 20 RPM) and the temperature of the slip.
- Cast: Casting is the same with that of NIO-CGO, except that blade gap is 0.0040–0.0042”

The cathode green tape had a measured thickness of 0.0007–0.00075” at the lead end of the cast, 0.00075–0.0008” on samples measured near the middle portion of the cast and 0.00075–0.0008” on samples measured at the trial end of the cast. In addition, the green bulk density of the cathode was measured to be between 3.56 g/cc–3.79 g/cc and the green oxide only density ranged from 3.13 g/cc–3.33 g/cc.

The lead foot and last several feet at the trial end of the cast, containing defects from the emptying of the doctor blade reservoir, was cut from the roll of the anode cathode and electrolyte green tapes and discarded.

3.2.2 Planar Cell Preparation

Multiple layers of green tapes were stacked together to reach the desired thickness of electrodes and electrolyte, and the thickness for each component was controlled by the number of layers, estimated based on the thickness of 20 µm for each tape. Figure 41 shows the planar cell preparation steps and they can be explained as follows:
• Step 1: Green body preparation of the anode, electrolyte and cathode (made by Maryland tape-casting company via tape-casting method)
• Step 2: The required number of anode green tapes were cut from the green tape rolls as 50 mm × 50 mm W×L and were layered upon each other to reach the desired thickness; secondly, the required number of layers of electrolyte tapes having the same width and length as anode were stacked on the anode surface; thirdly, the required number of layers of cathode tapes possessing the same width and length as anode and electrolyte were placed on the surface of electrolyte. The multi-layered stack was placed between two protective sheets, silicon coated PET release film, and pressed under different pressures and temperatures on a hot pressing machine (Carvel Heated Bench Top Hot Press, model: 3853CE-8).
• Step 3: Protective sheet was removed from the top and bottom surface of the green body of the cell after hot pressing.
• Step 4: The hot pressed cell was cut to 40 mm × 40 mm W×L and placed on a porous alumina substrate.
• Step 5: The cell was placed into a furnace and sintered at 1200˚C for 1 hour.

Figure 41 Schematic diagram of fabrication procedure of anode supported planar SC-SOFC procedure
3.2.3 Wavy Cell Preparation

Wavy cell green tape preparation is the same with planar cell preparation. It only differs at step 4 where alumina rods are utilised to make wavy structure with the help of insulating fire brick. Figure 42 shows the wavy cell fabrication steps. The method here is to control curvature formation normally occur almost equally at the each edge of the planar cells during sintering due to different shrinkage rate of each layers by preventing curvature evolution on one direction of horizontal plane while allowing it on the other direction with the help of alumina rods.

The wavy cell preparation steps can be explained as follows:

- Steps 1, 2 and 3 are identical to the planar cell preparation steps
- Step 4: The hot pressed cell was cut to 40 mm × 40 mm W×L and located, cathode facing downward, on two equidistant alumina rods (D: 3.4 mm) which were placed on a planar alumina substrate. Subsequently, an alumina rod (D: 3.7 mm, weighing from 1.02 g to 2.5 g according to the thickness of the underlying laminated cell) was positioned on the top of the cell in the geometric midpoint.

Two grooves were made under the insulating fire brick in order to place two alumina rods. The purpose of these two grooves is to allow small movement of the rods in horizontal plane on both X and Y directions while allowing the rods to rotate at its axis so as to mitigate any constraint caused by the rods.
The third groove was also made between two previous grooves but it had different height so as to allow the alumina rod could be placed on the top of the cell. The horizontal distance between each rod was 10 mm, considering the total cell size of 40 mm, and, as a result, cell was divided into four equal parts. This arrangement directs cell curvature formations to start at the touching points between the cell and rods during sintering, and thereby leading to a wavy cell structure. It also results in the wavy cell’s peak and base point distance to each other to be equal after sintering (see detailed illustration in Figure 43).

- **Step 5:** The green body of the wavy cell was placed into a furnace and sintered at 1200°C for 1 hour

The formation of wavy structure is quite straightforward. It can be defined as follow: firstly a planar green cell tape is placed and adjusted as Figure 43, cathode facing downward, and allowed to shape a wavy structure due to binder softening during debinding process by the help of alumina rods; secondly when main densification start, the curvature occurs from anode side to cathode side due to high densification and densification rate of cathode. This adjustment, cathode facing downward, allows curve formation direction at the sides at high densification to be the same with the curves formed during debinding because cell is bended downward at touching point of side rods owing to high cathode densification. If the anode was placed downward, then the direction of curves at the side would shift to opposite direction. Because the curve formed due to debinding would be cancelled at some point of sintering and form from opposite direction (from anode to cathode side, from bottom to up) at the later stage of sintering. This would result in either U-shape or cell crack. The purpose of middle alumina rod is to use its weight and cylindrical structure to form a wavy shape in the middle of the cell.
3.2.4 Hot Pressing

It is important to determine suitable hot pressing conditions so as to obtain acceptable compactness, good adhesion between each layer, prevent over-pressing and avoid inhomogeneous cell area distribution. For example, high pressure and temperature of hot pressing might lead to: (1) cell crushing or materials over penetrating into each other or (2) give rise to the cell face sticking to the protective sheet and hence makes it difficult to extract...
without damage whereas that of low pressure and temperature results in delamination due to poor adhesion. Similarly, inhomogeneous cell area due to uneven hot pressing causes different shrinkage and thereby leads to stress in the cell during sintering [129].

To find optimum hot pressing conditions, nine examples of anode-supported cell were prepared at a pressure from 1 MPa–3 MPa, temperature from 50°C–70°C with a dwelling time of 5 minutes using Carver bench top laboratory manual press with electrically heated platens (Figure 44A). All cells are 50 mm x 50 mm square with a thickness of 280 µm, including 200 µm (10 layers) for anode (A), 40 µm for electrolyte (E) and 40 µm for cathode (C), which give a thickness ratio of A:E:C as 10:2:2. All as-pressed green cells were sintered at 1200°C for 1 hour with a heating rate of 0.5°C min⁻¹ from room temperature to 500°C, 2°C min⁻¹ from 500°C to 900°C, 1°C min⁻¹ from 900°C to 1200°C, and cooling rate of 2°C min⁻¹ from 1200°C to room temperature. Through visual assessment of shape changes and integration, the optimum hot pressing conditions were determined.

Figure 44 (A) Carver bench top laboratory manual press for hot pressing and (B) Lenton box furnace for sintering
3.3 SINTERING

Prepared SC-SOFCs made of ceramic or/ and cermet green layers are not solid and they have some additives and binders in their structure. Therefore, these cells require heat treatment so as to remove those binders and densify to a certain solid form which has good properties such as conductivity, strength etc.

Sintering profile of cells in terms of the heating rate, dwelling and cooling rate, is one of the important aspects that should be taken into consideration so as to obtain cells with less defects by the single-step co-sintering method. In order to define the sintering profile, the debinding and shrinkage properties of each green layers should be known. This is so because, during the debinding, capillary force is created and this force leads to small shrinkage. If the solvents, binders or other additives in the green tapes are not removed in a controlled manner, i.e., if the evaporation rate of these additives is too fast, the capillary force will be too high and cause stress in each layer and even result in some defects in the cells. These defects and stress in the cells at low temperature then cause cracking, delamination or curvature formation during the latest stage of the sintering [129, 179]. Similarly, if the main shrinkage areas of each layers are known then one can control these temperature areas in order to control stress occurring between each layers (anode-electrolyte and electrolyte-cathode interfaces) during sintering. In addition, the cooling rate during cooling cycle is also important because each layer has different thermal expansion coefficient [75, 196], which might give rise to cracks during cooling if the cooling rate is too high.

Therefore, each component of cells’ thermal gravimetric analysis (TGA) and shrinkage measurement were taken to predict suitable sintering profiles. In addition to them the picture of anode, cathode and electrolyte sintered separately were taken to monitor their figural behaviour for the purpose of predicting better sintering profile. Additionally, in-situ monitoring by a long-distance microscope (Infinity K-2) was applied to examine the formation of different supported cells such as understanding at which temperature cracking or delamination occurs during sintering. Thereafter, the trial and error method was applied to find a proper co-sintering temperature, heating rate and holding time for SC-SOFCs sintering.

For the purpose mentioned above, five different sintering profiles were determined (see Figure 63 in section 4.3). In order to define the best sintering profile among that of five sintering, five similar anode supported planar SOFCs, (40 mm × 40 mm, cut from 50 mm × 50 mm hot pressed cells) which possess 10:2:2 (A:E:C) thickness ratio and 200:40:40 µm thicknesses, respectively, were made and sintered at different sintering conditions. All
sintering were carried out by using Lenton box furnace with 902 Eurotherm controllers (see Figure 44B).

3.4 PREPARATION OF SC-SOFCs WITH DIFFERENT THICKNESSES OF ANODE, ELECTROLYTE AND CATHODE

Thickness of each component in a cell can have direct impact on co-sintering. In order to evaluate this phenomenon, we prepared cell with different thicknesses and thickness ratios. They were hot pressed at 60°C and 2 MPa for 5 minutes, followed by sintering at 1200°C for 1 hour with a heating rate of 1°C min\(^{-1}\) from room temperature to 500°C, 2°C min\(^{-1}\) from 500°C to 900°C, 1°C min\(^{-1}\) from 900°C to 1200°C, and cooling rate of 3°C min\(^{-1}\) from 1200°C to room temperature. Some cells were sintered without any constraint but others were sintered with a 50 mm × 50 mm and 75 mm × 75 mm porous alumina cover plate on top of them.

3.5 POLISHING

In order to obtain optimum images from SEM for better understanding of pore structure, particle size and particle distribution of sintered cells, grinding and polishing of cells were carried out subsequently using semi-automatic Struers LaboSystem (see Figure 45A). In addition, mounting of cells were performed utilizing Struers CitoPress 5 with Bakelite and epoxy resin (see Figure 45B). In order to fill the pores and prevent particle to fill in the pores during grinding and polishing, cell were first mounted with epoxy resin. However, the SEM image quality for analysing pore size, particle size and pore distribution was not good enough and thus all cells were mounted with Bakelite. After each polishing, polished cross-sectional areas were examined with Leica CTR-advanced optical microscope (see Figure 46) before taking them to SEM. When the polishing was not as desired, all polishing steps were repeated until obtaining good polished cross-sectional areas for SEM. Grinding and polishing steps were summarized in Table 4.
A) Semi-automatic Struers LaboSystem for grinding and polishing and (B) Struers CitoPress 5 for hot mounting process

Figure 46 Leica, CTR-advanced optical microscope

Table 4 The summary of grinding and polishing steps of SC-SOFCs

<table>
<thead>
<tr>
<th>Grind</th>
<th>Consumable</th>
<th>Rotational Speed (rpm)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specimen mover plate-MD-disc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step 1</td>
<td>MD Piano 220, 250 mm diameter.</td>
<td>150-300</td>
<td>8</td>
</tr>
<tr>
<td>Step 2</td>
<td>MD Piano 550, 250 mm diameter.</td>
<td>150-150</td>
<td>3</td>
</tr>
<tr>
<td>Step 3</td>
<td>MD Piano 1200, 250 mm diameter.</td>
<td>150-150</td>
<td>5</td>
</tr>
</tbody>
</table>

Polishing

| Step 4| MD Plan cloths (250 mm diameter) with DiaPro Plan 9\(\mu\)m diamond suspension | 60-150 | 5 |
| Step 5| MD Dac cloths (250 mm diameter) with DiaPro Dac 3\(\mu\)m diamond suspension | 150-150 | 3 |
| Step 6| MD Nap cloths (250 mm diameter) with DiaPro Nap B 1\(\mu\)m diamond suspension | 150-150 | 3 |
3.6 CHARACTERIZATIONS

3.6.1 Thermal Gravimetric Analysis, Differential Scanning Calorimetry and Shrinkage Measurement

Thermal gravimetric analysis (TGA) of as-received tapes of anode, cathode and electrolyte was performed by TA Instruments Q5000IR by heating up to 1000°C at a heating rate of 5°C min⁻¹. In addition, differential scanning calorimetry (DSC) was conducted by Stanton Redcroft HT-DSC by heating up to 1200°C at a heating rate of 10°C min⁻¹ to measure the heat flow separately for electrodes and electrolyte with temperature increment in N₂ atmosphere with an alumina crucible. In-site observations of the shrinkage behaviours of each layer in with direction were done by using long-distance microscope installed on a furnace (Infinity K-20, Infinity Photo-Optical Company) (see Figure 47).

![Figure 47 Schematic illustration of anode, cathode and electrolyte shrinkage measurement by using long distance microscope](image)

The shrinkage measurement of the anode, cathode and electrolyte can be explained as follows:

- A small hole (30 mm diameter) was made in the furnace door and covered with an uncoated sapphire window so that pictures of the sample to be taken at different temperatures.
- Anode, cathode and electrolyte layers were made separately with dimensions of 40 mm × 40 mm, W×L, and a thickness of 0.4 mm, and each of them was placed in the
furnace on a reference polished alumina substrate, which is in the size of 50 mm × 50 mm, W×L, with 1 mm thickness, a CTE of 6.4 × 10⁻⁶ K⁻¹ and has a roughness of 0.6 μm (purchased from Goodfellow [197]). The cell layer (for all three instances) was placed so as to ensure that the edge of the layer and the alumina substrate were aligned along the length direction in order to be perpendicular to the long distance microscope).

- These samples were sintered at 1200°C for one hour with a heating and cooling rate of 5°C min⁻¹.
- A projected photo of each layer along length direction was taken every 50°C temperature increment up to 1200°C. Each photo was analysed in an image processing programme (ImageJ programme) with the help of reference alumina substrate to measure its shrinkage.
- Alumina expansion was theoretically calculated at each temperature on length direction using the linear thermal expansion equation.
- Actual length of the reference alumina at different temperatures was calculated.
- Images taken during sintering at different temperatures were separately sent to ImageJ programme for further analysis.
- A horizontal line equal in distance to length of the alumina was drawn on each image in ImageJ programme in order to set the scale of the real length of alumina in terms of pixel by using the calculated actual lengths of alumina at different temperatures.
- Once the scale was set, subsequently a second line which is equal distance to the anode length on the same image was drawn in order to find the actual length of the anode calculated by ImageJ programme.
- The actual length of the anode, cathode and electrolyte at different temperatures were calculated separately by the same method mentioned above for all images/increments.
- Once the actual length of each cell layer at different temperatures were found, they were then deducted from their initial lengths so as to find the individual expansion of the anode, cathode and electrolyte along the length direction at different temperatures. Subsequently, these values were divided by their initial length values (before sintering) and multiplied by 100 in order to calculate the shrinkage in terms of percentage (see Figure 55A).
- Shrinkage rates of each layer were calculated by dividing the difference in expansion along the length directions with the temperature differential \[\left(\frac{\Delta L_n - \Delta L_{n-1}}{T_n - T_{n-1}}\right)\], where n =
2 to 24, $\Delta L$ is the expansion on the length direction and $T$ is the temperature (see Figure 55B).

3.6.2 Visual Analysis of Anode, Cathode and Electrolyte Layers (Non-shrinkage) During Sintering

The purpose of this step is to replicate the initial four preparations steps for each of the three layers (anode, cathode and electrolyte) outlined above (see section 3.6.1) so as to conduct the visual inspection of the samples separately during/after sintering, to see the sintering results at different temperatures and provide an alternative visual perspective from pictures/images. This is to distinguish/discern the other effects in play during the sintering process such as debinding, warping, delamination, cracking etc. that were not the focus of the previous analysis from the long-distance shrinkage measurement.

- A small hole (30 mm diameter) was made in the furnace door and covered with an uncoated sapphire window so that pictures of the sample to be taken at different temperatures.

- Anode, cathode and electrolyte layers were made separately with sizes of 40 mm $\times$ 40 mm (W$\times$L) and a thickness of 0.4 mm, and each of them was positioned individually in the furnace on an alumina substrate (the edge of layers and alumina substrate along length direction was perpendicular to long distance microscope).

- These samples were sintered at 1200°C for one hour with a heating and cooling rate of 5°C min$^{-1}$.

- A photo of the projected view along the length direction was taken at every 50°C temperature increment up to 1200°C (for each of the anode, cathode and electrolyte respectively). A photo providing an isotropic view was also taken at these intervals for each layer separately.

3.6.3 Scanning Electron Microscopy, Energy Dispersive Spectroscopy and X-Ray Diffraction

Scanning electron microscopy (SEM) with Energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) were used to characterize microstructure of the cells, elemental and chemical analysis of a sample inside the SEM, and examine if any new phases formed during sintering such as impurities due to experimental conditions and so forth. In addition,
porosities of sintered cells were estimated by using SEM results of each cell’s cross-sectional area and ImageJ programing. SEM images and EDS of samples were taken utilising Zeiss 1530-VP FEGSEM with a field emission electron gun (see Figure 49). Acceleration voltage for imaging by secondary electrons and backscattered electrons was set to 5 kV and 20 kV. In order to make samples conductive for SEM imaging, polished and unpolished cells were sputtered with Au-Pd alloy. Furthermore, EDS of the cell was taken at the secondary electron stage, but the voltage was set to 20 kV with high current. For XRD measurement, standard powder XRD patterns were obtained using a Bruker D2 Phaser X-ray diffractometer (see Figure 48), fitted with a 1 dimensional Lynxeye detector and using Ni filtered Cu Ka radiation run at 30 kV and 10 mA. Patterns were recorded from 15–100°, using a step size of 0.02. Furthermore, before the measurement, cells were crushed into powder and placed into XRD machine.

*Figure 48 Bruker D2 Phaser X-ray diffractometer with sample loading illustration*

*Figure 49 Zeiss 1530-VP FEGSEM with a field emission electron gun*
3.6.4 Mean Porosity, Particle Size and Pore Size Measurement

The method utilised to estimate the mean porosity of the anode, cathode and electrolyte of different cells can be elaborated as follows:

- Back scatter SEM images of cross-sectional areas of each layer (anode, cathode and electrolyte) of different cells, which have a 10 µm scale, Mag 2.00 KX, and WD of 8.5 mm, were taken separately.
- Obtained images were sent to the ImageJ program for mean porosity, particle size and pore size measurement.
- Images were set to 8-bit image quality for threshold analysis.
- The threshold of each image was carefully adjusted.
- The percentage of black areas on the images, which corresponded to the percentage of the pore area, were read on the ImageJ program and recorded.

The estimation of mean particle size and pore size of the anode, cathode and electrolyte of different cells were obtained as follows:

- Once the mean porosity of each layers of different cell were measured, a horizontal line (equal in distance to the length of the scale bar shown on each image) was drawn on each picture in order to set the scale of each images’ pixel to the real length of the images.
- Once the scale was set, 50 random pore areas (25 small and 25 large pores) were chosen so as to draw a line which is equal to the diameter of the pore.
- The mean diameter of these pores was estimated from the ImageJ program.
- Similar to the mean pore size measurement, 50 random particles were chosen (25 small and 25 large particles) in order to draw a line which is equal to the diameter of the particle.
- The mean diameter of these particles was estimated from the ImageJ program.

3.7 FLUORESCENCE SPECTROSCOPY FOR DETERMINATION OF RESIDUAL STRESS

Fluorescence spectroscopy was chosen to measure residual stress between cathode and electrolyte of the cells. Fluorescence spectra was obtained from alumina located between cathode and electrolyte layers of the anode supported SC-SOFCs by using a true confocal
Raman microscope (The LabRAM HR High Resolution Raman/PL Microscope system, Horiba, Japan) over a spectrum of 14268 cm\(^{-1}\)–14539 cm\(^{-1}\) with a 633 nm red line of a 17 mW He-Ne laser. Measurements were taken by using a 50X objective lens together with a confocal setup that involved two 50 µm pinhole apertures at 90° to each other, which provides an approximate beam diameter of 1 µm on the specimen surface. In addition, the scanning spectrometry grating was set to 1800 cm\(^{-1}\). For each measurement, an area of interest was chosen by utilising the optical microscope focused on the top surface plane by altering of the height of the sample stage. All experiments (including calibration) were performed in a controlled environment at 22 ± 2°C. Measurements were taken with a step size of 1 µm for a 40 µm × 9 µm mapping, and acquire time was set to 10 seconds for each point. Afterward the obtained data were analysed with curve fitting algorithms involved in the Origin 2015 software. Furthermore, energy change (Δν) were obtained by subtracting R1 fluorescence peak of unstressed alumina from that of stressed alumina placed between cathode and electrolyte. In order to make cells for fluorescence spectroscopy, the fabrication method (lamination, hot pressing and sintering) mentioned in the previous chapter was applied. In addition to this fabrication method, alumina powder, having mean particle diameter of 200 nm, was distributed (with care taken to apply the powders for a reasonably homogeneous distribution) between cathode and electrolyte during lamination stage. Figure 50A shows the alumina distribution on the cathode surface before placing electrolyte layer on the top of them and Figure 50B depicts the Raman system for fluorescence spectra.

![Figure 50](image)

*Figure 50 (A) Alumina distribution on cathode surface and (B) Raman system for Fluorescence spectra*
3.8 PERFORMANCE TEST

When the required cells were obtained after sintering, then the performance of each cell was tested with methane-air gas mixture in a test rig (Elite split horizontal tube furnace with Eurotherm 2408 temperature control system, see Figure 51, which has a maximum temperature of 800°C, and their performance was compared with each other. Before the performance test, the reduction process was performed for the reduction of NiO-GDC anode into that of the Ni-GDC with a certain percentage of H₂ containing atmosphere at a certain period of time. The methane air mixture was prepared by sending certain percentage of CH₄, N₂ and O₂ into a gas chamber. Figure 51 shows testing system for OCV and polarization measurement of obtained cells.

![Testing system, gas supply system, horizontal split furnace and potentiostat for sintered SC-SOFCs](image)

OCV and polarization of cells were measured by utilising a potentiostat (Solarton Analytical 1280C) in concert with the CorrWare®/CorrView™ electrochemical suite (Scribner Associates Inc.). Gold as current collector was sputtered on both electrodes by using Q150T S/E/ES Turbo-Pumped Sputter Coater (see Figure 53), and silver paste was used to connect chromel (90% Ni, 10% Cr) wire to sputtered gold grids, as shown in Figure...
In addition, alumina paste (Ceramabond 552, bought from AREMCO), was also utilized to secure the connection of chromel wire to the cells surface. Cells were tested in a single chamber and were placed in an alumina tube perpendicular to flow direction, as shown in Figure 52A. In order to test cells, anode electrodes were first reduced at 600°C for 1 hour under gas mixed hydrogen and nitrogen with a flowing rate of 0.01 l/min, and 0.19 l/min respectively. After reducing, those cells were tested at 600°C under flowing mixed gas with different composition.

![Figure 52 Testing system: (A) sample holder placement in the furnace and (B) sample placement in the sample holder](image)

![Figure 53 Q150T S/E/ES Turbo-Pumped Sputter Coater](image)
CHAPER 4

DETERMINING OPTIMUM HOT PRESSING CONDITION AND SINTERING PROFILE FOR SINGLE STEP CO-SINTERING OF CELLS

In order to sinter three different layers in one step, it is important to know green tape composition of each layer (such as initial particle size, additives, etc.), their behaviours during sintering (for instance shrinkage or shrinkage rate) and heat flow for each layer. In addition, it is also crucial to comprehend hot pressing conditions for the cells made via tape casting, layering and hot-pressing processes so as to provide homogeneous cell area distribution after hot pressing. Furthermore, visual inspection of each separately sintered cell layer could be helpful to provide profound understanding of each layer’s sintering behaviour. Moreover, heating profile for sintering of a cell is also one of the significant characteristic that should be taken into consideration so as to mitigate stress development due to different shrinkage behaviour of layers and prevent any crack like defects during sintering. Therefore, in this chapter, these characteristics of each layer were investigated and optimum hot pressing condition and sintering profile were defined for single step co-sintering of SC-SOFCs.

4.1 TGA, DSC, IN-SITE SHRINKAGE MEASUREMENT OF LAYERS

The thermal behaviour of electrodes and electrolyte layers was examined by simultaneous TGA-DSC measurements and the results are shown in Figure 54. Figure 54A shows the TGA profiles of green tapes of anode, cathode and electrolyte. The profiles are similar in weight loss versus temperature. There is a little slope at the beginning which corresponds to a stage when mostly water is leaving the body and carbon oxidation starts [198]. Up to 400°C, almost all volatile constituents are burnt out. Whilst cathode and anode have the same weight loss of ~12.5%, electrolyte has slightly lower loss of 11.4%. Furthermore, at temperature from 400°C up to 800°C, all tapes have almost no weight change. Besides, from about 800°C to 900°C, the cathode tape has further weight loss, making a total loss of 12.98%, whilst the electrolyte and anode ones have no more weight loss. These measurements imply that almost all polymer components such as solvent, binder, plasticizer, lubricant and dispersant are completely burnt out before 400°C. The further loss for the cathode tape is likely due to volatilisation of one or more of the ceramic constituents; this
weight loss could also be attributed to oxygen evolution from the cathode required to maintain equilibrium oxygen vacancy concentration, or the combination of the two mechanisms.

Figure 54B depicts the differential scanning calorimetry of anode cathode and electrolyte. The purpose of DSC in this study is to observe if there is big heat flow difference when anode, cathode and electrolyte sintered separately. Because it is important to obtain as possible as close heat flow for each layer so as to prevent different temperature distributing during single step co-sintering of three layers and thereby mitigating thermal stress. As it can be seen from Figure 54B, the overall process for each layers are endothermic though there is a weak exothermic process for electrolyte. Moreover, three different layers possess similar heating flow while there are little differences. Heat flow differences for electrolyte at stage 1 might be due to different amount of additives in the green layer. There is a weak exothermic process for electrolyte at stage 2. This could be as a result of a chemical transformation or phase transition[198]. Another possibility could be the release of surface energy as densification (final stage of sintering) is known to be an exothermic process. It can be explained as such the exothermic process at stage 2 could be dominant than the existence of endothermic process occurring simultaneously with sintering process. Comparing NiO-CGO anode with other layers at stage 3, one can see that there is a small sudden drop which could be explained by phase change. Nevertheless, overall, there is no big differences in DSC results of each layers, that is to say, the thermal stress possibility is quite low and can be omitted for this study.
Figure 54 (A) Thermal gravimetric analysis (TGA) of the cathode, anode and electrolyte and (B) Differential scanning calorimetry (DSC) analysis of electrodes and electrolyte (heating rate for TGA is 5°C/min whereas it is 10°C/min for DSC)

Figure 55A and Figure 55B depict the shrinkage and shrinkage rate of each material, respectively. The main shrinkage occurs at temperature above 900°C. Moreover, the cathode possesses the highest shrinkage and shrinkage rate (13.25%, 0.029%/°C, respectively) at a temperature of 1200°C and the electrolyte has the lowest (4.74%, 0.014%/°C, respectively). Furthermore, the shrinkage behaviour of anode and electrolyte are a close match with each
other before 1100°C, but shrinkage differences increase between the temperature of 1100°C and 1200°C. These all are attributed to material properties and their grain size.

Figure 55 (A) In-situ shrinkage measurement of cathode, anode and electrolyte and (B) shrinkage rate measurement of cathode, anode and electrolyte (heating rate for shrinkage measurement is 5°C/min)

In addition, when one plot the shrinkage differences of anode and electrolyte and electrolyte and cathode versus temperature (see Figure 56), co-sintering behaviour of these two layer structures can be predicted. When anode-electrolyte is sintered together, it is expected to examine the curvature formation to occur from electrolyte to the anode side (see Figure 56). Likewise curvature formation should evolve from electrolyte to cathode direction when electrolyte and cathode sintered together. Accordingly, if anode, cathode and
electrolyte are sintered together, then the curvature tendency towards anode and that of cathode could either cancel each other and results in one curvature formation on dominant side or cause crack or delamination during sintering. Therefore it is important to control sintering of three different layers so as to prevent crack like defects.

Figure 56 Shrinkage differences of NiO/CGO-CGO and CGO-CGO/LSCF

In addition to these, Figure 57, Figure 58 and Figure 59 show the pictures taken of the anode, cathode and electrolyte during the sintering at different temperatures, and after sintering. It can be clearly seen that cathode has serious issues during the debinding process when heating rate is defined high (5°C per minute), especially in the temperature range from 200°C to 500°C. This might be because of the fact that cathode has larger particle size, thus the voids between particles is high compared to anode and electrolyte. Therefore, these large voids lead to more additive to be located between particles. As a result, the amount of evaporated additives at specific places becomes higher and causes big ripples on the surface (Figure 57 temperature between 200°C and 500°C for cathode) and inhomogeneous sintering. These problems might bring about interior stress or small cracks in the material itself and thereby cause the cathode to break at the latest stage of sintering (Figure 57, temperature 700°C and after sintering for cathode). Similarly electrolyte has inhomogeneous evaporation through the material itself (Figure 58, temperature from 200°C to 400°C for electrolyte) and becomes an issue at the early stage of sintering. However this issue is not as severe as that of
the cathode because it has smaller particle size and therefore the amount of additives between particles is less than that of the cathode. These factors result in better control of additives’ evaporation but still cause curvature formation (Figure 58, temperature from 200°C to 400°C for electrolyte). However, if the curvature formation of electrolyte at the early stage of sintering cannot be controlled then it can leads to permanent curvature formation of cell and even cause small cracks during sintering (Figure 58, at 1200°C and after sintering for electrolyte). Conversely, the anode has no problem during sintering even though heating rate is high. This might be ascribed to the anode material composition (NiO-CGO) (see Figure 59).
Figure 57 The picture of sintering results of cathode at different temperature, with dimensions of 40 mm x 40 mm and a thickness of 0.4 mm, heating rate 5°C/min
Figure 58 The picture of sintering results of electrolyte at different temperature, with dimensions of 40 mm x 40 mm and a thickness of 0.4 mm, heating rate 5°C/min
Figure 59 The picture of sintering results of anode at different temperature, with dimensions of 40 mm x 40 mm and a thickness of 0.4 mm, heating rate 5°C/min
4.2 HOT PRESSING ANALYSIS

Table 5 illustrates the photos of green cells after hot pressing under various pressing conditions and their sintering results. In addition, Figure 60 shows the expansion on width (ΔW), length (ΔL), and the two diagonals (ΔD and ΔT) after hot pressing. Furthermore, Figure 61 depicts the size of the sintered cell on width (W), length (L), D and T. Moreover, Figure 62 depicts the sintering profile of these nine cells. In order to define if cells are hot pressed homogeneously, the cells’ size were measured. To achieve a homogenous hot pressing, it is imperative that the measured cell dimensions satisfy the following criteria: (i) that ΔW ≅ ΔL; (ii) that \( \sqrt{\Delta W^2 + \Delta L^2} = \Delta D = \Delta T \). Similarly, it should follow that (iii) W ≅ L and (iv) D ≅ T.

According to Table 5, cells that were hot pressed at 70°C (cell 7, cell 8 and cell 9) were over-pressed because of pressure and temperature mismatch. In addition, it is observed in Figure 60A and Figure 60B that the intercept of these cells’ ΔW and ΔL, and ΔD and ΔT, respectively, are not on the line which has a slope of 1, which indicates that their expansion (either on width and length, or across diagonals) are different. This shows that there is inhomogeneous expansion in the cells during hot pressing, thus causing eccentric curvature formation and cracking during sintering. In order to avoid this over-pressing issue, hot pressing temperature was decreased to 50°C. However at this temperature, cell 1, cell 2, cell 3 had cracks and curvature formation after sintering despite the inhibition of cell over-pressing (Table 5). This might be as a result of different expansion of cell(s) at different edges during hot pressing. As temperature may not be sufficient enough to allow particle packages in cell green bodies to flow properly over protective sheet during hot pressing, this could have led to locally variable green body density in the cells. Moreover, the expansions ΔW and ΔL (see Figure 60A), and ΔD and ΔT (see Figure 60B) of cell 1, cell 2 and cell 3 are different, and support the claim that these cells were not hot pressed homogeneously. Increasing the hot pressing temperature from 50°C to 60°C had different effects on cells with regard to pressure change. Cell 4 and cell 5 were pressed homogeneously and possess reasonable sintering results whereas cell 6 was over-pressed and resulted in strange curvature evolution. According to Figure 60A, the intercept of the ΔW and ΔL of hot pressed cell 5 are just about on the line. It shows that their expansion on width and length directions is almost the same, (0.42 mm and 0.46 mm for ΔW and ΔL respectively). Likewise, the intercept of the ΔD and ΔT of the same cell are also coincident on the line, thus implying that their expansion is
nearly the same (0.628 mm and 0.623 mm for ΔD and ΔT, respectively, see Figure 60B). In addition, the root of the sum of the squares of ΔW and ΔL of the cell 5 was measured as the same with dimension change ΔD and ΔT. Furthermore, cell 4 also had acceptable hot pressing results because the intercept of ΔW and ΔL, and ΔD and ΔT of cell 4 (Figure 60A and Figure 60B, respectively) was also on the line and suggesting that it is also hot pressed homogeneously. Figure 61 also illustrates that cell 4 and cell 5 possess almost homogeneous sintering results, although there are curvature at the edges. In order to ensure good adhesion between each layer, it is determined that the hot pressing condition of cell 5 was to be used for this study rather than that of cell 4.

Hot pressing temperature might also have effect on solvents in green tapes, such as leading to a small decrease in the amount of solvent in green tapes by evaporation during hot pressing. This then helps sinterability of the green tapes during firing because solvent evaporation becomes less pronounced during sintering, and thus reduces possible defects in the green tape during burnout or debinding [129, 199]. This is posited as one of the possible reasons why cells hot pressed at 60°C at reasonable applied pressures possess better sintering results in comparison to cells hot pressed at 50°C.
Table 5 Hot pressing results for 9 anode supported cells, thickness ratio: 10:2:2 (A:E:C), thickness: 200:40:400 µm, at different pressure and temperature

<table>
<thead>
<tr>
<th>Cells</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Time (minute)</th>
<th>After Hot Pressing cell (50 mm x 50mm)</th>
<th>After Sintering cell (40 mm x 40mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 1</td>
<td>1</td>
<td>50</td>
<td>5</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 2</td>
<td>2</td>
<td>50</td>
<td>5</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 3</td>
<td>3</td>
<td>50</td>
<td>5</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 4</td>
<td>1</td>
<td>60</td>
<td>5</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>Cell 5</strong></td>
<td><strong>2</strong></td>
<td><strong>60</strong></td>
<td><strong>5</strong></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 6</td>
<td>3</td>
<td>60</td>
<td>5</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 7</td>
<td>1</td>
<td>70</td>
<td>5</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 8</td>
<td>2</td>
<td>70</td>
<td>5</td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 9</td>
<td>3</td>
<td>70</td>
<td>5</td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Figure 60 (A) Dimensional changes in anode-supported planar SC-SOFC after hot pressing on W and L directions, and (B) on T and D directions.
Figure 61 (A) The value of W and L, and (B) T and D of the cell after sintering
4.3 SINTERING PROFILE FOR SINGLE STEP CO-SINTERING OF CELLS

In order to find optimum sintering profile, five different sintering profiles were determined for the same five anode supported cells. All cells were placed on a porous alumina substrate, with the cathode adjacent to it (facing downward); through this, the aim is to suppress possible curvature formation (deriving from the high shrinkage of the cathode) by utilising the cell’s own weight against the shrinkage behaviour. In addition, the densification of the cathode was further impeded by the porous structure of substrate which has causes higher friction between cathode and substrate during sintering comparing to dense alumina substrate. Figure 63 illustrates different sintering profile and Figure 64 shows sintering results of five cells. It can be seen that heating rate up to 500°C and between 900°C and 1200°C was carefully defined to prevent any cracks. Figure 64 also shows that, cells sintered at sintering 1, 2, and 3 conditions have cracks and severe curvature formation due to stress occurred between layers. These cracks may have happened during sintering due to different sintering behaviour or during cooling owing to different CTE of each layer. In general, cooling rates were also carefully defined to allow stress relaxation to occur. Decreasing dwelling time and cooling rate (sintering 3 comparisons to sintering 1 and sintering 2) has no visible
enhancement on sinterability of the cell (see Figure 64). Decreasing heating rate after debinding, from 3 °C min\(^{-1}\) to 2 °C min\(^{-1}\) at the range from 500°C to 900°C and to 1°C min\(^{-1}\) between 900°C and 1200°C while increasing the cooling rate from 1°C min\(^{-1}\) to 3°C min\(^{-1}\) (sintering 5 comparison to sintering 1), enhanced cell sinterability (Figure 64). Cells sintered at sintering conditions 4 and 5 have only uniform curvature evolutions due to the fact that stress occurred between each layers were carefully controlled by defining suitable heating rates during sintering, especially at the stage of debinding, shrinkage and cooling. Sintering 5 describes that increasing heating rate during debinding and cooling has no big effects on cell formation in comparison to sintering 4 (Figure 64). However it decreases sintering time, thereby saving energy. Therefore, sintering profile of cell 5 is chosen to be used for sintering of final cells used in this study, which comprises sintering at 1200°C for 60 minutes with a heating rate of 1°C min\(^{-1}\) up to 500°C for debinding, 2°C min\(^{-1}\) up to 900°C and 1°C min\(^{-1}\) up to 1200°C while the cooling rate is 3°C min\(^{-1}\).

Figure 63 Different sintering profile for five similar anode supported cells, which has a thickness of 200:40:40 µm (A:E:C) and a thickness ratio of 10:2:2
When the sintering profile was determined, it was also vital to analyse hot pressing condition with new sintering profile so as to avoid any issue related to heating and cooling rate. Therefore, hot pressing test was repeated with the new sintering profile. Table S1 shows the green body of nine similar anode supported cells hot pressed under different pressing conditions and their sintering results. They all possess a thickness ratio of \(10:2:2\) and thickness of \(200:40:40\) µm (A:E:C, respectively). Furthermore, Figure S1 depicts the new sintering profile. Moreover, Figure S2A and Figure S2B shows the expansion on width (\(\Delta W\)), length (\(\Delta L\)), and the two diagonals (\(\Delta D\) and \(\Delta T\)), respectively, after hot pressing. In addition, the size of the sintered cell on \(W\), \(L\), \(D\) and \(T\) are shown in Figure S3. In order not to repeat the previous hot pressing test results, the test result hereby were shortly explained. Similar result with the previous hot pressing test was obtained for high pressure and temperature conditions (cell 6, cell 7, cell 8, and cell 9) by only observing sintering results in Table S1 (for the same reasons mentioned in the section of hot press analysis). In addition, when the hot pressing temperature was decreased to \(50\) °C, cell 2 has curvature formation and crack whereas cell 1 and cell 3 has only curvature formation after sintering. In addition, though cell 1 sintered without any crack, the sintering is not homogeneous because the dimension of \(L\) and \(W\) are not equal (the intercept of \(W\) and \(L\) is not on the line which has a slope of 1) (see Figure S3A). It can be ascribed to hot pressing results. Figure S2B shows the intercept of \(\Delta D\)
and ΔT of cell 1 is not 1 therefore the expansion on D and T direction are not equal and thereby inhomogeneous hot pressing results. However, comparing to first hot pressing test, there is an improvement for cell 1 sintering although heating rate during debinding increases. Similarly, there is a huge improvement for cell 3 in comparison the first hot pressing test the expansion on L and W as well as D and T are almost similar their intersect are on the line (see Figure S2). As a result its sintering looks almost homogeneous (see Figure S3). Changing the sintering profile also did not affect the hot pressing and the sintering results of cell 4 and cell 5, they both look homogeneously hot pressed and sintered according to Figure S2 and Figure S3. Their expansions (either on width and length or across diagonals) are equal thus resulting in homogeneous sintering even though there is curvature at the edges. As it is explained before, in order to ensure good adhesion between each layer, it is defined that the hot pressing condition of cell 5 was to be used for this study rather than that of cell 3 and cell 4.

4.4 SUMMARY

For the fabrication of an anode, cathode and electrolyte supported planar and/or wavy SC-SOFCs via tape casting, lamination, and single step co-sintering, it is important to optimise hot pressing condition and sintering profile. The materials were used for intermediate temperature SC-SOFC were NiO/CGO anode, CGO electrolyte and LSCF/CGO cathode. As it is well known that, cathode has lower sintering temperature than anode and electrolyte, therefore, the particle size of cathode was chosen harder than that of anode and electrolyte so as to retard its sinterability and bring its sintering temperature close to the anode and electrolyte sintering temperature and thereby balance the final density of each material. In order to analyse burn-out process, heat requirement during sintering and properties of these materials, the TGA, DSC and in-situ shrinkage measurement were conducted. In addition, pictures of the each separately sintered layer were taken so as to visually inspect them for better understanding of their behaviour during heating up. The results of these layers showed that, all additives were burned out up to temperature of 400°C, and there were no big differences in heat flow for each cell components. Furthermore, cathode showed highest shrinkage and shrinkage rate comparing to anode and electrolyte. Moreover, visual inspection of the cathode also showed that, when the heating rate is too high, the cell can possess defects during burn-out time and this could lead to the cracks or crack like defects at the later stage of sintering or during cooling. Thereafter, nine anode supported
cell were made in order to define better hot pressing condition for this fabrication method. According to experimental results, a temperature of 60°C, a pressure of 5 MPa and 5 minutes is optimum condition for hot pressing in order to obtain a homogeneous cell. Subsequently, five similar cells were made to determine optimum sintering profile. The result showed that sintering cell at 1200°C for 60 minutes with a heating rate of 1°C min\(^{-1}\) up to 500°C for debinding, 2°C min\(^{-1}\) up to 900°C and 1°C min\(^{-1}\) up to 1200°C while the cooling rate is 3°C min\(^{-1}\) could be optimum sintering profile for obtaining a cell via single step co-sintering. As a result, a planar anode supported cell made without any crack after optimizing all experimental conditions though there were curvature formation at the edges of the cell.
CHAPTER 5

SINGLE STEP SINTERING BEHAVIOUR OF AN ANODE SUPPORTED PLANAR CELL AND ITS PERFORMANCE

In order to obtain a curvature-free planar cell, in this chapter, the sintering behaviour of an anode supported cell was analysed in greater depth, in addition to the work performed in chapter 4. Furthermore, the effects of cell shape and thickness ratio on single step co-sintering of the cell were investigated. Moreover, a limiting constraint was applied to obtain a curvature-free cell. Furthermore, the total residual stress between cathode and electrolyte after sintering was measured using fluorescence spectroscopy. In addition, residual stress in cathode due to CTE mismatch during cooling at room temperature was calculated so as to estimate the sintering residual stress contribution. Finally, the cells were tested under single chamber conditions so as to examine/establish the following: (i) functionality of the sintered specimens as working electrochemical cells, and (ii) to identify the effects of increasing anode thickness and reducing electrolyte thickness, which were beneficial in obtaining reduced curvature, on the cell performance.

5.1 SINTERING BEHAVIOUR OF AN ANODE SUPPORTED CELL WITH TEMPERATURE INCREMENT

In order to investigate curvature direction of an anode supported SC-SOFC during sintering, pictures of the cell were taken at discrete temperature increments. The cells were positioned on a porous alumina substrate, with the cathode adjacent to it (facing downward) for the purpose of mitigating cathode shrinkage by utilizing the friction effect between substrate and cathode layer as well as using the cell mass to suppress curvature formation. Figure 65 shows the curvature formation and direction in relation to temperature change. According to Figure 65, slight curvature is formed towards the anode (towards the upward direction) up to 200°C. This is because the solid network is subjected to a compression on the drying surface (top surface). This causes the green body to warp upwards. Later into the drying process (above 200°C and until the end of the burn-out process 400°C or 500°C), the liquid vapour interface moves into the interior of the green body and pores are occupied with air. The green body network surrounding to air filled pores is relieved of any compressive
stress. However the lower part of the green body still contains liquid so that it is subjected to compressive stress owing to capillary forces. This causes the green body to warp into the opposite direction. In addition, when the debinding process is completed, the compressive stress mitigates due to the removal of the capillary forces. This results in a relieving of curvature formation and thus the curvature height decreases from 1.984 mm at 500°C to 1.628 mm at 900°C, curvature height, \( h_i \), from top surface of alumina substrate to the peak point of the top surface of the cell. When the temperature increases after the main shrinkage area (after 900°C according to Figure 55A), the cell curvature height increases further on the same direction. It is because of the fact that high shrinkage of cathode generates high compressive stress on the bottom of the cell and thereby causes more curvature formation of the cell towards the cathode side (from up to the bottom). It reaches its maximum value at 1200°C with a curvature height of 5.026 mm (see Figure 65).

According to Cai et. al. sintering damage such as crack or crack like defects and curvature formation may happen if the densification mismatch stress is greater than intrinsic sintering pressure of ceramic compact [200]. Experimental results show that there is no crack or crack like defects but curvature formation at the edges of the cell. Thus, intrinsic sintering pressure is smaller than densification mismatch stress of the cell.
Figure 65 Anode supported SC-SOFC’s sintering pictures during sintering with temperature increment
5.2 THE EFFECT OF SHAPE CHANGE ON SINGLE STEP CO-SINTERING OF THE CELL

Figure 66 shows the sintering results of square and rectangular planar SC-SOFCs. In order to distinguish the influence of width (W) and length (L) of the planar cells on cell sinterability, a square planar cell and two rectangular planar cells were made. The dimensions of the square cell are 40 mm × 40 mm W×L; those of first rectangular are 20 mm × 40 mm W×L and the second rectangular are 20 mm × 50 mm W×L. Their thickness ratio and thickness are all consistent, which are 10:2:2 and 200:40:40 µm (anode: electrolyte: cathode, A:E:C), respectively. In addition, they were hot pressed and sintered at the same conditions which were determined in chapter 4. Figure 66A depicts similar curvatures being formed at the edges of the square cell whilst the rectangular cell warps during free sintering. Decreasing the length of the rectangular cell (Figure 66C) give rise to the similar results with longer length of the rectangular cell (Figure 66B). This could be explained through the following interpretation: The square cell has symmetry in the planar dimensions, so the shrinkage mismatch between layers is equally shared in x-y directions (assuming z is vertical axis) and induced drawing stress is towards each corner symmetrically. The rectangular cell does not have this symmetry, and since one dimension (e.g. x length) is longer, the effect of mismatch stress will be more prominent along that edge/direction and so will cause the extensive warping/tube like formation etc.

Furthermore, when two light weight alumina rods were put on the top of the rectangular cell (20 mm × 40 mm W×L) perpendicular to longer edges, the warping effect was suppressed and the cell had similar curvature formation at the edge like square cell (see Figure 66D). In addition, the last-sintered rectangular cell was repeated to examine its reproducibility, and a similar result was obtained (Figure 66E). In the light of this information, it was determined that the best course of action was to carry on single step co-sintering of cells with square shape cells due to its simplicity and better quality after visual and handling examination.
Figure 66 Sintering results of square and rectangular cells with the same thickness ratio (10:2:2, A:E:C) and thickness (200:40:40 µm): (A) square cell with 40 mm x 40 mm WxL, (B) rectangular cell with 20 mm x 40 mm WxL, (C) rectangular cell with 20 mm x 50 mm WxL, (D) rectangular cell with 20 mm x 40 mm WxL and 2 rods on the top of the cell during sintering and (E) replication of the cell 3 with the same experimental conditions.
5.3 THE EFFECT OF THICKNESS AND THICKNESS RATIO ON SINGLE STEP CO-SINTERING OF THE CELL

The anode is required to possess enough thickness to provide resistance to deformation [25, 109] and to allow fuel reforming as well as electrochemical reactions for SC-SOFCs [8, 13]. Likewise, the cathode is also required to have optimum thickness for low concentration polarization while providing enough catalytic reaction favourability towards oxygen reduction. Previous experimental results show that the optimized hot pressing condition and sintering profile is not enough to obtain planar anode-supported SC-SOFC. Curvature formation still occurs though cracking and delamination issues were eliminated. Therefore, in the following work, the anode thickness was increased from 200 µm to 400 µm to 500 µm and to 800 µm, and cathode thickness was changed between 40 µm and 60 µm so as to examine the effect of anode and cathode thicknesses on cell sinterability by single step co-sintering at the sintering conditions defined above and on curvature formation. Similarly, electrolyte thickness decreased from 40 µm to 20 µm for the purpose of decreasing ohmic losses and to investigate its effect on single step co-sintering. To balance these increments, all cells were made with the same length and width (40 mm × 40 mm, WxL).

5.3.1 The Influence of Cathode and Electrolyte Thickness on Single Step Co-Sintering of the Cell

In order to investigate the cathode and electrolyte thickness on cell sinterability for anode supported SC-SOFCs, three anode supported cells, which have the same anode thickness (500 µm), were made. Thereafter, firstly, cathode thickness was kept constant (60 µm) while electrolyte thickness was reduced from 40 µm to 20 µm; secondly, the electrolyte thickness was fixed to the lowered value of 20 µm and cathode thickness was decreased from 60 µm to 40 µm (see Figure 67). Figure 67 shows that when anode and cathode thicknesses are the same, decreasing electrolyte thickness has a positive effect on cell sinterability and mean curvature height decreases from 2.87 mm (cell 1) to 2.39 mm (cell 2). This could be explained by the fact that when the electrolyte is sintered separately, it is expected to have no curvature or defects after sintering as anode sintered separately (Figure 59). However, one can observe that electrolyte has curvature at the edges due to interior stress caused by either non uniform burnout of binders or inhomogeneity of electrolyte (Figure 58). Thus, reducing electrolyte thickness may have decreased stresses caused by electrolyte. Furthermore, Figure
also shows that the mean curvature height decreases further to 2.28 mm when cathode thickness was decreased from 60 µm to 40 µm for the same anode and electrolyte thickness (cell 2 and cell 3). The reason behind that could be that the effect of cathode shrinkage (i.e. the cathode-electrolyte mismatch) on overall cell curvature was mitigated by decreasing cathode thickness. (Note the mean curvature height was calculated from the top surface of cathode to the peak point of curves as shown in Figure 67. The measurement was carried out from each side of the cells and the average of them was taken).

**Cell 1: 40 mm x 40 mm WxL, thickness ratio: 25:2:3, thickness 500:40:60 µm**

![Cell 1 view from anode side](image1.png)

![Cell 1 view from cathode side](image2.png)

Mean curvature-height: 2.87 mm

**Cell 2: 40 mm x 40 mm WxL, thickness ratio: 25:1:3, thickness 500:20:60 µm**

![Cell 2 view from anode side](image3.png)

Mean curvature-height: 2.39 mm

**Cell 3: 40 mm x 40 mm WxL, thickness ratio: 25:1:2, thickness 500:20:40 µm**

![Cell 3 view from anode side](image4.png)

Mean curvature-height: 2.28 mm

*Figure 67 The influence of cathode and electrolyte thickness on cell sinterability, 40 mm x 40 mm WxL*
5.3.2 The Influence of Anode and Electrolyte Thickness on Single Step Co-Sintering of the Cell

Figure 68 depicts the sintering results of cell 4, cell 5, cell 6 and cell 7 with their thickness ratio and thickness. It can be clearly seen that increasing anode thickness from 200 µm to 400 µm decreased the curvature formation significantly in the cell (Figure 68, cell 5, mean curvature height from 3.87 mm to 2.29 mm). This is likely because increasing anode thickness enhanced the cell inertia (resistance to deformation) and therefore led to the cell becoming more robust towards stress caused by thermal expansion mismatch between layers during sintering. In other words, the compressive and tensile stresses from the anode-electrolyte mismatch were decreased by increasing the cross-sectional area of the anode normal to the length direction. Therefore, the effect of cathode shrinkage (i.e. the cathode-electrolyte mismatch) on overall cell curvature was mitigated by increasing anode strength. In addition, decreasing electrolyte thickness from 40 µm to 20 µm gave rise to the similar influence on cell single step co-sintering mentioned in section 5.3.1 and curvature was mitigated further (Figure 68, cell 6, shows decrease in mean curvature height from 2.29 mm to 1.97 mm). This could be explained for the same reasons enumerated in section 5.3.1, namely lower the electrolyte thickness lower interior stress. When the anode thickness was increased from 400 µm to 800 µm, the curvature formation diminished further but there was still some observable curvature of the cell (Figure 68, cell 7, mean curvature height: 1.42 mm). Moreover, Figure 69 illustrates the graph of curvature height change of anode supported SC-SCFCs with anode thickness change for the same electrolyte and cathode thickness. It provides one correlative aspect about curvature decrease. For instance it can be seen that the curvature decrease is not linear with the linear increase of anode thickness. Moreover, according to Figure 69, the curvature height rate should generally decrease with anode thickness increment. Note that, the pictures of some specimens of the sintered cells for Figure 69 are hereby excluded for reason of clutter, they were placed in the appendix, see Figure S4.
Figure 68 The influence of anode and electrolyte thickness on cell sinterability, 40 mm x 40 mm WxL

Cell 4: 40 mm x 40 mm WxL, thickness ratio: 10:2:2, thickness: 200:40:40 µm

Cell 5: 40 mm x 40 mm WxL, thickness ratio: 20:2:2, thickness: 400:40:40 µm

Cell 6: 40 mm x 40 mm WxL, thickness ratio: 20:1:2, thickness: 400:20:40 µm

Cell 7: 40 mm x 40 mm WxL, thickness ratio: 40:1:2, thickness: 800:20:40 µm

Mean curvature-height: 3.87 mm

Mean curvature-height: 2.29 mm

Mean curvature-height: 1.97 mm

Mean curvature-height: 1.42 mm
CONSTRAINED SINTERING

Increasing anode thickness too much may have negative effects on the cell's performance due to imposing diffusion/gas transport impediments, particularly related to product removal in the case of a cell being situated as a flow-through (perpendicular to the gas flow) arrangement in the fixture. Thus, it is important to explore different methods to eliminate curvature formation rather than continuously increasing anode thickness. Therefore a dense alumina was placed on the green layer of different anode supported cells which possess the same electrolyte and cathode thickness. The dense alumina has a width and length of 50 mm × 50 mm, a thickness of 0.15 mm and a mass of 1.28 g. The aim is to suppress curvature formation during sintering by utilising the weight of alumina. Figure 70 shows cell 8, cell 9 and cell 10 with their thickness and thickness ratios. It can be clearly seen that using this alumina cover plate for curvature suppression caused severe cracks for the thin anode supported cell (cell 8). Cell 9 has less cracks compared to cell 8 when it was sintered with dense alumina on top of it. It is due to the gain in cell strength as a result of an increase in the anode thickness. When anode thickness increased further to 800 µm (cell 10) and sintered with dense alumina (see Figure 70), the crack formation was prevented and mean curvature
height decreased from 1.42 mm to 0.88 mm in comparison to cell 7 in Figure 68. However, as was pointed out and discussed prior, debinding process has some effects on stress evolution if the evaporation of additives is not easy and homogeneous. Thus, using a dense alumina layer on the top of the cell could block the release of evaporated gas and bring about extra stress generation during sintering. Therefore a porous alumina cover plate (7.31 g with a width and length of 50 mm × 50 mm, a thickness of 1 mm and 40% porosity) was placed on the top of the stacked green layer specimens to improve homogeneous evaporation during debinding and oppress curvature evolution during sintering. Figure 71, cell 11, depicts that there is quite small curvature formation (0.26 mm) when utilising a cover plate on the top of the cell during sintering. Curvature height could be further decreased by utilising heavier porous cover plate on the top of the cell.
Cell 8: 40 mm x 40 mm WxL, thickness ratio: 10:2:2, thickness: 200:40:40 µm, sintered with a dense alumina cover plate on the top of the cell

Cell 9: 40 mm x 40 mm WxL, thickness ratio: 20:2:2, thickness: 400:40:40 µm, sintered with a dense alumina cover plate on the top of the cell

Cell 10: 40 mm x 40 mm WxL, thickness ratio: 40:1:2, thickness: 800:20:40 µm, sintered with a dense alumina cover plate on the top of the cell

Mean curvature - height: 0.88 mm

Figure 70 Three different anode supported planar SC-SOFCs sintered with a dense alumina cover plate, which has a width and length of 50 mm x 50 mm, a thickness of 0.15 mm and a mass of 1.28 g
Cell 11: 40 mm x 40 mm WxL, thickness ratio: 40:1:2, thickness: 800:20:40 µm, sintered with a porous alumina cover plate on the top of the cell

Porous alumina cover plate
50 mm x 50 mm LxW and 1mm thickness
40% porosity; Total mass: 7.31 g

View from anode side
View from cathode side

Mean curvature-height: 0.26 mm

Estimated porosity
Anode: 32.32%
Electrolyte: 16.01%
Cathode: 30.53%

Figure 71 An anode supported cell sintered with a porous alumina cover plate on top of it, views from different perspectives
5.5 MICROSTRUCTURE CHARACTERIZATION OF SINTERED CELLS

As established in the methodology, the procedure now focuses on determining material and microstructural properties of the sintered cells using several discrete characterisation methods. The purpose in taking different type of SEMs (secondary electron (SE) SEM and the backscatter electron (BSE) SEMs) is to distinguish profoundly micro structural view towards the influence of cell thickness ratios, sintering conditions, cover plate presence on particle size densification, general porosity, and layer intermeshing as well as to distinguish phases in cells. EDS was employed to determine material composition through the thickness and determine layer homogeneity. In addition, XRD was used to determine presence of third phase formation after sintering.

5.5.1 SEM Images and EDS Maps

In order to examine the most real/representative structure of cells, SE SEM pictures of each of the sintered cells was taken in the unpolished state. However, it does not accurately provide the particle and pore sizes or their distribution. In addition, crack-like defects may not be distinguished clearly because they could be seen as part of pores in SEM images. Therefore, the cells were polished with different techniques. As is well known, polishing porous structure is not easy due to the possibility of the pull-out of particles and that these particles that are removed from the material can penetrate into pores. In order to prevent pull-out issues and particle penetration, epoxy resin can be utilized to fill out the pores. Figure 72A shows the SE SEM picture of unpolished cell 4, and Figure 72B and Figure 72C shows the SE SEM picture of cell 4 polished with Epoxy resin and Bakelite, respectively. The result showed that the cell polished with epoxy resin may have less susceptibility to issues related to pull-out and particle penetration; however, the pores size and distribution are not so clear in comparison to cell 4 sintered with Bakelite. Therefore, for the better understanding of pore size and distribution from SE SEM images, the polishing for the other cells were done with Bakelite though the removed particle penetration into pores and pull-out issues are more explicit with this technique.

According to Figure 72, the cathode of cell 4 has a coarser grain structure than the anode of the same cell due to over-sintering and the mean particle size was measured to be 3.26 ± 1.86 μm and 3.74 ± 1.97 μm for anode and cathode, respectively. In addition, the mean pore size is 3.1 ± 1.88 μm for anode and 3.31 ± 1.99 μm for cathode (see Table 6).
Across the cell, there is consistently good adhesion between anode-electrolyte, and cathode-electrolyte layers; however, the cell has a porous electrolyte that is acceptable in the SC-SOFC configuration. In addition, the estimated porosity of the anode, electrolyte and cathode of cell 4 was measured as 27.28%, 11.85% and 24.58%, respectively (Table 6). Furthermore, from the same figure, BSE SEM image of cell 4 (Figure 72D) also shows that there is a good connecting/networking of NiO phase on anode side and LSCF phase on cathode side. However, the continuity of CGO on both anode and cathode sides is not as good as required.

![Secondary electron (SE) SEM without polishing](image1)

![SE SEM polishing with Epoxy](image2)

![SE SEM polishing with Bakelite](image3)

![Backscatter electron (BSE) SEM polishing with Bakelite](image4)

Figure 72 Secondary and backscatter SEM results of cell 4, thickness ratio: 10:2:2, A:E:C, (A) secondary electron (SE) SEM without polishing, (B) SE SEM polishing with Epoxy, (C) SE SEM polishing with Bakelite and (D) backscatter electron (BSE) SEM polishing with Bakelite

Figure 73 shows different SEM results of cell 5. It can be seen from Figure 73B and Figure 73C that the cathode has a coarser grain structure than anode and electrolyte; likewise this is replicated in cell 4 as expected. There is also good connectivity of NiO on anode side and LSCF on cathode side whereas that of inadequate continuity of CGO is observed on both sides. Furthermore, the mean particle size of anode and cathode decreased from 3.26 ± 1.86 µm to 3.06 ± 2.07 µm and from 3.74 ± 1.97 µm to 3.53 ± 1.91µm, respectively, as compared
with cell 4 (see Table 6). Similarly, the mean pore size of anode decreased from $3.1 \pm 1.88 \mu m$ to $1.99 \pm 0.65 \mu m$ and that of cathode reduced from $3.31 \pm 1.99 \mu m$ to $2.19 \pm 0.78 \mu m$. However, there was an opposite trend for pore quantity and the estimated porosity increased from $27.28\%$ to $30.53\%$ for the anode, from $11.85\%$ to $14.82\%$ for the electrolyte and from $24.58\%$ to $29.8\%$ for the cathode, respectively, in comparison to cell 4. The reasons behind these could be that increasing anode thickness (increased from $200 \mu m$ to $400 \mu m$ for the same thickness of electrolyte and cathode (cell 4 and cell 5)), improved the cell resistance to deformation and fracture, and thus led to the cell becoming more robust towards stress caused by thermal expansion mismatch between layers during sintering. Therefore, the effect of cathode shrinkage on thicker anode sinterability becomes less. In addition, the aforementioned cathode shrinkage was suppressed by increasing anode resistance to deformation. Consequently, the shrinkage led to deformation or fracture of anode and electrolyte in general were mitigated.

Figure 73 Secondary and backscatter SEM results of cell 5, thickness ratio: 20:2:2, A:E:C, (A) secondary electron (SE) SEM without polishing, (B) SE SEM polishing with Bakelite and (C) backscatter electron (BSE) SEM polishing with Bakelite
The SEM results of cell 6 are shown in Figure 74. They show that similar microstructural results were obtained from cell 6 in terms of particle and pore connectivity in comparison with cell 4 and cell 5. Decreasing electrolyte thickness for the same anode and cathode thickness has little effect on porosity as compared with cell 5 (small reduction in general, see Table 6) and the estimated porosity of the layers were measured to be 30.25%, 14.5% and 29.12%, for anode, electrolyte and cathode, respectively. This could be explained by the fact that the compressive stress caused by cathode layer has more effect on a thinner electrolyte and thus improved the sinterability of electrolyte and thereby resulted in less porous structure. Moreover, there is a slight reduction in mean pore size of both electrodes and the mean particle size of cathode in comparison to cell 5. However, there is a slight increase in the mean particle size of anode (see Table 6).

Figure 74 Secondary and backscatter SEM results of cell 6, thickness ratio: 20:1:2, A:E:C, (A) secondary electron (SE) SEM without polishing, (B) SE SEM polishing with Bakelite and (C) backscatter electron (BSE) SEM polishing with Bakelite
The similar particle and pore connectivity was observed from SEMs results of cell 7 (see Figure 75) as compared with previous cells. In addition, cathode has a coarser structure than anode as with other cells. Increasing anode thickness from 400 µm to 800 µm for the same electrolyte and cathode thickness (cell 6 and cell 7, respectively) has substantial effects on both porosity and mean particle and pore size on both electrodes (see Table 6). The estimated porosity of anode, electrolyte and cathode increased from 30.25% to 33.43%, from 14.5% to 17.03% and from 29.12% to 32.25%, respectively. As the shrinkage effect of cathode on a thicker anode become less effective on anode sinterability as well as whole cell. Moreover, the shrinkage of cathode was also mitigated due to constrain imposed by thicker anode. Therefore, in general, the sinterability of each layer was mitigated and thus resulted in higher porosity of electrodes and electrolyte. Furthermore, the mean particle and pore sizes of cell 7 reduced compared to cell 6. The mean particle and pore sizes of anode were measured to be 2.60 ± 1.61 µm and 1.24 ± 0.47 µm, for cells 7, respectively, while that of cathode were measured to be 3.01 ± 1.51µm and 1.6 ± 0.77 µm, respectively (see Table 6).
Figure 75 Secondary and backscatter SEM results of cell 7, thickness ratio: 40:1:2, A:E:C, (A) secondary electron (SE) SEM without polishing, (B) SE SEM polishing with Bakelite and (C) backscatter electron (BSE) SEM polishing with Bakelite.

The SEM images of cell 11 are shown in Figure 76A, 76B and 76C. It shares the same thickness and thickness ratio with cell 7 (see Figure 75 and Figure 76). In addition to SEM results, Figure 76D also shows the phase image of cell 11 from Energy Dispersive Spectroscopy (EDS) analysis. The SEM pictures as well as phase image of cell 11 illustrates that the anode and cathode possess a similar micro structure with cell 7 and others in terms of particle and pore connectivity as well as adhesion of both electrode to electrolytes. Likewise, the cathode has a coarser structure compared to anode due to over-sintering. Moreover, there is no new phase formation after sintering observed from phase image. In addition, putting a porous alumina cover plate on cell 11 resulted in slightly decreasing in the anode, electrolyte and cathode porosities (see Table 6). They were measured to be 32.32% for anode, 16.01% for electrolyte and 30.53% for cathode. This could be explained by the fact that grains in
Electrolyte and electrodes were forced by internal stresses caused by interface stresses responsible for in-plane shrink rather than curvature formation. This phenomenon might have increased their sinterability but resulting in decreased porosity. In addition, the mean particle and pore sizes of cell 11 reduced as compared with cell 7. The mean particle size of anode and cathode were measured to be $3.08 \pm 1.45 \, \mu m$ and $3.66 \pm 1.62 \, \mu m$, respectively and the mean pore sizes of anode and cathode were measured to be $1.70 \pm 0.64 \, \mu m$ and $2.17 \pm 0.92 \, \mu m$, respectively.

![Figure 76](image1.png)

Figure 76 Secondary and backscatter SEM results of cell 1, thickness ratio: 40:1:2, A:E:C sintered with porous cover plate. (A) secondary electron (SE) SEM without polishing, (B) SE SEM polishing with Bakelite, (C) backscatter electron (BSE) SEM polishing with Bakelite and (D) Phase image from EDS analysis.

Figure 77 also shows the EDS maps and spectrum of cell 11. It can be seen that the distribution of Ni, Ce, Fe, Sr, O, La, Gd and Co elements is in the expected regions and there is no other elements (such as impurities due to experimental conditions) observed from EDS maps (see Figure 77A). However, this result by itself cannot demonstrate that there are no unwanted elements in the cells. This is because the small amount of elements is not easily
seen in the EDS maps. However, they could be seen in the EDS spectrum (see Figure 77B). It can be observed that there are some impurities in the cell for instance, gold (Au), palladium (Pd), yittria (Y), silicon (Si) and aluminium (Al). Au and Pd are introduced from the sputtering of cells with these materials so as to make the cells conductive for SEM analysis. Yittria might be introduced during ball milling due to milling media is made of yittria stabilized zirconia (YSZ). Al was most probably introduced during sintering from alumina substrate or cover plate. Furthermore, Si could be coming from any stage of cell preparation, sintering, polishing and even during cell characterization as silicon elements could be found in any of these stages. These unwanted elements could seriously affect the performance of the cells. Therefore, they should be prevented to present in the cell, or the amount of these should be curtailed to an acceptable level. It can be seen that their amounts are quite small (Figure 77B).

Furthermore, the estimated porosity, mean particle and pore sizes of anode and cathode of cell 4, cell 5, cell 6, cell 7 and cell 11 are summarised in Table 6.

<table>
<thead>
<tr>
<th>Table 6 Porosity measurement of anode, cathode and electrolyte with mean particle and pore sizes of electrodes</th>
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<td><strong>Cell 4 (200:40:40 µm, A:E:C), free sintering</strong></td>
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<td>Porosity (%)</td>
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<td>Mean particle size (µm)</td>
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<td>Mean pore size (µm)</td>
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<td><strong>Cell 5 (400:40:40 µm, A:E:C), free sintering</strong></td>
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<td>Porosity (%)</td>
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<tr>
<td>30.53</td>
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<td>Mean particle size (µm)</td>
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<td>Mean pore size (µm)</td>
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<td><strong>Cell 6 (400:20:40 µm, A:E:C), free sintering</strong></td>
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<td>Porosity (%)</td>
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<td>Mean particle size (µm)</td>
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<td>Mean pore size (µm)</td>
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<td>Mean pore size (µm)</td>
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<td><strong>Cell 11 (800:20:40 µm, A:E:C), sintered with a porous cover plate</strong></td>
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<tr>
<td>Porosity (%)</td>
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<tr>
<td>Mean particle size (µm)</td>
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<td>Mean pore size (µm)</td>
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A) EDS Maps of cell 11

B) Map Sum Spectrum of cell 11

Figure 77 (A) EDS Maps and (B) Map Sum Spectrum cell 11, which has a thickness of 800:20:40 µm, A:E:C, sintered with porous cover plate
5.5.2 X-Ray Diffraction of Cell 4, Cell 5, Cell 6 and Cell 11

Figure 78 and Figure 79 show XRD of cell 4, cell 5, cell 6 and cell 11. According to these figures, there is no unwanted phase formation after sintering aside from the desired phases (NiO, CGO and LSCF) for cell 4, cell 5, cell 6 and cell 11. All cells possess highly similar XRD results. It might be because of the fact that each cell has the same anode, cathode and electrolyte material, and they were all made with the same fabrication process. The only difference is their layer thickness. Therefore, it is highly likely to expect similar XRD results. Furthermore, no further crystalline phases are present in any of the cells. The EDS data also supports the elements which could cause the formation of these phases in cell 11 (see the elemental analysis from Figure 77B). Furthermore, all elements in cell 11 using EDS can be attributed to the three phases found in XRD. However, the XRD technique performed on cell 11 did not detect or show additional phases representing the trace elements of Pd, Al and Si, due to the limitation of the XRD technique in detecting trace amounts of phases.
Figure 78 (A) X-Ray Diffraction of cell 4 and (B) that of cell 5
Multi-layered ceramic composites may experience significant magnitude of residual stress during cooling from sintering temperature, specifically when they are composed of comparatively thick layers made of different layers. Residual stress occurs due to different
CTE between layers [200, 201] and elastic constants between the constituent phases and among adjacent layers. In addition, it should also be noted that the geometry of the layered structure, in particular on layer thickness, significantly affect resistance of a cell to residual stress induced deformation or cracking. In general, the overall stress field is influenced by different shrinkages during sintering, CTE mismatch between constituent layers/phases, mismatch in elastic constants between different phases/layers and layers` geometry [201]. The general stress field may be rather complex and therefore difficult to envisage by theoretical calculations. An accurate control of both magnitude and distribution of residual stress is required so as to avoid delamination and cracking. The development of reliable experimental technique for the assessment of the residual stress in multi-layered ceramic components is highly desired. There are several techniques available for the evaluation of the residual stress in ceramic materials, including neutron diffraction, X-ray diffraction and piezo-spectroscopic analysis of photo-stimulated fluorescence [201, 202]. In this study, fluorescence spectroscopy was chosen to measure residual stress between cathode and electrolyte of the cells. In order to use this technique the material must have the luminescent ability (those defined as luminescent material include Al₂O₃:Cr³⁺, BaSO₄, etc.; for more information about luminescence materials see reference [203, 204]). Moreover, an energy source is required to stimulate luminescence; there are a wide range of energy sources that can be utilised, for instance, X rays, cathode rays, UV emission of a gas discharge and so forth, and their variety provides a suitable classification for luminescence phenomena [203, 204].

It is well known that most of the ceramics are optically transparent, with exception of pore scattering and grain boundary, due to their large band gaps. However, the existence of trace impurities in polycrystalline ceramics, largely rare-earth ions and transition-metal ions, can bring about intense fluorescence when suitably excited. These specific lines typically arise from electronic transition of dopant ions. Furthermore, these characteristic lines are also highly sensitive to local ionic environment in the host crystal, which can be described by ligand field theory. As a consequence, deformation which shifts the interionic distances can lead to change in the characteristic lines. In addition, the existing degeneracy of the energy states will be removed by that deformation which decreases the symmetry of the crystal, and therefore results in splitting and shifting of the lines in the spectra. The connection between the change in energy of the electronic state and strain (equivalently stress) is known as the piezo spectroscopic effect [205, 206].
For cathode (LSCF-CGO) and electrolyte (CGO), they both do not have luminescent ability and therefore Al$_2$O$_3$:Cr$^{3+}$ polycrystalline ceramics powders will be utilized between these two layers. The reasons for selecting Al$_2$O$_3$ corundum are (1) chemical and thermal stability, and relatively good strength [207]; (2) it is inert toward electrolyte material at 1200˚ [208, 209]; (3) sintering temperature is over 1400˚C [210] as per CGO; (4) it can improve the ionic conductivity of the electrolyte (CGO) [209, 211]. However, using alumina powder between anode and cathode for measuring stress between these layers may have negative or positive effect on cell sinterability as well as cathode catalytic and electrical properties. These effects are not investigated in this study.

Chromium ions (Cr$^{4+}$) fluorescence spectroscopy can be used to investigate the residual stress for alumina based ceramics. The method is based on the shift in the fluorescence bands associated with Cr which is persistent impurities in alumina (Al$_2$O$_3$) [205, 206, 212, 213]. The crystal field result from the octahedral arrangement of oxygen ions surrounding the chromium ions in alumina results in two closely-separated R1 and R2 bands that fluoresce at a wavelength of roughly 694 nm [213, 214]. Stress application, different chromium composition and temperature change all distort octahedral and related crystal field and results in changes in the energies of the R1 and R2 fluorescence peaks (see Figure 81). In other words, Huang et al. simply explains this technique as a laser being focused on the sample surface by utilising an optical microprobe. The chromium ions in alumina interact with the laser and leads to luminescence. When the materials undergo to a stress the peaks of the luminescence frequency in the spectrum changes correspondingly. This phenomenon allows us to obtain the indication of the mean stress distribution in materials [212]. When the materials are subject to compressive stress, fluorescence spectra shifts towards lower wavenumber, and vice versa when they are subject to tensile stress [215]. The relationship between energy change, $\Delta v$, (in wavenumbers, cm$^{-1}$), and stress, $\sigma$, in the Al$_2$O$_3$ corundum structure is given as following base equation [202, 205, 206, 213, 214, 216, 217]:

$$\Delta v = \Pi_{11}\sigma_{11} + \Pi_{22}\sigma_{22} + \Pi_{33}\sigma_{33}$$ (14)

Where the tensor axes (1, 2, and 3) represents the corundum crystallographic axes (a, m, c). The $\Pi$ is the piezo-spectroscopy coefficient. Furthermore, the three-fold rotational symmetry about the corundum c axis should principally bring about the a and m axes to be equivalence. Therefore, it is assumed here to utilize conventional notation of $\Pi_{11}$, $\Pi_{22}$, $\Pi_{33}$ as $\Pi_{11} = \Pi_{22} = \Pi_a$ and $\Pi_{33} = \Pi_b$. In addition, these two coefficients ($\Pi_a$ and $\Pi_b$) are different for the R1 and
R2 fluorescence lines. Under the hydrostatic conditions ($\sigma_{11} = \sigma_{22} = \sigma_{22} = \sigma$), the equation 14 can be written as follow [213, 214]:

$$\Delta v = (2\Pi_a + \Pi_b) \sigma$$

(15)

Although the piezo-spectroscopic coefficients, $\Pi_a$ and $\Pi_b$, for R1 and R2 fluorescence lines are different[205, 213, 218], their pressure sensitivity ( $2\Pi_a + \Pi_b$ ) is almost the same [219–221]. Here, R1 line shifts will be interested in order to calculate residual stress. The piezo-spectroscopic coefficient for R1 line is $2/3$ of ( $2\Pi_a + \Pi_b$ ) for polycrystalline alumina, which is equal to $(7.59 \times 2) / 3 = 5.06 \text{ cm}^{-1} \text{ GPa}^{-1}$ [202, 205].

Figure 80 shows a general representative illustration of alumina placement between cathode and electrolyte layers of different SC-SOFCs. In addition, it also shows that mapping on alumina for fluorescence spectra measurement points and its starting point. Measurements were taken with a step size of 1 µm for a 39 µm × 8 µm map (40 × 9 points on x and y direction, respectively). Out of these, a representative 25 points on x direction for each 9 points along y direction were chosen for stress measurement in order to obtain reasonable and non-distorted fluorescence spectra from the points on alumina particles, as shown in Figure 80. Moreover, the illustration in Figure 80 is only for visual representation, and is not the actual figure of alumina location and fluorescence map in each and every one of the measured cells. The alumina particle location(s) along the y direction is generally consistent between layers for all the cells; however, the location along x directions are different because samples for fluorescence spectra measurement were taken at different parts of the cells due to difficulty in finding the location of alumina in the cell by using the Raman microscope. Therefore, for simplicity, fluorescence spectrum measurements were taken on the places where appropriate alumina was found. In addition, the particle size of alumina which the fluorescence spectra measurement was taken was different for each cell based on the visual inspection.

Figure 81 depicts one of the fluorescence spectrum measurement of one of the cells (cell 4, thickness ratio: 10:2:2) and fluorescence spectra result of reference alumina. It also shows that the shift ($\Delta v$) of a peak after sintering. It can be seen that the shift is towards lower wavenumber (from 14404 cm$^{-1}$ to 14398.9 cm$^{-1}$); indicating a compressive stress at that point of the cell. According to our results, all measurements from all cells possess shift towards lower wavenumber, therefore, they all are under compressive stress.
Figure 80 A representative illustration of alumina placement between cathode and electrolyte layers of a SC-SOFCs and mapping positions on alumina for fluorescence spectra measurement.

Figure 81 Representative fluorescence spectra from cell 1, (thickness ratio: 10:2:2, A:E:C) and the shift (Δv) from reference peak position after sintering.

Figure 82 and Figure 83 show the residual stress measurement between cathode and electrolyte of five different anode supported SC-SOFCs at room temperature (cell 4, cell 5, cell 6, cell 7 and cell 11 mentioned in the previous sections, but this time they were sintered with some alumina powders distributed between cathode and electrolyte). The residual stress...
measured between these layers after sintering is the combination of the sintering stress due to different shrinkage from layers and CTE mismatch layers during cooling. Sintering of these cells may have been affected by alumina powder in comparison to the same cells sintered without alumina powder. Therefore, the residual stress in cells sintered with alumina powder may be different than that of the actual cells sintered without alumina powders. However, for the sake of simply measuring residual stress in the cells by utilising fluorescence spectroscopy, this effect was ignored. Though the residual stress might be different in actual cells comparing to residual stress found in the same cells that alumina powders were placed, finding residual stress of the cells by utilising fluorescence spectra can help one to evaluate the stress distribution in the cells and thereby attain better understanding of sintering.


Figure 82 Residual stress results of (A) cell 4, (B) cell 5 and (C) cell 6 from Fluorescence spectroscopy
According to Figure 82 and Figure 83, the maximum residual stress occurred at the location close to electrolyte layers for cell 4, cell 5, cell 6, and cell 7, with a maximum compressive residual stress of -2065 MPa, -1274 MPa, -1084 MPa, and -730 MPa, respectively. However, it was measured to be -740 MPa for cell 11 at the location close to cathode layer. The reason for the residual stress location of cell 4, cell 5, cell 6, and cell 7 could be the higher densification of electrolyte comparing to cathode (from the SEM images electrolyte has less porosity than cathode) which might impose more pressure on alumina section in the electrolyte. For all cells, the common point observed is a lack of symmetrical residual stress distribution along the x direction from the alumina particles. This is manifest most obviously in the results from cells 4–7, having a region of comparatively higher stress close to the region of x = 0–10. However, the maximum stress region for the cell 11 is the region of x = 15–25. This might be because of the fact that for all these cells, the location of the measured alumina particles is not equidistant to the cells’ edges. Therefore, bending due to the cathode’s high shrinkage has asymmetrical effects to the alumina powders. For
instance, if the measured alumina powder is closer to one edge of the cell, the influence of compressive stress will be higher at the edge of the alumina which is facing the cell edge further away from it. Note: Fluorescence spectra R1 shift was plotted and shown in Figure S5 and Figure S6 in Appendix.

The mean residual stress along the y direction for each point of x direction was also calculated (see Table 7). The results show that increasing anode thickness from 200 µm to 400 µm (cell 4 and cell 5) mitigated compressive stress substantially for all points along x direction. This might be as a result of the fact that when anode thickness was increased, the effect of cathode shrinkage on overall cells became less effective, and therefore, the electrolyte become more porous comparing to cell has less anode thickness (see SEM results of all cells), and thereby, the densification pressure on alumina decreases. However, increasing anode thickness from 400 µm to 800 µm (cell 5 and cell 7) has comparatively less effect on mean compressive stress; there are even instances of increase in the mean residual stress along x direction. For the same anode thickness, decreasing electrolyte thickness (from 40 µm to 20 µm, cell 5 and cell 6) do not have substantial influence on mean residual stress. The mean compressive residual stress showed slight increases and decreases at different points along the x direction. For the same anode, electrolyte and cathode thickness (cell 7, and cell 11 which is sintered with 5 cm × 5 cm porous alumina cover plate in order to oppress the curvature formation), the maximum compressive stress is quite different and its location is opposite of each other along the x direction. The mean residual stress of cell 11 significantly decreased compared to the cell 7 (from around -700 MPa to around -450 MPa) (cell 11, see Table 7). To conclude, it can be established that, increasing anode thickness has positive effect on cells sinterability by observing stress evolution between two different layers.
In addition, residual stress in the cells after sintering is as a result of first stress developed during sintering due to different shrinkage rate of layers and second thermal expansion misfit of layers during cooling from 1200°C to room temperature (assumed to be 20°C). If the residual stress of cells at room temperature owing to different thermal expansion mismatch is calculated, then the residual stress developed during sintering can be estimated from residual stress measurement at room temperature using fluorescence spectroscopy technique. In order to find residual stress contribution because of CTE misfit, the equation 16 can be simply used for two different layers. However, for the cells sintered together, they have three different layers, anode, electrolyte and cathode. Nonetheless, this equation can be used for the cells in this study if we assume anode and electrolyte (CGO) as one composite layer since composite anode consist of 40% of electrolyte (CGO) material and 60% of NiO before sintering. In addition, they have close shrinkage properties (see Figure 55) and CTE (see Table 8). Furthermore, the thickness of electrolyte is comparatively small for anode

### Table 7 Mean stress measurement along y direction on alumina sintered with SC-SOFCs

<table>
<thead>
<tr>
<th></th>
<th>X direction</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 4</td>
<td>X direction</td>
<td>-1675.45</td>
<td>-1545.89</td>
<td>-1587.62</td>
<td>-1541.5</td>
<td>-1447.08</td>
<td>-1438.3</td>
<td>-1416.34</td>
<td>-1488.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell 7</td>
<td>X direction</td>
<td>-51.182</td>
<td>-70.383</td>
<td>-675.337</td>
<td>-739.017</td>
<td>-675.337</td>
<td>-721.45</td>
<td>-721.45</td>
<td>-686.316</td>
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<table>
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<th>X direction continue</th>
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<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
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</thead>
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<td>X direction continue</td>
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<td>17</td>
<td>18</td>
<td>19</td>
<td>20</td>
<td>21</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>Cell 5</td>
<td>X direction continue</td>
<td>-1207.73</td>
<td>-1238.47</td>
<td>-1207.73</td>
<td>-1236.28</td>
<td>-1157.22</td>
<td>-1216.51</td>
<td>-1220.9</td>
<td>-1106.72</td>
</tr>
<tr>
<td>Cell 6</td>
<td>X direction continue</td>
<td>-663.295</td>
<td>-674.274</td>
<td>-691.841</td>
<td>-779.676</td>
<td>-685.254</td>
<td>-726.975</td>
<td>-656.707</td>
<td>-619.378</td>
</tr>
<tr>
<td>Cell 7</td>
<td>X direction continue</td>
<td>-725.077</td>
<td>-696.531</td>
<td>-703.118</td>
<td>-736.056</td>
<td>-676.768</td>
<td>-692.139</td>
<td>-707.51</td>
<td>-685.551</td>
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</tbody>
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<table>
<thead>
<tr>
<th></th>
<th>X direction continue</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
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<td>X direction continue</td>
<td>-1214.32</td>
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<tr>
<td>Cell 5</td>
<td>X direction continue</td>
<td>-726.975</td>
</tr>
<tr>
<td>Cell 6</td>
<td>X direction continue</td>
<td>-677.984</td>
</tr>
<tr>
<td>Cell 7</td>
<td>X direction continue</td>
<td>-640.203</td>
</tr>
<tr>
<td>Cell 11</td>
<td>X direction continue</td>
<td>-446.966</td>
</tr>
</tbody>
</table>
supported SC-SOFCs, and thus, electrolyte/anode layers can be assumed to be one composite layer consisting of NiO-CGO materials with certain porosity and it is named as single composite new layer. In addition, cathode also is made of different materials (50%LSCF-50%CGO) before sintering, but the shrinkage rate and CTE of cathode and CGO electrolyte are quite different (see Figure 55 and Table 8). Furthermore, cathode of the cells also has certain porosities after sintering. Therefore, the percentage of porosity and composition of each material should be taken into account so as to find true value of thermal expansion coefficient, Young’s modulus and Poisson ratio of these materials. In order to find these values, the inclusion principle was simply utilised. Table 9 gives the estimated composition of LSCF, CGO and porosity for cathode, and NiO, CGO and porosity for single composite new layer (composed of anode and electrolyte) in terms of volume ratio (note the mass ratio of each layer in the green tape was assumed to be the same with the volume ratio). They were calculated based on the material composition table, Table 3, and porosity table, Table 6. In addition, Table 9 also gives the new values of Young’s modulus, CTE, and poission ratio of these two layers for different anode supported SC-SOFCs. Furthermore, the new thickness of each cells’ layer were calculated based on around 18% shrinkage of each layer from SEM results.

\[
\sigma_1 = \frac{(\alpha_2 - \alpha_1)\Delta T}{E_1 + t_1 E_2} \quad \text{and} \quad \sigma_2 = \frac{(\alpha_1 - \alpha_2)\Delta T}{E_2 + t_2 E_1} \quad [222] \quad (16)
\]

\[
\hat{E} = \frac{E}{1-\nu} \quad [222] \quad (17)
\]

\[
\nu = \frac{E}{2G} - 1 \quad [223] \quad (18)
\]

Where \(\sigma\) is the residual stress in layers, \(\alpha\) the thermal expansion coefficient, \(E\) the young’s modulus, \(t\) the layer thickness, \(\nu\) the Poisson ratio, and \(G\) the shear modulus. Subscripts 1 and 2 represent the cathode and the single composite new layer, respectively.
Table 8 Estimated properties of some materials (around 99% relative density) used in this study.

<table>
<thead>
<tr>
<th>Material properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE (K⁻¹)</td>
</tr>
<tr>
<td>NiO</td>
</tr>
<tr>
<td>CGO</td>
</tr>
<tr>
<td>LSCF</td>
</tr>
</tbody>
</table>

Table 9 New material properties calculated based on their composition and porosity ratio using simple inclusion principle

<table>
<thead>
<tr>
<th>%LSCF</th>
<th>%CGO</th>
<th>%NiO</th>
<th>Porosity</th>
<th>CTE (K⁻¹) x 10⁻⁶</th>
<th>E (GPa)</th>
<th>ê (GPa)</th>
<th>v</th>
<th>t (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode supported SC-SOFC (cell 4) (10:2:2, A:E:C, thickness ratio, 200:40:40 µm thickness) before sintering</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode</td>
<td>37.5</td>
<td>37.5</td>
<td>0</td>
<td>25</td>
<td>10.91</td>
<td>133.9</td>
<td>175</td>
<td>0.236</td>
</tr>
<tr>
<td>Single composite new layer</td>
<td>0</td>
<td>38.7</td>
<td>36</td>
<td>23.3</td>
<td>9.8</td>
<td>156.6</td>
<td>206</td>
<td>0.24</td>
</tr>
<tr>
<td>Anode supported SC-SOFC (cell 5) (20:2:2, A:E:C, thickness ratio, 400:40:40 µm thickness) before sintering</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode</td>
<td>35.1</td>
<td>35.1</td>
<td>0</td>
<td>29.8</td>
<td>10.21</td>
<td>125.3</td>
<td>160.9</td>
<td>0.221</td>
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<tr>
<td>Single composite new layer</td>
<td>0</td>
<td>33</td>
<td>37.9</td>
<td>29.1</td>
<td>9.31</td>
<td>149.38</td>
<td>193</td>
<td>0.226</td>
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<tr>
<td>Anode supported SC-SOFC (cell 6) (20:1:2, A:E:C, thickness ratio, 400-20-40 µm thickness) before sintering</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cathode</td>
<td>35.44</td>
<td>35.44</td>
<td>0</td>
<td>29.12</td>
<td>10.31</td>
<td>126.52</td>
<td>162.8</td>
<td>0.223</td>
</tr>
<tr>
<td>Single composite new layer</td>
<td>0</td>
<td>30.6</td>
<td>39.9</td>
<td>29.5</td>
<td>9.27</td>
<td>149</td>
<td>192.2</td>
<td>0.225</td>
</tr>
<tr>
<td>Anode supported SC-SOFC (cell 7) (40:1:2, A:E:C, thickness ratio, 800:20:40 µm thickness) before sintering</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode</td>
<td>33.75</td>
<td>33.75</td>
<td>0</td>
<td>32.5</td>
<td>9.81</td>
<td>120.49</td>
<td>153.1</td>
<td>0.213</td>
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<tr>
<td>Single composite new layer</td>
<td>0</td>
<td>28.06</td>
<td>38.97</td>
<td>32.97</td>
<td>8.82</td>
<td>141.85</td>
<td>141.1</td>
<td>0.213</td>
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Table 10 Total mean residual stress between cathode and electrolyte obtained by using fluorescence spectroscopy and estimated residual stress due to CTE mismatch during cooling

<table>
<thead>
<tr>
<th>Cell 4</th>
<th>Cell 5</th>
<th>Cell 6</th>
<th>Cell 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mean stress on alumina placed in different cells from fluorescence result (MPa) (including sintering stress during sintering and CTE mismatch stress during cooling)</td>
<td>-1315.06</td>
<td>-758.508</td>
<td>-765.13</td>
</tr>
<tr>
<td>σ (estimated compressive stress in cathode due to CTE mismatch during cooling), MPa, from modelling</td>
<td>-200</td>
<td>-159</td>
<td>-185</td>
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</table>

Table 10 shows the total mean residual stress on alumina particles placed between cathode and electrolyte of cell 4, cell 5, cell 6 and cell 7 measured at room temperature by fluorescence spectroscopy and the estimated residual stresses in cathode of cells due to CTE
misfit during cooling. According to Table 10 the stress developed during sintering due to different shrinkage behaviour of layers are dominant factor in the total mean residual stress since stress due to CTE mismatch is low in comparison to residual stress occurred during sintering.

5.7 CELL PERFORMANCE TESTS

Performance testing was carried out with two aims: to establish functionality of the sintered specimens as working electrochemical cells, and to identify the effects of increasing anode thickness and reducing electrolyte thickness, which were beneficial in obtaining reduced curvature, on the cell performance. Figure 84 and Figure 85 shows OCV measurements of cell 4 and cell 5, and cell 6 and cell 11, respectively, at different flow rates and gas mixture ratios and Table 11 shows their maximum OCV results and power densities. When cell 4 and cell 5 are compared to each other, it can be seen that the OCV measurement of cell 5 in almost all gas mixtures (except gas mixture 2) is higher than that of cell 4 (see Figure 84). This might be as a result of improvement of methane reforming on anode side, which leads to oxygen partial pressure decrease locally, hence increasing the partial pressure differential of oxygen across the electrodes. However, when electrolyte thickness is reduced (comparing cell 5 and cell 6), OCV is decreased in all different gas flow rates and even less than the OCV measurements of cell 4 (see Figure 84 and Figure 85). This could be as a consequence of: (1) decreasing electrolyte thickness resulting in better ionic conductivity, therefore enabling faster oxygen ion transfer from cathode to anode side, and permitting oxygen reduction reaction to proceed at the fastest rate for the present condition and thus using up oxygen gas at the cathode membrane, and/or (2) reaction products (H₂ and CO) on anode side can migrate easily to cathode side and react with oxygen. In both cases, oxygen partial pressures differences between anode and cathode sides decrease, thereby decreasing OCV; the second case will also reduce fuel partial pressure and, could limit the utilisation of these fuels for electrochemical reaction, in favour of direct chemical oxidation/reforming. In addition, increasing anode thickness (cell 11) improves OCV in all the different gas mixtures in comparison to cell 6 and the OCV of cell 11 becomes a closer match to that of cell 5 (see Figure 84 and Figure 85 and Table 11). As a result, the OCV fall due to reduction in electrolyte thickness was compensated to a certain extent by increasing anode thickness (cell 11). Furthermore, the oscillation of OCV of some cells (cell 6, cell 11 and even cell 5) might be attributed to anode oxidation and reduction cycling and related temperature fluctuations.
Table 11 OCV measurements and maximum power density at these OCVs of cell 4, cell 5, cell 6 and cell 11 at 600°C at different gas mixtures

<table>
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<tbody>
<tr>
<td></td>
<td>OCV (V)</td>
<td>Power density (mW cm(^{-2}))</td>
<td>OCV (V)</td>
<td>Power density (mW cm(^{-2}))</td>
</tr>
<tr>
<td>Fixed CH(_4) (40ml/min) And Fixed N(_2) (200 ml/min) gas mixture 1 (R:1)</td>
<td>0.69</td>
<td>2.82</td>
<td>0.73</td>
<td>21.15</td>
</tr>
<tr>
<td>Fixed CH(_4) (50ml/min) And Fixed N(_2) (200 ml/min) gas mixture 2 (R:1.2)</td>
<td>0.6</td>
<td>2.23</td>
<td>0.6</td>
<td>18.30</td>
</tr>
<tr>
<td>Fixed CH(_4) (50ml/min) And Fixed N(_2) (200 ml/min) gas mixture 3 (R:1)</td>
<td>0.67</td>
<td>2.65</td>
<td>0.69</td>
<td>27.12</td>
</tr>
<tr>
<td>Fixed CH(_4) (50ml/min) And Fixed N(_2) (200 ml/min) gas mixture 4 (R:1.2)</td>
<td>0.62</td>
<td>2.35</td>
<td>0.65</td>
<td>23.67</td>
</tr>
</tbody>
</table>

Figure 86 and Figure 87 shows the power density of these cells in different gas composition, and the highest power density was observed as 2.82 mW cm\(^{-2}\), 23.64 mW cm\(^{-2}\) and 30.69 mW cm\(^{-2}\) from cell 4, cell 6 and cell 11 at gas mixture 1 (see Table 11). However, the highest power density was obtained from cell 5 as 27.12 mW cm\(^{-2}\) at gas mixture 3. When cell 4 and cell 5 are compared with each other (see Figure 86), increasing anode thickness improved cell performance significantly across the current draw range in all gas flow rates. This might be explained by the fact that, in addition to likely reforming improvement, the thicker anode volume for cell 5 implies a larger three-phase region throughout the layer (as SC-SOFCs are porous throughout, with the phases distributed along the cell), suggesting that more electrochemical oxidation of the fuel is facilitated. As a result, increasing cell anode thickness not only improved cell OCV in general and decreased curvature formation, but also improved cell power density substantially. Furthermore, it is likely that gains will be made in obtaining higher power density when electrolyte thickness is reduced owing to reduction in electrolyte ohmic losses. For the same anode thickness, cell 5 and cell 6, decreasing electrolyte thickness resulted in increased cell performance at gas mixture 1 and 2 (from 21.15 mW cm\(^{-2}\) to 23.64 mW cm\(^{-2}\) and from 18.3 mW cm\(^{-2}\) to 18.8 mW cm\(^{-2}\), respectively) (see Figure 86, Figure 87 and Table 11). However, for the gas mixture 3 and 4, the power density of cell 6 decreased in comparison to cell 5 (from 27.12 mW cm\(^{-2}\) to 23.01 mW cm\(^{-2}\)
and from 23.67 mW cm\(^{-2}\) to 19.3 mW cm\(^{-2}\), respectively). This may be ascribed to the fact that the negative effect of product gas cross-over from anode to cathode side is higher than the positive effect of ohmic loss reduction on cell performance. In addition to these, further increasing the anode thickness (Figure 87, cell 11) enhanced cell performance even greater in comparison to cell 6 (29.82%, 42.5%, 22.46% and 14.55% improvement at gas mixture 1, 2, 3 and 4, respectively). Moreover, the power density of cell 11 is also higher than that of cell 5 at gas mixture 1, 2 and 3 whereas it is less at gas mixture of 4. As a consequence, the increased anode and decreased electrolyte thickness resulted in not only better sintering result but also power density in this study.

However, in general, both overall current draw and power density are relatively low in comparison to the available results obtained in the literature. The cell performance might be affected adversely by various reasons commonly afflicting both cells. The thick and porous electrolyte leads to more ionic transport losses as well as a minimisation of the oxygen partial pressure differential across the cathode and anode membranes from gas crossover, which determines the establishment of OCV. The usage of CGO electrolyte in reducing conditions facilitates the electronic conduction through the electrolyte [227] which would enable short circuit current through the cell. Furthermore, methane partial oxidation may not be sufficient enough because of low working temperature (600°C). Best reforming can be achieved at temperature over 700°C which is not acceptable for low temperature SC-SOFCs [8, 114]. In addition, oxygen from the mixed gas phase could react more strongly/favourably with syngas (H\(_2\) and CO from methane reforming) than oxygen ions coming from the electrolyte [116] and thereby causing a reduction in cell performance. The other consideration is that LSCF perovskite cathode is known to be catalytically active towards HC/methane oxidation [8], [228] and hence the cathode could facilitate methane oxidation catalysis and minimise its role as an mixing ionic electronic conductive (MIEC) membrane for oxygen reduction. Given that this is the first step in the SC-SOFC to establish OCV, as well as the fact that the cell is arranged perpendicular to the flow with cathode layer facing first, it is important that the cathode remains more selective to the oxygen reduction. The attainment of OCV levels for all cells closer to 0.7V suggests that the electrochemical oxidation of species (H\(_2\) and CO) is still taking place. Moreover, the coarseness of the cathode microstructure for both cells may adversely impact performance, given that surface exchange rather than bulk/porous diffusion is more likely the rate limiting step, given that best performance is achieved in the relatively rich mixtures. The coarser structure would reduce the possible number of three phase sites across the same volume of material; in addition, electronic and ionic conduction would be
impeded by the extra length of transport pathways due to the discontinuity of CGO material in both electrodes (see SEM results of these cells from section 5.5).

Moreover, as observed from Figure 52B in chapter 3 section 3.8, the current collection material was not spread at high density or complete uniformity, which can also adversely influence the cell’s performance under load. What is more, silver diffusion from one electrode to another one due to porous electrolyte can provide short circuit pathways and thereby result in reducing both OCV and power density, which was observed during experiment. In addition to silver diffusion, sputtered gold as current collector on both sides diffused from one electrode to another one through porous structure due to its nano-size and caused a short circuit as well. It was also observed that nano-level (250 nm) sputtered gold as current collector on both electrodes disappeared due to gold volatilization even at 600°C. As a consequence of poor current collection and short circuit, cell performance might have been suppressed. Beside which, the testing chamber might have influenced the cell performance, because narrow gas outlet might have caused gas stagnation as well as intermixing of gases which have negative effects on cell performance (i.e. non-catalytic, non-electrochemical interaction and reactions). Finally, the influence of flow distribution and operating conditions on SC-SOFC performance are highly sensitive, and the presence of curvature along the edge of cells (cell 4, 5 and 6) could change the flow conditions locally; in conjunction with non-optimised (i.e. narrow window of investigation) fuel: oxygen ratios and temperature levels, the ideal operating parameters for this cell are not exactly determined. The testing chamber did not ‘funnel’ the supplied fuel-air mixture exactly onto the cell, not did it incorporate dedicated flow field design, and these could have significant impact on cell operation, fuel utilisation and performance.
Figure 84 Open circuit voltage (OCV) measurement of (A) cell 4 and (B) cell 5 at different flow rate and gas mixture. R, fuel to oxygen ratio
144

Figure 85 OCV measurement of (A) cell 6 and (B) cell 11 at different flow rate and gas mixture, R, fuel to oxygen ratio
Figure 86 Polarization curve of (A) cell 4 and (B) cell 5 at different flow rate and gas mixture, R, fuel to oxygen ratio.
Figure 87 Polarization curve of (A) cell 6 and (B) cell 11 at different flow rate and gas mixture, R, fuel to oxygen ratio
5.8 SUMMARY

In this study an anode-supported SOFC for single chamber conditions was manufactured via single step co-sintering method. The results show that single step co-sintering is possible to be applied to the fabrication of SOFCs though there are certain problems to be overcome such as obtaining dense electrolytes (electrolyte layer obtained in all examples here are porous). The results also indicate that curvature formation can be suppressed by a combination of defining better sintering conditions, changing the thickness of anode or electrolyte and utilising alumina porous cover plate on the top of the cell during sintering. Increasing the thickness of anode led to increase of the resistance of the cell strength to deformation. Decreasing electrolyte thickness also resulted in a decrease in curvature formation. However, increasing anode thickness and decreasing electrolyte thickness were not enough to obtain curvature-free anode-supported SC-SOFC. Therefore a porous alumina cover plate (7.31 g) was used on the top of anode to oppress curvature formation during sintering. By applying optimized anode, electrolyte and cathode thickness as well as utilizing alumina porous cover plate, an anode supported planar SC-SOFC was successfully made. In addition, some of the sintered cells were characterised with SEM, EDS, XRD for understanding sintering profoundly and measure the porosity of anode, electrolyte and cathode as well as pore and particle sizes of electrodes. Furthermore, the residual stress between cathode and electrolyte after sintering was measured by applying the fluorescence spectroscopy technique. The residual stress in cathode due to CTE mismatch during cooling was measured at room temperature for each cell except cell 11. The results show that there is a high total mean residual stress between cathode and electrolyte and the main contribution of this residual stress is the stress developed during sintering owing to different shrinkage behaviour of neighbouring layers.

The fabricated cell’s performance was investigated with different mixed gas composition at a temperature of 600°C. The maximum OCV was measured from the cell 5 (thickness ratio 20:2:2, thickness 400:40:40 µm) as 0.73 V with a gas mixture of 40 mL min⁻¹ CH₄, 40 mL min⁻¹ O₂ and 200 mL min⁻¹ N₂. In addition, maximum voltage and power density of the cell were obtained as 0.71 V and 30.69 mW cm⁻², respectively, from the thicker cell (cell 11) at a fuel to oxygen ratio of 1 (40 mL min⁻¹ of CH₄, 40 mL min⁻¹ of O₂ and 200 mL min⁻¹ N₂). The results showed that increased anode thickness (from 200 µm to 400 µm and to 800 µm) with that of reduced electrolyte (from 40 µm to 20 µm) not only improved cell strength and removed curvature formation but also enhanced cell performance. However, the
power densities obtained were comparatively low, suggesting that further work is needed to find solutions to the issues pertaining to electrolyte stability, electrolyte porosity, current collection and optimised flow conditions.
CHAPTER 6

SINGLE STEP SINTERING BEHAVIOUR OF A CATHODE SUPPORTED PLANAR CELL AND ITS PERFORMANCE

For the anode supported SOFCs, potential anode reoxidation is a serious problem which cause cells to break after a certain cycle of cell usage [65, 67]. It is because the thicker anode (based on Ni catalyst) oxidation and reduction lead to cell to shrink and expand in time. This uncontrolled shrinkage and expansion leads the cell to crack. Therefore, a new configuration of SOFCs, named as cathode supported SOFC, were proposed by researchers to overcome this issue [8, 9]. This configuration of SOFC has showed the longest lifetime among all categories of SOFCs [229]. In general, these types of cells were sintered using at least two step sintering process. In this chapter, the single step co-sintering of cathode supported SC-SOFCs was investigated profoundly. Moreover, the effect of layer thickness, cell size and sintering temperature on cell sinterability were analysed. Furthermore, a limiting constraint was applied on the top of the cells so as to achieve a curvature free cathode supported cell. In addition, characterization techniques were applied to the cells to understand microstructure of sintered cells. Finally, the fabricated cells were tested under single chamber conditions in order to observe the functionality of the cells as working electrochemical cells and to analyse the effect of thickness and thickness ratio change on the cell performance.

6.1 SINTERING BEHAVIOUR OF A CATHODE SUPPORTED CELL WITH TEMPERATURE INCREMENT DURING HEATING AND WITH TEMPERATURE REDUCTION DURING COOLING

Figure 88 depicts the picture of a cathode supported cell taken during sintering at different temperatures (thickness ratio and thickness of the cell is 3:2:10 and 60:40:200 µm (anode-electrolyte-cathode), respectively, with a 40 mm x 40 mm width (W) and length (L)). The cell was placed on a porous alumina substrate, with the cathode adjacent to it (facing downward). According to Figure 88, there is no observable/substantial curvature formation up to 200°C. However, when temperature reached 250°C, there is a visible curvature formation (towards the upward direction, \( h_1 = 1.384 \) mm, curvature height, \( h_1 \), from top surface of alumina substrate to the peak point of the top surface of the cell). This might be as
a result of additives removal in the green body during debinding stage. Because, the top surface of the cell is the drying surface and additives will be first evaporated from the top surface. This phenomenon leads to a capillary force in the top surface and cause a compressive stress in this area. Therefore, cells curved towards upward. Moreover, when the temperature reached to 300°C, the cell curvature was relieved, the $h_1$ decreased to 0.462 mm. This could be explained by the fact that later into the drying process (above 250°C and until the end of the additive removal process), the liquid vapour interface is subjected to changes from the top surface to the interior of the green body and pores are occupied with air. This results in a reduction in compressive stress on the top surface. In addition, the lower part of the green body still contains liquid therefore it is exposed to compressive stress due to capillary forces. This brings about the tendency of the green body to warp into the opposite direction. In general, the effect of capillary force, at the lower part of the cell at the later stage of sintering was not big enough to curve cell downward. Thus, the cell curvature was still upward after the burn-out stage. Additionally, the curvature direction is still upward until 800°C, and the curvature height reached to 1.260 mm. It might be as a result of particle rearrangement. However, when the main densification started (after 800°C), the cells edges tended to curve downward due to higher shrinkage rate of cathode. The curvature height became 3.39 mm at 900°C though the effect of additive removals on curvature formation was still at present (see Figure 88). Moreover, in the main densification area, cell curvature directed downward and it reached its maximum value of 6.678 mm at 1200°C (see Figure 89).

In addition, the main observation from these figures was that it was expected for the cell to crack when it reached at 1200°C or after dwelling at 1200°C. However, surprisingly, there was no cracking or delamination during heating and after dwelling as shown in Figure 88 and Figure 89. Nevertheless, when the cell was cooled down, the cell did not break until 800°C (see Figure 90). It might not even have broken at a temperature of less than 800°C. However, the cell broke into many pieces during cooling owing to residual stress in the cell (see Figure 90). It might be explained by the fact that, at elevated temperature, the ceramic cell might have possessed plastic properties and thus withstood high residual stress. However, when the temperature decreased, the cell became more brittle and the contribution of CTE mismatch stress became higher at room temperature. Consequently, the cell could not withstand the amount of residual stress due to its brittle crystal structure.
Figure 88 The pictures of a cathode supported cell taken during sintering at different temperatures
6.2 THE EFFECT OF THICKNESS, THICKNESS RATIO AND CELL SIZE ON SINGLE STEP CO-SINTERING OF THE CELL

As stated in the previous chapters, the cells must have enough thickness to provide mechanical supports. For the cathode supported cells, the cathode thickness should provide

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**Figure 89** The picture of a cathode supported cells taken during sintering at different temperatures

**Figure 90** The picture of a cathode supported cells taken during cooling at different temperatures
this support. However, its thickness should be optimized for low concentration polarization while ensuring enough catalytic reaction sufficiency towards oxygen reduction. In addition, for single step co-sintering of anode supported cells, increasing anode layer thickness improved single step co-sintering of the cell (see chapter 5). Therefore, in this section, the effect of cathode and electrolyte thickness on cell’s single step co-sintering was examined for cathode supported cells at the optimum hot pressing and sintering condition defined in the previous chapters. Furthermore, since SOFCs can be made in different size, the cell size on such possibility was also investigated.

6.2.1 The Influence of Cathode Thickness and Cell Size on Single Step Co-Sintering of the Cell

In order to investigate the cathode thickness and the cell size on the single step co-sintering of the cell, two types of cells with different cathode thicknesses were made and sintered at 1200°C. The first type of cell possessed a width and length of 40 mm and 40 mm (named cell type 1) respectively while the second type had a 30 mm × 30 mm W×L (named cell type 2). For both type of cells, cathode thickness increased from 200 µm, to 300 µm, to 400 µm, and to 500 µm while anode and electrolyte thickness were kept constant with a thickness of 60 µm and 40 µm, respectively.

Figure 91 shows the sintering results of these cells. It can be clearly seen from the figure as a visual inspection for both type of cells, increasing cathode thickness improved cell single step sinterability. Because the following reasons are put forth: firstly, the cathode layer became more dominant in overall cell composition, thus, the effect of anode and cathode become less effective during sintering. Secondly, increased cathode thickness improved cell resistance to deformation and breaking, and therefore, the cells become more robust towards withstanding either sintering stress during heating or CTE mismatch stress during cooling as a result of increased cross-sectional area of the cathode normal to the length direction. Furthermore, it can also be seen from the Figure 91, increasing cell size from 30 mm × 30 mm to 40 mm × 40 mm (W×L) has negative effect on single step co-sintering of the cell. For instance, cell type 1 with a cathode thickness of 200 µm broke into numerous pieces while cell type 2 splintered into fewer pieces. Similarly, cell type 1 with a cathode thickness of 400 µm broke into three parts whereas cell type 2 has no carks present after sintering.
Figure 91 The influence of cathode thickness and cell size on cell sinterability sintered at 1200°C
6.2.2 The Influence of Cathode and Electrolyte Thickness on Single Step Co-Sintering of the Cell

Figure 92 shows the sintering results of three different cathode supported cells. Cell 1 and cell 2 possess the same anode and cathode thickness (60 µm and 400 µm, respectively) while their electrolyte thickness is 40 µm and 20 µm, respectively. The figure shows that decreasing electrolyte thickness improved single step co-sintering of the cell. The cell mean curvature height decreased from 4.29 mm to 3.87 mm and there was no crack after sintering (see Figure 92, cell1 and cell 2). This might be as a result of the electrolyte mismatch stress contribution mitigation. Furthermore, for the same anode and electrolyte thickness (60 µm and 20 µm), increasing cathode thickness enhanced cell`s single step co-sintering, and cell`s curvature diminished further from 3.87 mm to 3.45 mm (see Figure 92, cell 2 and cell 3) because of higher resistance to breakage resulting from either sintering stress during heating and CTE mismatch stress during cooling. In addition, comparing to anode supported cell, higher mean curvature height was measured for the similar thickness of the cells after sintering (see Figure 68 and Figure 92) as expected due to comparatively thicker cathode layer, which is the main source of the mismatch stress.
Cell 1: 40 mm x 40 mm WxL, thickness ratio: 3:2:20 (A:E:C), thickness: 60:40:400 µm

Mean curvature – height: 4.29 mm

Cell 2: 40 mm x 40 mm WxL, thickness ratio: 3:1:20 (A:E:C), thickness: 60:20:400 µm

Mean curvature – height: 3.87 mm

Cell 3: 40 mm x 40 mm WxL, thickness ratio: 3:1:25 (A:E:C), thickness: 60:20:500 µm

Mean curvature – height: 3.45 mm

Figure 92 The influence of cathode and electrolyte thickness on cell sinterability
6.3 CONSTRAINED SINTERING OF CATHODE SUPPORTED CELLS

For the cathode supported cell, increasing cathode thickness continuously and decreasing electrolyte thickness was not enough to obtain curvature free cell as seen in previous sections. In addition, concentration polarization becomes a serious problem when the cathode thickness is increased too much. This is because the thicker cathode causes impediments to the gas transport from top surface of the cathode to the inner pore of cathode layer and product removal from triple phase boundary. This issue becomes more vital when a cell is placed as a flow-through (perpendicular to gas flow) arrangement in the fixture. Therefore, it is important to investigate different methods to remove curvature formation rather than continuously increasing cathode thickness. Placing a limiting constraint on the top of the cell was a useful approach to obtain curvature-free cells without changing the thickness of the cell as demonstrated in chapter 5. Therefore, five cells with the same size, thickness and thickness ratio were made and sintered either free or with limited constraint on the top of the cells. For that purpose, either one or multiple alumina porous cover plates were located on the top of the cells so as to investigate the effect of the limited constraint on cell sinterability, the ability to suppress curvature formation, and finally to obtain curvature free cell. The cells were made with a 40 mm × 40 mm of W×L and a thickness of 60:20:800 µm, A:E:C, (thickness ratio of 3:1:40), and were sintered at 1200°C. Figure 93 and Figure 94 depicts the sintering results of these cells. The cell sintered without any cover plate was named as cell 4 while cells sintered with a 50 mm × 50 mm porous alumina cover plate (cell 5) has less mean curvature height (h = 1.18 mm) in comparison to the cell sintered without cover plate (cell 4, h = 1.93 mm). However, this mass of cover plate is not enough to suppress curvature evolution of the cell while it was enough for the anode supported cell. Furthermore, increasing cover plate mass (from 7.31 g to 16.45 g) by simply using a bigger size of porous cover plate (75 mm × 75 mm, W×L) reduced mean curvature height further (to 0.65 mm, cell 6). Increasing porous cover plate mass has no linear effect on curvature reduction as can be seen from cell 6, cell 7 and cell 8 shown in Figure 93, Figure 94 and
Figure 95. Figure 95 shows the relation of porous alumina cover plate mass with the mean curvature height that can be used to predict the mean curvature height with the change of the cover plate mass for the cathode supported SC-SOFCs. Though the Figure 95 has limited data for its reliability, it can still give an approximate idea about required cover plate mass for curvature free cathode supported cell for this type of cells with the same size, thickness and thickness ratio. According to Figure 95, the mean curvature height becomes almost stable after using two or more 75 mm × 75 mm cover plates on top of the cell (around 0.47 mm for two cover plate and 0.41 mm for three cover plates). To conclude, a cell (cell 8) with a low mean curvature height (0.41 mm) was obtained after using three 75 mm x 75 mm, W×L, alumina porous cover plates on the top of the cell during sintering.

In comparison to the anode supported cells mentioned in chapter 5, cathode supported cells displayed more severe curvature formation during sintering due to significantly increased cathode volume (high shrinkage and shrinkage rate of cathode become more severe when the volume of cathode layer increased). In addition, cathode supported cell required heavier porous cover plate for curvature suppression as compared with anode supported cells for the same electrolyte and support thickness.
**Figure 93** Free and limited constraint sintered of cathode supported cells having the same width, length, thickness and thickness ratio (40 mm, 40 mm, 3:1:40 (A:E:C) and 60:20:800 µm (A:E:C), respectively)
CSC 8: 40 mm x 40 mm WxL, thickness ratio: 3:1:40 (A:E:C), thickness 60:20:800 µm, sintered with three 75 mm x 75 mm LxW porous alumina cover plates on the top of the cell, 40% porosity with a total mass of 49.35 g

Figure 94 Limited constraint sintered of cathode supported cell (cell 8) with a width, length, thickness and thickness ratio of 40 mm, 40 mm, 3:1:40 (A:E:C) and 60:20:800 µm (A:E:C), respectively, and with an estimated porosity

View from anode side

View from cathode side

Mean curvature -height: 0.41 mm

Estimated porosity:
- Anode: % 24.31
- Electrolyte: % 12.43
- Cathode: % 26.04
6.4 CHARACTERIZATION OF SELECTED OPTIMUM SPECIMENS OF SINTERED CELLS

6.4.1 SEM Images and EDS Maps

Figure 96 shows the SE and BSE SEM images of polished cell 1, cell 2 and cell 4. In addition, Figure 97 depicts the SE SEM images, BSE SEM images and EDS maps of polished cell 8 with unpolished SE SEM images. Furthermore, Table 12 summarizes the estimated porosity of the anode, cathode and electrolyte as well as estimated mean particle size and pore size of the anode and cathode of cell 1, cell 2, cell 4 and cell 8.

When inspecting the SE and BSE SEM images in Figure 96 and Figure 97, all cells appear to have highly similar microstructures respective to their anode, electrolyte and cathode layers, in terms of particle size and distribution. Across all cells, there is consistently
good adhesion between anode-electrolyte, and cathode-electrolyte layers; however they all have a porous electrolyte (acceptable in the SC-SOFC configuration). Moreover, in general for all cells, there is a good connection of NiO phase on anode side and LSCF phase on cathode side. However, the CGO continuity on both sides is not as good as desired. In addition, there is normal grain growth in all section of all cells; however, the cathode in all the cells possesses coarser microstructure than the anode as a consequence of over-sintering (see Table 12).

Furthermore, from Figure 96: cell 1, the electrolyte section close to cathode side has lower porosity than that close to anode side from visual inspection. This might be due to the compressive stress generated from high shrinkage of cathode is higher at this side compared to another side of the electrolyte. However, the same influence was not observed on the cell that has the thinner electrolyte (cell 2 and cell 4). The estimated porosity of the anode, electrolyte and cathode for cell 1 was measured to be 27.35%, 12.93% and 29.2%, respectively. Furthermore, for the same cell, the mean particle and mean pore size was found to be 3.394 ± 2.464 µm and 1.509 ± 0.693 µm for anode, respectively, and that of 3.645 ± 2.454 µm and 1.812 ± 0.738 µm, respectively, for cathode. It can be generally seen that cathode has higher porosity and mean pore size compared to that of the anode (see Table 12). This might be as a result of coarser microstructure of cathode because the increase in mean grain size is accompanied by a rise in the mean pore size.

Additionally, for the same anode and electrolyte thickness (60 µm and 20 µm, respectively, cell 2 and cell 4), increasing cathode thickness from 400 µm to 800 µm resulted in a slight increase on cathode porosity (from 24.58% to 25.13%) while that of little decrease on anode and electrolyte (from 26.62% to 23.72% for anode and 14.96% to 12.73% for electrolyte). The reason behind this could be that the increased cathode thickness made the cathode more effective in the cell during sintering. As a result, compressive stress on both anode and electrolyte due to high shrinkage of cathode increased further and led to these two layers to shrinking more in comparison to the cell with a thinner cathode layer.

Furthermore, for the same anode, electrolyte and cathode thickness (cell 4 and cell 8), the cell sintered without any constraint (cell 4) and the cell sintered with three 75 mm × 75 mm porous alumina cover plates on the top of the cell (cell 8) possessed slight differences in terms of porosity, mean particle and mean pore size. The porosity of anode and cathode of the cell 8 increased slightly when limited constraint was applied to it (from 23.72% to 24.11% for anode and from 25.13% to 26.04% for the cathode) whereas electrolyte porosity little diminished (from 12.73% to 12.43%) comparison to cell 4.
Figure 96 (A) SE SEM images and (B) BSE images of cell1, cell 2 and cell 4
CSC 8: 40 mm x 40 mm WxL, thickness ratio: 3:1:40 (A:E:C), thickness: 60:20:800 µm sintered with three 75 mm x 75 mm LxW porous alumina cover plates on the top of the cell

Figure 97 (A) SE SEM image of polished cell 8, (B) BSE image of polished cell 8, (C) unpolished SE SEM image of cell 8 and (D) EDS layered image of cell 8 from SE imaging
Table 12 Porosity measurement of anode, cathode and electrolyte with mean particle and pore sizes of electrodes for cathode supported SC-SOFCs

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell 1 (60:40:400 µm, A:E:C), free sintering</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>27.35</td>
<td>12.93</td>
<td>29.2</td>
</tr>
<tr>
<td>Mean particle size (µm)</td>
<td>3.394 ± 2.464</td>
<td>3.645 ± 2.454</td>
<td></td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
<td>1.509 ± 0.693</td>
<td>1.812 ± 0.738</td>
<td></td>
</tr>
<tr>
<td><strong>Cell 2 (60:20:400 µm, A:E:C), free sintering</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>26.62</td>
<td>14.96</td>
<td>24.58</td>
</tr>
<tr>
<td>Mean particle size (µm)</td>
<td>3.244 ± 1.798</td>
<td>3.771 ± 2.871</td>
<td></td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
<td>1.501 ± 0.769</td>
<td>1.774 ± 0.801</td>
<td></td>
</tr>
<tr>
<td><strong>Cell 4 (60:20:800 µm, A:E:C), free sintering</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>23.72</td>
<td>12.73</td>
<td>25.13</td>
</tr>
<tr>
<td>Mean particle size (µm)</td>
<td>2.966 ± 2.086</td>
<td>3.569 ± 2.244</td>
<td></td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
<td>1.47 ± 0.66</td>
<td>1.85 ± 0.803</td>
<td></td>
</tr>
<tr>
<td><strong>Cell 8 (60:20:800 µm, A:E:C), sintered with three 75x75 porous alumina cover plate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>24.11</td>
<td>12.43</td>
<td>26.04</td>
</tr>
<tr>
<td>Mean particle size (µm)</td>
<td>2.895 ± 1.864</td>
<td>3.645 ± 2.27</td>
<td></td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
<td>1.267 ± 0.723</td>
<td>1.603 ± 0.736</td>
<td></td>
</tr>
</tbody>
</table>

Figure 98 and Figure 99 depict the EDS maps and spectrum of cell 8 from anode and cathode side, respectively. The purpose taking of EDS analysis of cell 8 is to investigate possible impurities introduced during fabrications process. The EDS analysis of cell 8 either from anode side or cathode side showed that there were no impurities and the distribution of Ni, Ce, O, Fe, Sr, La, Co and Gd elements is in the projected area (Figure 98A and Figure 99A). However, due to the difficulty of observing the small amount of elements from the EDS maps, it is useful to have a typical EDS spectrum measured. The spectrum shows all elements in the scanned region. Figure 98B shows the Map Sum Spectrum of cell 8 from the anode side, and it can be observed that there is a small amount of Au, Pd, Al, Zr, Si, Sr and Co. The existence of Au and Pd is due to the sputtering of these elements before SEM imaging in order to make the cell conductive. Aluminium might have been introduced during sintering either from porous alumina substrate or cover plate. Zirconium might have been introduced during ball milling by ball milling medium which is made of yittria stabilized zirconia (YSZ). However, the existence of strontium and cobalt was due to the diffusion of these elements from cathode sides. Furthermore, silicon might be coming from different stages of the fabrication process since Si elements could be present in any of these stages. In addition, from the cathode side EDS spectrum (Figure 99B), there were also Au, Pd, Al, Zr,
and Si elements on the cathode side due to the same respectively reasons mentioned for EDS spectrum analysis from the anode side. In addition to these contaminations, nickel was also detected on cathode side because of the nickel diffusion from the anode side. These impurities were not observed from EDS spectrum when the EDS of cathode and anode were taken together (see Figure S7) owing to limited area of EDS scanning. To conclude there were same contaminations on both sides of electrodes, and small amounts of anode- and cathode-side elements diffused from anode to cathode and cathode to anode, respectively. It is important to avoid or to minimize this contamination to a reasonable level so as to obtain better performance from the cells, with regards to catalytic selectivity and favourable reactant concentration gradients at the respective electrodes.
Figure 98 (A) EDS Maps of cell 8 and (B) Map Sum Spectrum of cell 8 taken from anode side, the cell possess a thickness of 60:20:800 µm, A:E:C, sintered with three 75 mm x 75 mm alumina porous cover plate
A) EDS Maps of cell 8, from cathode side

B) Map Sum Spectrum of cell 8, from cathode side

Figure 99 (A) EDS Maps of cell 8 and (B) Map Sum Spectrum of cell 8 taken from cathode side, the cell possess a thickness of 60:20:800 µm, A:E:C, sintered with three 75 mm x 75 mm alumina porous cover plates
6.4.2 X-Ray Diffraction of Cell 1, Cell 2, and Cell 8

Figure 100 displays XRD patterns of cell 1, cell 2, and cell 8. According to these figures, there is no undesired phase formation after sintering except the required phases (NiO, CGO and LSCF) for cell 1, cell 2 and cell 8. In addition, the elements which could bring about the formation of the main phases in cell 8 are also supported by the EDS data (see the elemental analysis from Figure 98 and Figure 99). Though there were some impurities detected from EDS analysis in the previous section (see Figure 98 and Figure 99), their reaction with other elements which could form new phases such as SiO, ZrO, CoO and so forth were not observed in XRD patterns of cell 8 due to the limitation of XRD technique to detect these possible phases because of their small amount. Moreover, there are no further crystalline phases present in any cells. In addition, each cell`s XRD results shows that these cells are identical. This is as a result of possessing the same anode cathode and electrolyte material. The fabrication process for each cell is the same and the only difference they have is their layer thickness. Thus, it is most likely to expect the similar XRD results.
Figure 100 (A) X-Ray diffraction patterns of cell 1, (B) cell 2 and (C) cell 8
6.5 CELL PERFORMANCE TESTS

Cathode supported cells were also tested as anode supported SC-SOFCs in order to examine the functionality of sintered samples as working electrochemical cells, and to investigate the influence of electrolyte and cathode thickness on the cell performance. During performance testing of cells, 100 mL min\(^{-1}\) nitrogen gas was used as diluting agent at different fuel/oxygen gas mixture so as to reduce the danger of explosion, improve the diffusion and flow of the fuel and oxygen gases as well as for the reactant adsorption and product desorption processes on the anode and cathode [110]. The gas mixture was sent as a flow through (gas flow perpendicular to cathode layer). Figure 101, Figure 102, and Figure 103 show the open circuit voltages (OCV) and polarization results of cell 1, cell 2 and cell 8, respectively, at different flow rates and gas mixture ratios. Additionally, Table 13 depicts the maximum OCV and power density measurements of these cells.

According to Figure 101, the OCV of cell 1 diminishes with the increased amount of oxygen gas at both fixed amounts of 50 mL min\(^{-1}\) CH\(_4\) and 40 mL min\(^{-1}\) CH\(_4\). Maximum OCV and power density of cell 1 were found to be 0.56 V and 25 mW cm\(^{-2}\), respectively, in a quite fuel rich gas mixture (gas mixture 4). This can be explained as follows: a fuel rich condition is required to supply more methane to anode surface because of lack of fuel reforming on anode side due to the thin anode thickness in a cathode supported cell. As a result of increased fuel reforming, more syngas such as H\(_2\) and CO were generated, and these syngas react with oxygen ions migrating from the cathode side. Therefore, partial pressure differences between two layers increases and thus led to improved OCV and power density. In addition, the formation of volatile nickel hydroxide Ni(OH)\(_2\) due to presence of water vapour leads to nickel loss and it becomes severe in oxygen-rich mixture where a higher quantity of water vapour was produced [8, 65]. This could be among the reasons why cells’ OCV and power density reduced with increased amount of oxygen gas. However, having high power density at fuel rich condition brings certain problems, for instance, coking of nickel catalyst interfaces, and chemical reactions between methane and oxygen gas or ion could occur on cathode side, and thereby resulting in cell degradation and low cell performance.

The OCV and power density of cell 1 at gas mixture 4 (R: 2.4) and gas mixture 5 (R: 1.6) are higher than that at the gas mixture 1 (R: 2.4) and gas mixture 2 (R: 1.6), respectively whereas the OCV and power density of cell 1 at gas mixture 3 (R: 1) are greater than that of at gas mixture 6 (R: 1). Therefore, the OCVs and power densities of cell 1 at fixed methane
of 40 mL min⁻¹ are generally higher than that of fixed methane of 50 mL min⁻¹ at the same fuel/oxygen ratio. In general, increasing gas mixture flow rate has positive effects on cell performance owing to the improved gas exchange at both electrodes which results in reduction in overpotential relating to gas diffusion at both electrodes [8, 9, 110, 116]; however, for cell 1, reduction in the amount of gas mixture by decreasing the fixed amount of CH₄ from 50 mL min⁻¹ to 40 mL min⁻¹ (resulting in reduced total flow rate) for the same fuel/oxygen ratio improved cell’s OCV as well as its power density (see Figure 101 and Table 13). This could be attributed to the increased residence time of reactant gases on anode electrode where the reforming was limited due to the insufficient anode thickness [116].

Furthermore, for the same anode and cathode thickness (cell 1 and cell 2), decreasing electrolyte thickness from 40 µm to 20 µm had severe effect on power density especially at rich fuel/oxygen condition. Moreover, there is a little reduction in OCV at gas mixture 1 and gas mixture 5 with comparison to cell 1. However, at gas mixture 3 and gas mixture 6, the OCV of cell 2 is more than two folds higher than that of cell 1. Therefore, one can generally define that there is an OCV reduction at fuel rich gas mixture (R: 2.4 and R: 1.6) while an increase in OCV is observed at fuel lean condition when cell thickness was reduced. The OCV reduction could be attributed to reduced electrolyte thickness leading to better ionic conductivity, thus enabling faster oxygen ion travel from cathode to the anode side. Consequently, oxygen reduction reaction proceeds at the fastest rate for the present condition and therefore depletes oxygen gas at the cathode membrane. The OCV decrease could also be as a result of gas cross-over, since, cells possessing porous electrolytes usually have gas cross-over problem. Product gases generated from anode side such as H₂ and CO can diffuse to the cathode side via porous electrolyte and react with oxygen gases and thereby causing simply chemical reaction which is not beneficial for SOFCs [8, 112, 116]. For the cell possessing thinner electrolyte and higher porosity, the gas cross over becomes more severe due to easy diffusion of these syngas. Cell 2 possess thinner electrolyte and higher porosity in comparison to cell 1 (see Table 12), thereby facilitating higher gas cross-over. In both cases, oxygen partial pressure differences between anode and cathode sides reduce, therefore decreasing OCV, and also further impeding the favourable conditions for methane reforming [8, 116]. The reason for the OCV increment with decreased electrolyte thickness at oxygen rich condition (gas mixture 3 and gas mixture 6) could be explained by the fact that the thinner and more porous electrolyte could allow faster oxygen and methane gas transport from cathode side to anode side since the gas mixture contacts first to the cathode and pass through electrolyte to anode layer. However, the increment in the amounts of methane
diffusion to the anode side will be higher than that of oxygen gas, because, methane possess
higher diffusivity rate than oxygen gas due to its lower molar mass comparing to O\textsubscript{2}. This
leads to more methane reforming on the anode side and thus resulting in more oxygen gas
consumption. Therefore, the partial pressure of oxygen increases between two electrodes and
thus OCV rises.

The gas cross-over problem does not just lead to OCV reduction but also results in
fuel partial pressure and limits the use of these fuels for electrochemical reaction, in favour of
direct chemical oxidation/reforming. This could explain why less power was obtained from
cell 2 in comparison to cell 1 though it is likely that the ohmic losses decreased due to
reduction in electrolyte thickness. In addition, the general trend was that the maximum OCV
and power density were obtained at fuel rich condition, similar to cell 1. The maximum OCV
and power density of cell 2 were found to be 0.38 V and 3.32 mW cm\textsuperscript{-2}, respectively at gas
mixture 2 (see Figure 102 and Table 13) (around 87% reduction in power density compared
to cell 1). According to Figure 102 and Table 13, the OCV of cell 2 generally mitigates with
the increased amount of oxygen gas at both fixed amount of 50 mL min\textsuperscript{-1} CH\textsubscript{4} and 40 mL
min\textsuperscript{-1} CH\textsubscript{4} as cell 1. Furthermore, in both cells, the lowest OCV and power density were
obtained at lean condition, R = 1, and the OCVs were not stable. The oscillation of OCVs
might be as a consequence of oxidation-reduction cycle of Ni-cermet anode and
accompanying temperature fluctuation at rich oxygen condition [8].

Moreover, for the same anode and electrolyte thickness (cell 2 and cell 8), increasing
cathode thickness from 400 µm to 800 µm led to considerable OCV and power density
reductions at all gas mixtures. Additionally, there were almost no OCV and power density at
the oxygen rich gas mixtures (gas mixture 3 and gas mixture 6, see Table 13 and Figure 103).
The maximum power and OCV were found to be 0.2 V and 1.71 mW cm\textsuperscript{-2}, respectively, at
gas mixture 2 (around 51% power density reductions comparing to cell 2). Figure 103 also
shows that the OCV and power density of cell 8 generally diminished with the increased
amount of oxygen gas at both fixed amount of 50 mL min\textsuperscript{-1} CH\textsubscript{4} and 40 mL min\textsuperscript{-1} CH\textsubscript{4} as cell
1 and cell 2. The low OCV and power density of the cell 8 might be ascribed to the thicker
cathode, because thick cathode causes high concentration polarization on the cathode side of
the cell due to increased difficulties of oxygen gas movement into the inner part of cathode
and distance for oxygen ion diffusion from cathode side to anode side of the cell [75].
However, cathode thickness increment also leads to an increase in triple phase boundary for
oxygen gas reduction and thus alternately could result in better cell performance. However,
the results demonstrated that the benefit of increased triple phase boundary is much less than
the negative effect of cathode concentration polarization (mass transport limitation). Furthermore, the LSCF cathode material can also oxidize methane (parasitic catalytic combustion) [8, 13, 228], therefore the increased cathode thickness could lead to more methane oxidation which consume oxygen gas on the cathode side and thereby resulting in low OCV due to decreased oxygen partial pressure difference between cathode and anode. In addition, the reaction product (CO and H₂) after methane reforming on cathode side can be adsorbed on the cathode surface and leads to a reduction in active area for oxygen gas adsorption [116].

To sum up, the reduced electrolyte thickness and increased cathode thickness selected for the benefit of obtaining planar cathode supported cell via single step co-sintering unfortunately resulted in severe performance degradation: this is contrary to the situation of the anode supported cell mentioned in chapter 5, where the thicknesses conducive to better sintering results could also yield better performance.
Figure 101 (A) OCV Measurement and (B) polarization results of cell 1 thickness 60:40:400 μm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio.
Figure 102 (A) OCV Measurement and (B) polarization results of cell 2, thickness 60:20:400 µm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio.
Figure 103 (A) OCV Measurement and (B) polarization results of cell 8, thickness 60:20:800 µm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio.
Table 13 The maximum OCV and power density results of cell 1, cell 2 and cell 8 at different gas mixtures

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<tr>
<td></td>
<td>OCV (V)</td>
<td>Power density (mW cm(^{-2}))</td>
<td>OCV (V)</td>
</tr>
<tr>
<td>Fixed CH(_4) (50 ml/min) And Fixed N(_2) (100 ml/min)</td>
<td></td>
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<td></td>
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<tr>
<td>gas mixture 1 (R:2.4)</td>
<td>0.4</td>
<td>11.1</td>
<td>0.37</td>
</tr>
<tr>
<td>gas mixture 2 (R:1.6)</td>
<td>0.36</td>
<td>7.5</td>
<td>0.38</td>
</tr>
<tr>
<td>gas mixture 3 (R:1)</td>
<td>0.124</td>
<td>1.85</td>
<td>0.28</td>
</tr>
<tr>
<td>Fixed CH(_4) (40 ml/min) And Fixed N(_2) (100 ml/min)</td>
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<td></td>
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<tr>
<td>gas mixture 4 (R:2.4)</td>
<td>0.56</td>
<td>24.79</td>
<td>0.33</td>
</tr>
<tr>
<td>gas mixture 5 (R:1.6)</td>
<td>0.394</td>
<td>8.13</td>
<td>0.32</td>
</tr>
<tr>
<td>gas mixture 6 (R:1)</td>
<td>0.05</td>
<td>1.69</td>
<td>0.2</td>
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In general, the performance of the cathode supported SC-SOFCs were found comparatively low with comparison to available results presented in the literature for cathode supported SC-SOFCs. The cells’ performance could be adversely influenced by various reasons and they could be explained as follows. Lack of fuel utilization due to low selectivity of anode and cathode towards their corresponding gases is a general problem for all type of SC-SOFCs [8, 116] and this results in quite low cell performance and fuel utilization. The thick cathode (from 400 µm to 800 µm for this study) leads to more concentration polarization owing to oxygen gas diffusion inhibition from outer surface to the reaction areas and increased distance for oxygen ion transport. Furthermore, the thick and porous electrolyte (thickness varies from 20 µm to 40 µm and porosity around 14%) result in high ohmic losses due to increased ionic transport losses. What is more, reaction products (H\(_2\) or CO) can move from anode side to cathode side because of porous electrolyte and reacts with oxygen gases and thus minimization of the oxygen partial pressure differential across the cathode and anode electrodes, which define the establishment of OCV.

In addition, CGO electrolyte could be partially reduced at high temperature and low oxygen partial pressure since 600°C working temperature is a critical temperature for CGO functionality [6, 230], as predominant on the anode side. This reduction brings about electronic conductivity in a great volume fraction of the electrolyte extending from anode side. Thus electrons flow from anode side to cathode side through electrolyte even at open circuit, and consequently resulting in low power output [6, 8, 23]. Furthermore, the reactivity
of oxygen gas is higher than the oxygen ion, thus the oxygen gas easily react with H$_2$ or CO in comparison to O$^2^-$ on the anode side. Additionally, methane full oxidation could occur on both electro sides. These parasitic reactions in the fuel air mixture do not contribute electricity generation, however, only to the heat generation, and consequently lowering the performance of the cells [8, 116].

Another reason for low power output could be the lack of fuel reforming at 600°C. Near-complete methane reforming is only achieved at temperatures above 600°C. Therefore, for better cell performance, more active fuels such as higher chain hydrocarbons ethane, propane etc. should be used at low temperatures [8]. Furthermore, the design of testing chamber has a substantial role regarding cell performance. The testing chamber should allow good flow of the reaction gases with less stagnation and decent exposure of reaction products to the electrodes. The testing chamber used for cell 1, cell 2 and cell 3 was a closed chamber design with small diameter for inlet and outlet pipes. This might have resulted in gas stagnating as well as intermixing of gases in the chamber and thereby lowers power output. Therefore an open chamber design with reasonable diameter should be employed for better cell performance.

Moreover, The increased sintering temperature of composite cathode (from 1000°C [84] to 1200°C) caused coarse structure of cathode as well as low porosity (see Table 12, Figure 96 and Figure 97). This leads to reduction in the reaction area, and therefore a lack of oxygen reduction reactions [84, 231]. The limitation of oxygen gas transportation through cathode due to low porosity mitigate cell performance owing to increased concentration polarization [232]. Good bonding is also required between particles for better electrical conductivity [84]. However, the CGO conductivities are not as good as it should be on both electrodes (see SEM images of cell 1, cell 2 and cell 8), this could lead to the oxygen ion interruption through the electrolytes. The weak connections between agglomerated particles escalate the resistance of oxygen ion as well as electrons transfer through the porous cathode [233].

Besides, carbon deposition on catalyst surfaces due to the cracking of methane (CH$_4$ into C + 2H$_2$) can deteriorate the cell performance in time [8, 119]. This carbon layer then causes: (1) catalyst redistribution/non continuity in anode by pushing Ni particles apart, and (2) forming a barrier at the nickel surface, preventing gas reactions [6]. In addition, impurities in electrolyte as well as electrodes have also adverse effect on cell performance. Si can poison the electrolyte material and thus reduce the performance. For instance, silicon can segregate at the grain boundaries of the electrolyte materials, forming insulating siliceous
(SiO\textsubscript{2}) and thus decreasing conductivity. Si has also detrimental effect on cathode electrode. It can cause serious surface exchange coefficient degradation especially in humidified atmosphere [234–236]. For instance, Si can react with Sr in LSCF cathode and cause cathode degradation [237]. The EDS analysis of the cell 8 shows that there were small amount of Si contamination on both electrodes (see Figure 98 and Figure 99). Furthermore, SrCO\textsubscript{3} is formed on LSCF cathode in atmosphere of O\textsubscript{2}-CO\textsubscript{2} [82, 238] and thus oxygen activity and surface adsorption on LSCF decreases and it becomes worse with the existence of H\textsubscript{2}O. The existence of H\textsubscript{2}O with CO\textsubscript{2} also give rise to SrO on LSCF cathode [239]. Zhao et al. [238] defines that the existence of H\textsubscript{2}O aggravates the interaction of carbon dioxide with perovskite oxide. Because the H\textsubscript{2}O-CO\textsubscript{2} van der Waals complex is formed and later is transformed to bicarbonate at oxygen vacancies and it thereby reduces oxygen reduction reaction. CH\textsubscript{4} was used for testing of these cathode supported cells therefore, it is highly possible the formation of CO\textsubscript{2} and H\textsubscript{2}O due to the fuel reforming and electrochemical or chemical reaction of H\textsubscript{2} or CO with oxygen species. Consequently, the formation of SrCO\textsubscript{3} or SO insulating layers could have caused lower power density. In addition, Ni could be poisoned by the sulphur compounds in the gas mixture (hydrocarbon fuels), even at concentration of 0.1 ppm sulphur compounds [6]. This could also have caused low performance results, because, the methane used in these experiments has 96% purity. Diffusion of strontium out of LSCF cathode brings about strontium depletion in the cathode and considerably mitigates performance of the cell [75]. The EDS result of cell 8 (see Figure 98) shows that there is not only diffusion of Sr out of LSCF but also Co and Fe, and they were also observed on the anode side. Similarly, Ni was also observed on cathode side (see Figure 99). In addition to these impurities, small amount of Al and Zr was also detected on both electrodes. These impurities could also cause less performance by blocking active surface area for either fuel oxidation or oxygen reduction on anode and cathode, respectively.

In addition, Au current collector on anode side could cause low performance [8, 9] because gold is inert to fuel reforming and could occupy the active surface area of anode since there is not enough anode thickness for reforming. Furthermore, sputtered gold thickness was in nano-level, and thus evaporated during experiments. This could cause the low current collection from the cell. Another factor to consider is that of direct chemical reaction of methane with O\textsubscript{2} gas on the electrode surfaces. This also gives rise to energy loss in the fuel cell. Finally, there was a short circuit observed during experiment of these cells due to silver and gold diffusion from one side to another sides through porous electrolyte. The magnitude of this short circuit was quite high and thereby leading to high power losses.
Lastly, Ni oxidation (NiO due to existence of O₂) increases the cell resistance [240] and thus causing low cell performance.

6.6 SUMMARY

A cathode supported planar SOFC for single chamber conditions was made via single step co-sintering method. Our study showed that determining optimum thickness and thickness ratio of the cell with the optimized hot pressing and sintering conditions leads to better co-sintering results: no crack and delamination but limited curvature at the edge of the cell. Decreasing electrolyte thickness and increasing cathode thickness led to curvature decrease at the edges, but these adjustments were not enough to obtain curvature free cathode supported cell. Three porous alumina cover plates with a 75 mm x 75 mm WxL and mass of 49.35 g was utilized to suppress curvature formation, and as a result, almost a curvature free cathode supported cell was obtained (cell 8). The sintered cells were then polished and characterized with SEM, EDS and XRD for microstructure analysis of the cells. The results also showed that decreasing electrolyte thickness has negative effect on electrolyte porosity (increased from 12.93% to 14.96%) while increasing cathode thickness have positive effect on electrolyte porosity (reduced from 14.96% to 12.43%).

The fabricated cells performances were investigated with different gas mixture at 600°C. The results indicated that increasing cathode thickness and reducing electrolyte thickness had detrimental effects on cell performance despite improved single step co-sinterability of the cell. Furthermore, the maximum power density and OCV were measured from the cell 1 (thickness ratio 3:2:20, thickness 60:40:400 µm, A:E:C) as 24.79 mW cm⁻² and 0.56 V, respectively, in a fuel rich condition (R:2.4, 40 mL min⁻¹ of CH₄, 17 mL min⁻¹ of O₂ and 100 mL min⁻¹ N₂). In general, the performance of the cells were quite low, suggesting that additional work is required to find solutions to the problems mentioned in the previous section such as electrolyte porosity, current collection issue, ceria reduction at low oxygen partial pressure or high temperature, methane reforming and so forth.
CHAPTER 7

SINGLE STEP SINTERING BEHAVIOUR OF AN ELECTROLYTE SUPPORTED PLANAR CELL AND ITS PERFORMANCE

Electrolyte supported (ES) SOFCs were suggested by researchers in order to overcome the problems that either anode or cathode supported SOFCs possess. For the anode and cathode supported cells, the common issue is the mass transport limitation of the gases due to thick support layer (anode layer for the anode supported cells and cathode layer for the cathode supported cells). In addition to this, the sluggish reaction of the cathode due to lower conductivity becomes a serious issue for the cathode supported cells. For the anode supported cells, the potential reoxidation is another problem that limits the long term stability of the cells. Compared to these, electrolyte supported cells have relatively strong structural support from electrolyte, and they are less susceptible to failure owing to anode reoxidation and have relatively low mass transport limitations. However, ohmic losses due to thick electrolyte could be a serious problem [6, 20].

An electrolyte supported single chamber SOFC was fabricated using the single step co-sintering methodology established for the other configuration of cells (cathode/anode supported cells). The study is extended to evaluate the applicability of this co-sintering approach to the electrolyte supported cells, considering that these may bring certain benefits to performance and/or ease of sintering and curvature suppression. As per previous iterations, determining optimum thickness and thickness ratio of the cell with the optimized hot pressing and sintering conditions leads to better co-sintering results, avoidance of cracking and delamination but there persists some curvature at the edge of the cell. In keeping with the established methodology, and to apply consistency for comparative evaluations, the same subsequent steps were taken, i.e the cells were polished and given different characterisation techniques such as SEM, XRD, and EDS. The measurements and images were taken for analysing porosity, microstructure, layer adhesion and impurities/formation of other phases. The representative specimens of each type were then tested in different gas mixtures to evaluate both the effects of sintering modifications on the cell performance, as well as to see the relative energy conversion capability of these cells.
7.1 SINTERING BEHAVIOUR OF AN ELECTROLYTE SUPPORTED CELL WITH TEMPERATURE INCREMENT DURING HEATING

Figure 104 shows the image of an electrolyte supported cell taken during sintering at different temperatures. The cell possess a thickness of 60:200:40 µm (A:E:C, thickness ratio: 3:10:2) with a 40 mm × 40 mm width and length. The cell was also positioned on a porous alumina substrate, with the cathode adjacent to it. According to Figure 104, there is no observable change on cell at temperature 100°C but a slight direction towards upwards at the edges. As is now well established, this is due to additive removals starting on the top of the surface, which leads to the compressive stress caused by capillary forces. When the temperature is increased further, curvature direction begins to change its direction to the downwards at 250°C due to changed capillary force direction, resulting in a chamber formation. Once the all additives are removed in the green body at 400°C, the cell structure becomes almost uniform until the main shrinkage area (900°C), and the distance from top surface of the alumina substrate to the peak point of the top surface of the cell (h₁) at this temperature was measured to be 1.405 mm, despite little reduction comparing to h₁ at 500°C (1.465 mm); this is due to the possibility of particle rearrangement after the debinding process. When the temperature is increased to 1100°C and to 1200°C, the h₁ raises to 5.471 mm and 5.726 mm, respectively. This is mainly because of the high shrinkage behaviour of the cathode layer (as it can be seen curvature is towards cathode layer (downwards)). Furthermore, at room temperature, there were no cracks or crack-like defects according to our visual observation. The cell was strong enough to withstand the residual stress generated during sintering and CTE mismatch during cooling. In addition, the h₁ at 1200°C for electrolyte supported cell was found to be smaller than that of the cathode supported cell (6.252 mm, see chapter 6) and higher than the anode supported cell (5.439 mm, see chapter 5) as expected. To conclude, electrolyte supported SC-SOFC has overall different shrinkage behaviour compared to the anode and cathode supported cells, in spite of the similar reasons for the curvature direction changes.
Figure 104 The pictures of an electrolyte supported cell taken during sintering at different temperatures.
7.2 THE INFLUENCE OF ELECTROLYTE THICKNESS AND CELL SIZE ON SINGLE STEP CO-SINTERING OF THE CELL

For the electrolyte supported cell, the thickness of electrolyte should be sufficient enough to support the cell whilst not causing overly high ohmic losses. Therefore, initially, the electrolyte thickness was determined to be 200 µm with a 60 µm anode thickness and 40 µm cathode thicknesses (cell 1, thickness ratio: 3:10:2). For this thickness and thickness ratio, the mean curvature was measured to be 5.87 mm (see Figure 105). Thereafter, the electrolyte thickness was increased from 200 µm to 300 µm so as to increase the cell resistance to deformation further and suppress curvature formation as per the anode and cathode supported cells. The curvature height was decreased to 5.56 µm (see Figure 105). This could be attributed to the fact that electrolyte material (CGO) became more dominant in electrolyte supported cell by increasing the electrolyte thickness, and thus the negative effect of the cathode shrinkage become less. In other words, the increased cross section area of the electrolyte normal to the length direction resulted in an increase in the inertia (\(I = b^2h^3/12\), \(b\) is the width and \(h\) is the thickness in this study) and therefore increased resistance to bending (\(\sigma = M*y/I\), \(\sigma\) is the bending stress, \(M\) is the internal bending moment, \(y\) the perpendicular distance from neutral axis to a point on the section, and \(I\) is the inertia). Furthermore, the cell size was decreased from 40 mm \(\times\) 40 mm \(W\times L\) to 30 mm \(\times\) 30 mm \(W\times L\), and as a result, the mean curvature height decreased further to 4.11 mm (see Figure 105; cell 2 and cell 3). However, decreasing cell size is not beneficial in order to obtain high power output, and thus the cell width and length was kept constant as 40 mm and 40 mm, respectively for the rest of the study.
7.3 CONSTRAINED SINTERING OF ELECTROLYTE SUPPORTED CELLS

Limited constraining was also applied to electrolyte supported cell to suppress curvature formation and thus obtaining curvature free cell. Figure 106 shows the image of three electrolyte supported cells sintered with different mass of porous alumina cover plates and Figure 107 depicts the final curvature free cell from different views.
shows the relationship between the cover plate mass and the mean curvature height with, that can be utilized to envisage the mean curvature height with the change of the cover plate mass for the electrolyte supported SC-SOFCs. The cell has a thickness of 60:300:40 µm, thickness ratio: 3:15:2, A:E:C, with a 40 mm × 40 mm W×L. When a 75 mm × 75 mm W×L alumina cover plate (a mass of 16.45 g) was placed on the top of the cell, the curvature height decreased from 5.56 mm to 1.11 mm (almost 80% drop) (see Figure 105; cell 2, and Figure 106; cell 4). However, this mass was not enough to obtain a curvature-free electrolyte supported cell. Therefore, the mass of alumina porous alumina cover plate was increased to 32.9 g by simply utilising two cover plates. As a result the mean curvature height dropped to 0.38 mm. As can be seen from Figure 106 and Figure 108 the reduction in mean curvature height is not linearly proportional to the rise in mass of the cover plate. Furthermore, the mass of the cover plate was increased to 49.35 g, and as a consequence, almost a curvature free electrolyte supported cell was obtained (see Figure 106 and Figure 107; cell 6). Compared to the cathode supported cell, the electrolyte supported cell via single step co-sintering possesses much lower mean curvature height after using 49.35 g alumina cover plate. The cathode supported cell has a mean curvature height of 0.41 mm (see Figure 94 in chapter 6) whilst that of the electrolyte supported cell is 0.07 mm (see Figure 107). This could be because of the fact that electrolyte layer is the dominant layer in electrolyte supported cell since anode and cathode layers consisting of 40% and 50% electrolyte material, respectively. Therefore, the cell might have behaved as one layer mostly composed of CGO electrolyte, and thereby provided better sintering results after limited constrained sintering.
Limited constraint sintered of electrolyte supported cells having the same width, length, thickness and thickness ratio (40 mm, 40 mm, 3:15:2 (A:E:C) and 60:300:40 μm (A:E:C), respectively)

**Cell 4:** 40 mm x 40 mm WxL, thickness ratio: 3:15:2 (A:E:C), thickness: 60:300:400 μm, sintered with a 75 mm x 75 mm LxW porous alumina cover plate on the top of the cell, 40% porosity with a total mass of 16.45 g

**Cell 5:** 40 mm x 40 mm WxL, thickness ratio: 3:15:2 (A:E:C), thickness: 60:300:40 μm, sintered with two 75 mm x 75 mm WxL porous alumina cover plate on the top of the cell, 40% porosity with a total mass of 32.9 g

**CSC 6:** 40 mm x 40 mm WxL, thickness ratio: 3:15:2 (A:E:C), thickness: 60:300:40 μm, sintered with three 75 mm x 75 mm WxL porous alumina cover plate on the top of the cell, 40% porosity with a total mass of 49.35 g

*Figure 106 Limited constraint sintered of electrolyte supported cells having the same width, length, thickness and thickness ratio (40 mm, 40 mm, 3:15:2 (A:E:C) and 60:300:40 μm (A:E:C), respectively)*
Figure 107 The views of almost curvature free electrolyte supported cell (cell 6) from different perspectives with estimated porosities

Mean curvature -height: 0.07 mm

Estimated porosity:
Anode: % 27.11
Electrolyte: % 18.48
Cathode: % 26.56
7.4 CHARACTERIZATION OF SELECTED OPTIMUM SPECIMENS OF SINTERED CELLS

Figure 109 depicts the SE SEM images of polished and unpolished cell 1 and cell 2 as well as with polished BSE SEM images of these cells. In addition, Figure 110 shows the final curvature free cell’s SE and BSE SEM images with EDS layered image. Furthermore, Table 14 shows the estimated porosity of the anode, cathode and electrolyte. In addition, it also summarizes the estimated mean particle size and mean pore size of anode and cathode of cell 1, cell 2 and cell 6. According to Figure 109 and Figure 110, cathode layer has coarser grain structure in comparison to anode layers for each cells; this is as expected owing to higher sintering temperature for LSCF cathode. All cells possess porous electrolyte structure due to the sintering temperature lower than the temperature required for fully sintered CGO materials. Furthermore, there is a steadily good adhesion across all cells between layers.
Moreover, it generally appears that the connectivity of NiO on the anode side and LSCF on the cathode side is reasonable, but there is low connectivity of the CGO on both sides, which may reduce the triple phase boundary for electrochemical reactions.

Additionally, the density of the electrolyte close to the cathode layer is greater than that adjacent to the anode layer for all cells from visual inspection, see Figure S8. This is because compressive stress generated by the cathode is normally higher between cathode/electrolyte layer and decreases along the thickness direction towards the anode layer. These types of properties were also observed in the anode and cathode supported planar SC-SOFCs explained in the previous chapters. However, when comparing electrolyte porosities of the electrolyte supported cells with the electrolyte porosities of the anode and cathode supported cells (all of which have similar cell thicknesses), there are considerable differences. For example, the estimated porosity of the electrolyte for the anode and cathode supported cells was measured to be around 14% with small differences while it was measured to be around 18% for the electrolyte supported cells (see Table 6, Table 12 and Table 14). This could be ascribed to the effect of the cathode’s high shrinkage, which causes compressive stress on electrolyte, wherein this effect becomes less pronounced on the electrolyte supported cells due to the greater electrolyte layer thickness.

In addition, according to Table 14, the estimated anode, electrolyte and cathode porosity of cell 1 is 29.58%, 16.19% and 27.57%, respectively. Moreover, the mean particle and pore sizes were found to be 2.301 ± 1.485 μm and 1.124 ± 0.604 μm, respectively, for anode layer and 2.902 ± 2.28 μm and 1.656 ± 0.783 μm, respectively, for cathode layer. These mean particle and pore sizes of cathode layer are greater than that of anode layer due to the coarse grain structure of cathode. Furthermore, when the thickness of the electrolyte was increased from 200 μm to 300 μm (cell 1 and cell 2) the electrolyte porosity increased to 18.89% while there were minimal changes on the anode and cathode porosity as well as their mean particle and pore sizes. In addition, for the same anode cathode and electrolyte thickness (cell 2 and cell 6), when the cell was constrained with three alumina cover plates (cell 6), the cathode and anode porosity decreased from 28.17% to 26.56% and from 30.03% to 27.11%, respectively whereas there were small reduction in electrolyte porosity (18.89% to 18.45%). Similarly, the mean particle and pore of the anode and cathode layers slightly decreased. This might be elucidated by the fact that particles in each cell’s layers were forced by internal stresses caused by interface stresses to in-plane shrink instead of causing curvature formation. This event might have improved their sinterability, however simultaneously it may have brought about lower electrode porosity.
**Cell 1 thickness ratio: 3:10:2 (A:E:C)**

**Cell 2 thickness ratio: 3:15:2 (A:E:C)**

---

**A**) Secondary electron (SE) SEMs of cell 1 and cell 2 without polishing

**B**) SE SEM images of cell 1 and cell 2, polished

**C**) Backscatter electron (BSE) SEM images of cell 1 and cell 2, polished

*Figure 109 The SE SEM images of polished and unpolished cell 1 and cell 2 with polished BSE SEM images of these cells*
Cell 6 thickness ratio: 3:15:2 (A:E:C), thickness: 60:300:40 µm, sintered with three 75 mm x 75 mm LxW porous alumina cover plates on the top of the cell

Figure 110 (A) SE SEM image of polished cell 6, (B) BSE image of polished cell 6, (C) unpolished SE SEM image of cell 6 and (D) EDS layered image of cell 6 from SE imaging
Table 14 Porosity measurement of anode, cathode and electrolyte with a mean particle and pore sizes of electrodes for electrolyte supported SC-SOFCs

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell 1 (60:200:40 µm, A:E:C), free sintering</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>29.58</td>
<td>16.19</td>
<td>27.57</td>
</tr>
<tr>
<td>Mean particle size (µm)</td>
<td>2.301 ± 1.485</td>
<td>2.902 ± 2.28</td>
<td></td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
<td>1.124 ± 0.604</td>
<td>1.656 ± 0.783</td>
<td></td>
</tr>
<tr>
<td><strong>Cell 2 (60:300:40 µm, A:E:C), free sintering</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>30.03</td>
<td>18.89</td>
<td>28.17</td>
</tr>
<tr>
<td>Mean particle size (µm)</td>
<td>2.276 ± 1.493</td>
<td>3.029 ± 2.273</td>
<td></td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
<td>1.21 ± 0.7</td>
<td>1.697 ± 0.823</td>
<td></td>
</tr>
<tr>
<td><strong>Cell 6 (60:300:40 µm, A:E:C), sintered with three 75x75 porous alumina cover plate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>27.11</td>
<td>18.48</td>
<td>26.56</td>
</tr>
<tr>
<td>Mean particle size (µm)</td>
<td>2.307 ± 1.715</td>
<td>2.767 ± 2.343</td>
<td></td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
<td>1.102 ± 0.621</td>
<td>1.342 ± 0.682</td>
<td></td>
</tr>
</tbody>
</table>

The EDS Maps of cell 6 and its spectrum from anode and cathode side are shown in Figure 111 and Figure 112, respectively. According to the Figure 111A, the Ce, O, Ni and Gd elements are in the expected region of the composite anode electrode (consisting of NiO-CGO material). There were no observable impurities in the anode layer, whether they were those that diffused from cathode layer or contaminated during the fabrication process. However, Figure 111B depicts that there are in fact some impurities in the anode component. There were some elements observed on the anode side such as Al, Si, Fe and Co. Some of these impurities such as Fe and Co had most likely diffused from the cathode side throughout electrolyte layer although the cell electrolyte is quite thick in comparison to the anode and cathode supported cells. Furthermore, as with the anode and cathode supported specimens, the existence of Au and Pd is due to sputtering of these elements on the cell before SEM imaging so as to make them conductive whereas that of Al was likely coming from either porous alumina cover plate or substrate. In addition, Si could be introduced during the any stage of fabrication process. Similarly, Figure 112A shows that cathode elements La, Sr, Co, Fe, Ce, O, and Gd which make the cathode electrodes are also in the projected area. Similar impurities (Al, Si and Pd) were also observed on the cathode side due to the same reasons mentioned previously (Figure 112B). However, there was no Ni diffusion from the anode side. The amounts of these impurities on both sides seem quite small, but, they could block the active reaction areas of the cell and thereby cause low cell performance.
In addition, Figure 113 illustrates the XRD diffraction patterns of cell 1 and cell 6. According to this figure, a phase of NiO, CGO and LSCF for the anode, electrolyte and cathode layers, respectively, were observed. As per the previous iterations performed in chapter 5 (cell 11, anode supported) and chapter 6 (cell 8, cathode supported), EDS data for cell 6 also supports the presence of the main elements which could give rise to the formation of the main cell phases (see the elemental analysis from Figure 111B and Figure 112B). Furthermore, there was no undesired phase formation in both cells after sintering. There were some impurities observed in the Map Sum spectrum of the cell 6 as well as some elemental diffusion either from anode to cathode side or from cathode to anode side (see Figure 111B and Figure 112B). These impurities as well as diffused elements from one side to another could cause some additional phase formations. However, there are no additional crystalline phases observed in XRD patterns owing to limitation of XRD technique to detect these possible phases due to their small amount. Moreover, cell 6 and cell 11 are identical according to their XRD results. This is as a consequence of having the same anode, cathode and electrolyte material (NiO-CGO, LSCF-CGO and CGO, respectively). Each cell has the same the fabrication process and the only difference they possess is the thickness of their layer. Therefore, it is very likely to expect the similar XRD results.
A) EDS Maps of cell 6, from anode side

B) Map Sum Spectrum of cell 6, from anode side

Figure 111 (A) EDS Maps of cell 6 and (B) Map Sum Spectrum of cell 6 taken from anode side, the cell possess a thickness of 60:20:800 µm, A:E:C, sintered with three 75 mm x 75 mm alumina porous cover plate
A) EDS Maps of cell 6, from cathode side

B) Map Sum Spectrum of cell 6, from cathode side

Figure 112 (A) EDS Maps of cell 8 and (B) Map Sum Spectrum of cell 8 taken from cathode side, the cell possess a thickness of 60:20:800 µm, A:E:C, sintered with three 75 mm x 75 mm alumina porous cover plate
Figure 113 (A) X-Ray Diffraction patterns of cell 1 and (B) cell 6

7.5 CELL PERFORMANCE TESTS

Figure 114 and Figure 115 indicate the OCV and polarization results of cell 1 and cell 6, respectively. According to Figure 114, the high power density and OCV of cell 1 were obtained at fuel-rich gas mixture (R: 2.6). The maximum OCV of cell 1 was measured as 0.65 V at gas mixture 4 (80-31-100 ml min⁻¹, CH₄-O₂-N₂, R: 2.6) with a maximum power density of 24.32 mW cm⁻². However the maximum power density was obtained at gas mixture 7 (100-38-100 ml min⁻¹, CH₄-O₂-N₂, R: 2.6) and it was measured to be 29.39 mW cm⁻² with an OCV of 055 V (Figure 114 and Table 15). The similar trends were also observed from cell 6, the maximum power density and OCV as measured at fuel rich conditions (R:...
Furthermore, when the electrolyte thickness was increased from 200 µm (cell 1) to 300 µm (cell 2), the cell OCV and power density decreased almost at all fuel/oxygen ratio (R) of 2.6 and 1.8, but generally increased at R: 1. The maximum OCV and power density of cell 6 were obtained at gas mixture 7 and measured to be 0.55 V and 14.4 mW cm^{-2}, respectively (see Table 15 and Figure 115). The reason for the mitigated cell performance due to increased electrolyte thickness could be mainly attributed to fact that the increased electrolyte thickness causes high ohmic losses [233, 241] owing to the increased O^2^- pathway from cathode side to anode side. However, the increased electrolyte thickness also reduces the gas cross-over (H_2 and CO) from anode side to cathode side due to increased distance for gases to travel from cathode to anode and thereby resulting in better cell performance. The decreased cell performance demonstrated that the benefit of increasing electrolyte thickness is less than the negative effects of thickness increment. The cell performance increment at lean gas conditions (R: 1) could be explained as follows: the O_2 diffusion might have been more mitigated than the CH_4 to anode side from cathode side due to the thicker electrolyte layer, since the O_2 has lower diffusion rate in comparison to CH_4 because of its high molar mass, therefore, the partial pressure of O_2 increased on the cathode side while it decreased on the anode side. This could lead to an increase in OCV establishment due to increased partial pressure differences between anode and cathode layers. This phenomenon could also be seen at fuel rich gas conditions, however, it becomes more important at fuel lean conditions (R: 1) due to the lower percentage of methane in the gas mixture. In addition, the OCV oscillation in both cells at different gas mixtures could be mainly due to Ni oxidation/reduction since anode possesses a thin layer [240, 242].

Moreover, the increased the amount of total gas at fuel-rich gas mixture (R: 2.6) by increasing the amount of methane and oxygen gases has generally beneficial effects on the performance of cell 1 and cell 6 (gas mixture 1, 4 and 7) whereas it has predominantly detrimental influence at R: 1.8 and R: 1. This could be articulated by the fact that the surface exchange co-efficient and temperature increases with the increased gas flow rate [241, 242], therefore cell performance increases. However, when the proportion of methane decreases in the total gas mixture, increasing total gas mixture could have negative effects on cell performance in comparison to the fuel rich conditions. Because there would be enough percentage of methane at fuel rich gas mixtures on the anode side, the resulting decreased residence time could facilitate more methane to be reformed. However, if there is not enough methane on the anode side, the decreased residence time could cause a situation where less
methane but more oxygen gas is adsorbed on the anode surface in comparison to fuel-rich gas mixtures, therefore yielding less reforming and thus a reduction in cell performance.

Furthermore, Figure 114 and Figure 115 also show that the increased amount of $O_2$ has negative effects on cell’s OCV and power density at all fixed methane gases for the same reasons (see chapter 6) for the cathode supported SC-SOFC, namely the resultant effects of the minimised anode thickness. The anode is required to have enough active surface to reform methane gas as well as electrochemical reaction of syngas ($H_2$ and $CO$) with oxygen ions [243, 244]; if there is not enough methane reforming, the oxygen partial pressure increases on the anode side, and thus oxygen partial pressure difference decreases and thereby OCV decreases according to Nernst equation. Therefore, it is expected that a more fuel rich gas sent [244] to the thin anode will partly redress the adverse partial pressure gradient and aid in more methane being reformed in order to compensate the decreased methane reforming due to the lack of effective reforming catalytic area from thin anode layer. In addition, in the case of oxygen increment, the proportion of methane in the total gas mixture decreases, thus the surface areas in anode will be occupied more by oxygen adsorption due to the increased amount of oxygen gas. In other words, oxygen gas competes with the methane gas for the adsorption areas on nickel surface and that increased $O_2$ has an inhibitory effect on the partial oxidation of $CH_4$ [244]. Hence, complete methane reforming is less favoured, and thus OCV and power density diminish. Furthermore, the higher formation of $H_2O$ and $CO_2$, which do not partake in the electrochemical reactions of the cell, increases with the increased $O_2$ [244], and therefore the cell performance decreases.

To sum up, the performance results of thicker electrolyte supported cell (cell 6) shows that the increased electrolyte thickness for the benefit of obtaining planar electrolyte supported cell via single step co-sintering has negative influence on cell’s performance in comparison to thinner cell (cell 1) as is the case with the cathode supported cell. Overall, the cell performance was found to be relatively low in comparison to the electrolyte supported cells in the literature. This is likely an aggregate of all the explanations provided for the low cell performance of anode and cathode supported SC-SOFCs mentioned in chapter 5 and chapter 6 such as impurities (see Figure 111 and Figure 112) in both electrodes, carbon cooking, reduction of CGO electrolyte and so forth.
Figure 114 (A) OCV Measurement and (B) polarization results of cell 1, thickness: 60:200:40 µm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio.
Figure 115 (A) OCV Measurement and (B) polarization results of cell 6, thickness: 60:300:40 µm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio.
7.6 SUMMARY

An electrolyte supported planar SC-SOFC was manufactured utilising the single step co-sintering technique established for the configuration of the anode and cathode supported cells. The results show that optimum thickness and thickness ratio of a cell manufactured with the optimized hot pressing and sintering conditions showed in improved co-sintering results, no delamination and no cracking, but curvature was still maintained at the edges of the cell. Porous alumina cover plate was used to suppress curvature formation and to achieve planar and curvature-free cell as done in other configuration of the cells. By using three alumina cover plates with a total mass of 49.35 g on the top of the cell, an almost curvature free electrolyte supported cell was successfully obtained. SEM, EDS and XRD techniques were used to characterize the sintered cell in order to measure its estimated porosity, mean particle and pore size, and to detect possible impurities and undesired phase formations in the cell. The result showed that there were no unwanted phase formations in the cell but some elements diffused from cathode to anode layer such as Fe and Co, and other elements e.g. Al, Si, etc. were introduced during any stage of the fabrication. Moreover, increasing electrolyte
thickness led to an increase in the cell porosity which has detrimental effect on cell performance.

In addition, the cells were tested to investigate its relative energy conversion capability and the effect of electrolyte thickness on cell’s performance. The maximum power density was obtained from thin cell (cell 1) with a measurement of 29.39 mW cm\(^{-2}\) at quite fuel-rich conditions (gas mixture 7, 100-38-100 ml min\(^{-1}\), CH\(_4\)-O\(_2\)-N\(_2\), R: 2.6). At this gas mixture, the maximum OCV was measured to be 0.55 V. When the electrolyte thickness increased (cell 6), the cell performance substantially decreased, which is assumed due to the increased ohmic losses. Therefore, increasing electrolyte thickness for the benefit of obtaining curvature-free planar cell has negative effects on cell’s performance.
CHAPTER 8

SINGLE STEP SINTERING BEHAVIOUR OF AN NOVEL ANODE SUPPORTED WAVY CELL AND ITS PERFORMANCE

A wavy anode supported SC-SOFC was fabricated by using previously recommended co-sintering techniques for planar, curvature-free SC-SOFCs (anode, cathode and electrolyte supported cells). The purpose of making a wavy structure is to investigate the effect of wavy structure on cell performance. In addition, it is also assumed that the wavy structure could absorb more shock than its planar counterpart due to its unique shape.

8.1 FABRICATION OF THE ANODE SUPPORTED WAVY SC-SOFC

A similar set of laminating and hot pressing techniques were applied for the fabrication of the initial green tape for wavy structure. Anode, electrolyte and cathode layers were sandwiched upon each other and hot pressed at 60°C with a pressure of 2 MPa for 5 minutes. Similarly, the cell was sintered as follows: at 1200 °C for 60 minutes with a heating rate of 1°C min\(^{-1}\) up to 500°C for debinding, 2°C min\(^{-1}\) up to 900°C and 1°C min\(^{-1}\) up to 1200°C while the cooling rate was set at 3°C min\(^{-1}\).

In order to produce a wavy structure, the cell was initially placed on two alumina rods which have equal diameters of 3.4 mm, with the cathode layer contacting to them (facing downward) (see Figure 116, first design for a wavy cell fabrication). The aim here was to control curvature formation, which normally happens towards the cathode layer during sintering due to high shrinkage rate of the cathode. Firstly, it is assumed that the cell could curve from the contact points with rods towards the cathode layer due to (1) gravitational effect during debinding process where the binders become soft and (2) mismatch force generated between layers owing to the high shrinkage of the cathode layer during the main densification periods. This could result in formation of half of the wave. Secondly, a bell shape curve could be formed in the middle of the cell as a result of the fact that the mass of the cell could pull down the cell from the centre point during debinding process due to gravitational effect on softened green tape and resulting in permanent bell shape in the middle of the cell during sintering. These two occurrences could complete a wavy structure, thus leading to a wavy SC-SOFC.
The cell possesses dimensions of 15 mm × 60 mm W×L and a thickness of 200:40:40 μm, A:E:C. The horizontal distance and the distance from the cell short edge to their closest alumina rods were defined as being 30 mm and 15 mm, considering the total length of 60 mm. This arrangement is assumed to produce a result such that the wavy cell’s peak and base points’ distance to each other to be equal after sintering. In addition, the alumina rods were not fixed in order to allow smooth movement of particles at the contacting areas with alumina rods (see Figure 116). According to Figure 116, the first predicted design for fabrication of wavy cell structure unfortunately failed. As was expected, the cell curved towards cathode layer; however, there was no wave shape formed in the middle of the cell, and the cell cracked at the contact area between cell and one of the alumina rods. The unsuccessful result could be attributed to several reasons. For example, during the debinding stage, the cell forms a wavy structure by the help of alumina rods and gravitational effect; however, when the cell starts to densification, the driving force between particles pulls them to each other and particles rearrange themselves. This pulling effect might have led to removal of the bell type shape in the middle of the cell as well as increasing the stiffness of the cell which resists deformation in response to gravitational force (see Figure 116, there is no wavy shape in the middle of the cell). Furthermore, the crack at the contact point could be ascribed to the fact that the cell lower part is under compressive stress while the upper part is under tensile stress due to the high shrinkage of the cathode causing curvature towards the cathode layer. When the material withstands this tensile stress, no cracks or crack-like defects occur after sintering. However, if the material cannot resist the tensile stress, it fails. In the case of wavy cell fabrication method shown in Figure 116, an additional bending stress is imposed on the contact regions of the cell with alumina, and this increases the total intrinsic stress (both tensile and compressive stress) at these areas in comparison to other part of the cell. This bending stress was as a result of gravitational force caused by the mass of the cell section which is between alumina rod and short side of the cell edge as seen in Figure 116 (F = mg). Therefore, when the cell became brittle, the increased tensile stress might have led to the cell to crack at the contact area. In addition, the material microstructure could differ at the touching sections (or bending areas) than other parts of the cell, as the alumina rods would restrict particle motion in the contact areas while the particles on top surface of the same region would have no restriction. This could cause a different cell microstructure at the region and different intrinsic stress in comparison to the other parts of the cell. As a result, the cell becomes quite weak at this sections and any small impact or shock could cause the cell to break at this section.
In addition, as a second trial, the cell this time was placed on the top of two alumina rods which as a diameter of 2.7 mm with the anode layer contacting to them (facing downward). These two rods also located on two insulating fire brick as in the Figure 117, 2A (second design for a wavy cell fabrication). Two grooves were made on the insulating brick to allows alumina rods to move at its centre whereas no movement on the other directions in order to prevent anisotropy due to possible motion of alumina rods owing to particle movements. Furthermore, an alumina rod with amass of 0.67 g was placed in the middle of the cell so as to aid gravitational force that leads to the formation of a bell type shape curve in the middle of the cell (see Figure 117, 2A). Moreover, the cell thickness and thickness ratio was preserved (thickness = 200:40:40 μm, A:E:C) while the width and length were defined to be 40 mm and 40 mm respectively. The distance between each rod is defined to be 10 mm in
order to divide the cell into four equal sections (see Figure 117, 2A) for the purpose of achieving the peak and base points of the cell to be equal after sintering. Two additional alumina rods were also placed at the edge of the cell so as to prevent the cell movement on y direction before debinding process. Thereafter, the cell was pre-heated until 80˚C in order to allow the green body of the cell to soften and to be formed to a wavy shape by the help of the gravity and alumina rod located in the middle of the cell. Afterward, the alumina rods placed at the edge of the cell and in the middle of the cell were removed. Figure 117, 2B shows that the cell formed to a wavy structure before sintering after pre-heating and removal of alumina rods. Subsequently, the cell was sintered at 1200˚C. It was assumed that the pre-formed shape of the cell would try to preserve its shape during sintering though cathode causes cell to curve upwards. However, the result shows that (see Figure 117, 2C) the cell broke and formed a cylindrical shape after sintering. This is mainly attributed to the high shrinkage of cathode. Because cathode layer forced the cell to curve upward (from anode to cathode side, from bottom to up) and this tendency of curvature formation towards upward initially cancelled the wavy structure formed during debinding at some point of sintering and later caused the cell to become cylindrical shape and to crack. Therefore it is important to place cathode face facing downward.

Furthermore, a similar cell which possess the same size with the previous one (40 mm × 40 mm W × L, 200:40:40 µm, A:E:C) was placed on two alumina rods (diameter = 3.4 mm) (named third design) as the first design for the wavy cell fabrication but this time an alumina rod with a mass of 3.45 g were placed on the middle of the cell (see Figure 117,3) for the same purpose explained for the alumina rods positioned on the cell in the second design for the cell fabrication. As a result, although the cell curved at the contact areas with the rods, the cell broke into two pieces due to excessive mass of the alumina rod.
2) Second design for a wavy cell fabrication, cell size: 40 mm x 40 mm WxL before sintering, thickness: 200:40:40 μm, thickness ratio: 20:2:2, A:E:C

A) The cell placement on the alumina rods before sintering

B) The cell formation and alumina rod removal after 80 °C

C) After sintering

3) Third design for a wavy cell fabrication, cell size: 40 mm x 40 mm WxL before sintering, thickness: 200:40:40 μm, thickness ratio: 20:2:2, A:E:C

Alumina rods

Alumina supporting rods

Alumina rods for suppressing cell edges

Insulating firebrick

Figure 117 (2) Second design for a wavy cell fabrication: (A) before heat treatment, (B) after heat treatment at 80 °C and (C) after sintering, and (3) third design for wavy cell fabrication
Finally, the last design, the combination of third and second design (named as forth design for wavy cell fabrication), was assumed to overcome the issues mentioned above. Figure 118 illustrates the wavy cell fabrication design and the placement of green tape in the design. Two insulating fire bricks were employed so as to allow small motion of the rods on the X and Y direction while allowing the rods to rotate at its axis in order to soften any constraint instigated by the rods. In order to place alumina rods in the fire brick, two grooves were formed under the insulating fire brick (see Figure 118A). Furthermore, the third groove also made between two previous grooves however, it has different height so that allowing an alumina rod can be positioned on the top of the cell. The aim of middle alumina rod is to utilise its mass and cylindrical structure to form a wavy shape in the middle of the cell. Moreover, the diameter of the substrate rods has the same diameter with rods in the third design (3.4 mm), and the rod located on the middle of the cell possess a diameter of 2.7 mm and a mass of around 1.02 g. Besides, in order to increase the cell strength, the anode thickness of the cell was increase from 200 µm to 400 µm. In addition, in order to divide cell into four equal parts, the distance between the rods was defined being 10 mm, considering the total cell sizes of 40 × 40 mm W × L. Moreover, the cell placed as cathode facing downward. This arrangement leads to wavy cell structure due to the directing cell curvature formation to begin at the touching areas between the cell and rods during the sintering. it is also assumed to ensure the wavy cell’s base and peak point distance to each other to be the same after sintering.

The fabrication of wavy cell in this design can be explained as follows: Firstly, a planer anode supported green cell tape was positioned and adjusted on two alumina rods, cathode facing downward, then an alumina rod was placed on the top of the cell as per Figure 118B. This arrangement allows a wavy structure to be formed owing to binder softening during debinding process: secondly, when main densification starts, the curvature occurs from anode side to cathode side as a result of high densification of the cathode. This arrangement, with cathode facing downward, allows the direction of curvature formation at the sides at high densification to be the same with the curves formed during debinding because cell is bent downward at the areas in contact with the side rods due to high cathode densification. If the anode was located downward, then the direction of curves at the side would shift to opposite direction and lead to a cylindrical type shape or crack at the later stage of sintering as demonstrated in second design for the wavy cell fabrication. Finally, an anode supported SC-SOFC, which has a thickness of 400:40:40 µm, A:E:C (thickness ratio = 20:2:2, A:E:C) with a roughly wavy shape was obtained (see Figure 118C).
4) Forth design for a wavy cell fabrication, cell size: 40 mm x 40 mm WxL before sintering, thickness: 400:40:40 µm, thickness ratio: 20:2:2, A:E:C

A) The substrate alumina rods

B) The cell placement on the alumina rods before sintering

C) Cell 1 Anode Supported wavy SC-SOFC after sintering 40 mm x 40 mm WxL before sintering, thickness ratio: 20:2:2, (A:E:C), thickness 400:40:400 µm

Figure 118 Forth design for a wavy cell fabrication: (A) the illustration of substrate rods in fire brick, (B) the placement of cell on the alumina rods and (C) sintering results of an anode supported cell

In addition, for the same anode and cathode thickness as well as with the same width and length, an anode supported wavy cell with less electrolyte thickness (electrolyte thickness
20 µm, see Figure 119, cell 2) was fabricated with the similar technique. The mass of the alumina placed on the top of the cell during sintering was the same (D: 2.7 mm, Mass: 1.02 g). However, one should bear in mind that although the cell has a wavy structure, it must have different dimensions in terms of wave height, wavelength etc. in comparison to the cell 1 in Figure 118. Furthermore, in order to make a thicker anode supported cell, the anode thickness increased from 400 µm to 800 µm while the electrolyte and cathode thickness was kept constant. However, using the same mass of the alumina on the top of the cell utilised in cell 2 and cell 1 for curvature formation was not sufficient to lead a curve in the middle of the cell. Therefore, the mass of the alumina was increased to 2.5 g while its diameter was not altered. As a consequence of that, the cell was broken into two parts as shown in Figure 119, cell 4. It is mainly attributed to the cell strength not being sufficient to withstand the pressure generated by the alumina rod placed on the top of the cell. Therefore, the mass of the alumina was reduced from 2.5 g to 1.9 g. However, this mass was also excessive and caused the cell to break as depicted in the Figure 119, cell 5. Afterward, the mass of the alumina was decreased further to 1.49 g. Finally, a wavy anode supported cell with a thickness of 800:20:40 µm, A:E:C, was obtained (see Figure 119, cell 6). Furthermore, the wavy structure could withstand high force when the force is applied vertically to the top surface of the cell in comparison to the planar counterpart because of the fact that the pressure in a wavy structure is distributed evenly and thus there is no concentration of force. However, the cells were easily broken in comparison to the planar anode supported cells when a horizontal force was applied to the wavy structure with a manual test done by hands. It shows that the wavy structure is quite weak at the peak sections under the horizontal forces. In addition, a wavy cell with more isotropic and smooth shape as well as required peak and wavelength could be obtained by this fabrication technique if the right diameter of the all rods and the mass of the middle rod are defined suitably.
Cell 2: 40 mm x 40 mm WxL before sintering, thickness ratio: 20:1:2 (A:E:C), thickness: 400:20:400 μm, an alumina rod placed on the top of the cell, which has a mass of 1.02 g and diameter of 2.7 mm

Cell 3: 40 mm x 40 mm WxL before sintering, thickness ratio: 40:1:2 (A:E:C), thickness: 800:20:400 μm, an alumina rod placed on the top of the cell, which has a mass of 1.02 g and diameter of 2.7 mm

Cell 4: 40 mm x 40 mm WxL before sintering, thickness ratio: 40:1:2 (A:E:C), thickness: 800:20:400 μm, an alumina rod placed on the top of the cell, which has a mass of 2.5 g and diameter of 2.7 mm

Cell 5: 40 mm x 40 mm WxL before sintering, thickness ratio: 40:1:2 (A:E:C), thickness: 800:20:400 μm, an alumina rod placed on the top of the cell, which has a mass of 1.9 g and diameter of 2.7 mm

Cell 6: 40 mm x 40 mm WxL before sintering, thickness ratio: 40:1:2 (A:E:C), thickness: 800:20:400 μm, an alumina rod placed on the top of the cell, which has a mass of 1.49 g and diameter of 2.7 mm

Figure 119 Sintering results of different anode supported wavy SC-SOFCs
8.2 CHARACTERIZATION OF SELECTED OPTIMUM SPECIMENS OF SINTERED WAVY CELLS

Figure 120 shows the polished and unpolished SE SEM images of cell 1 and cell 2 along with their polished BSE SEM images. In addition, Figure 121 depicts the SEM images of cell 6 as well as its EDS maps. All cells possess highly comparable structure respective to their cathode, electrolyte and anode, in terms of pore and particle sizes and their distributions. In addition, these cells’ microstructures are also very close to the planar anode supported cells which have the same thicknesses and thickness ratios. There is a sufficient adhesion between cathode and electrolyte, anode and electrolyte layers across all cells. However, they all have porous electrolyte and coarse cathode microstructure due to the low sintering temperature of electrolyte and high sintering temperature of cathode, respectively as mentioned in previous chapters. Furthermore, from the BSE images of all cells, one can define that the NiO and LSCF connectivity are sufficient enough in their respective electrodes but CGO seems to have some discontinuity in both electrodes that could reduce the cells’ performances because of insufficient effective electrochemical reaction area (TPB) in the anode and cathode layers for an electrochemical reaction in the gas mixture during operation.

Beside, Table 16 shows the estimated porosity of anode cathode and electrolyte of each cell along with their mean particle and pore sizes of anode and cathode. It can be seen that cell 1 (thickness: 400:40:40 μm, A:E:C) has an estimated 31.85% porosity of anode, 15.93% of electrolyte and 31.39% porosity of cathode. The mean particle and pore sizes of anode were measured as being 2.603 ± 1.706 μm and 1.201 ± 0.524 μm, respectively, whereas they were found to be as 3.026 ± 2.315 μm and 1.685 ± 0.613 μm, respectively, for cathode layer. Moreover, decreasing electrolyte thickness (cell 2) has positive effect on electrolyte porosity, and it mitigated to 15.12% in comparison to cell 1. It could be as a result of the fact that high cathode shrinkage (induced compressive stress on electrolyte) becomes more dominant on a thinner electrolyte. In addition, the anode and cathode estimated porosity of cell 2 was measured to be 31.26% and 33.59%. When the anode thickness increased from 400 μm to 800 μm (μm) (cell 6), the estimated electrolyte porosity increased to 16.25% due to the similar reasons, cathode high shrinkage effect decreases on overall cell as a result of the increased cell thickness. Similar observations were detected for the planar anode supported SC-SOFCs. Furthermore, the cell 6 possesses a porosity of 32.71% for anode layer.
and 34.74% for cathode layer. In general, it can be emphasized from Table 16 that cell 1, cell 2 and cell 6 have a closely matching porosity, particle and pore sizes.

Table 16 Porosity measurement of anode, cathode and electrolyte with a mean particle and pore sizes of electrodes for anode supported wavy SC-SOFCs

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Porosity (%)</strong></td>
<td>31.85</td>
<td>15.93</td>
<td>31.39</td>
</tr>
<tr>
<td><strong>Mean particle size (µm)</strong></td>
<td>2.603 ± 1.706</td>
<td>3.026 ± 2.315</td>
<td></td>
</tr>
<tr>
<td><strong>Mean pore size (µm)</strong></td>
<td>1.201 ± 0.524</td>
<td>1.685 ± 0.613</td>
<td></td>
</tr>
<tr>
<td><strong>Cell 2 (400:20:40 µm, A:E:C), free sintering</strong></td>
<td>31.26</td>
<td>15.12</td>
<td>33.59</td>
</tr>
<tr>
<td><strong>Mean particle size (µm)</strong></td>
<td>2.313 ± 1.659</td>
<td>3.129 ± 2.456</td>
<td></td>
</tr>
<tr>
<td><strong>Mean pore size (µm)</strong></td>
<td>1.213 ± 0.64</td>
<td>1.86 ± 0.763</td>
<td></td>
</tr>
<tr>
<td><strong>Cell 6 (800:20:40 µm, A:E:C), free sintering</strong></td>
<td>32.71</td>
<td>16.25</td>
<td>34.74</td>
</tr>
<tr>
<td><strong>Mean particle size (µm)</strong></td>
<td>2.559 ± 1.882</td>
<td>2.857 ± 2.295</td>
<td></td>
</tr>
<tr>
<td><strong>Mean pore size (µm)</strong></td>
<td>1.118 ± 0.455</td>
<td>1.772 ± 0.908</td>
<td></td>
</tr>
</tbody>
</table>
**Figure 120** The SE SEM images of polished and unpolished cell 1 and cell 2 with polished BSE SEM images of these cells
Cell 6 thickness ratio: 40:1:2 (A:E:C), thickness: 800:20:40 µm

A) Secondary electron (SE) SEMs of cell 6 without polishing

B) SE SEM images of cell 6, polished

C) Backscatter electron (BSE) SEM images of cell 6, polished

D) EDS Maps of cell 6, polished, 25 µm

Figure 121 (A) Unpolished SE SEM images of cell 6, (B) SE SEM image of polished cell 6, (C) BSE image of polished cell 6 and (D) EDS Maps of cell 6 from SE imaging
When inspecting EDS maps of cell 6 in Figure 121D, the Ni, O, Ce, Gd, La, Sr, Co, and Fe elements are in the expected regions, and it looks there are no impurities on anode and cathode sides. However, Figure 122 demonstrated that there are actually some impurities in the cell 6 after sintering. According to Figure 122B, anode layer has small weight percentage of cathode elements in its structure (Co: 1.4wt.% and Sr: 0.1wt.%), which could be as a result of surface diffusion of these elements throughout the porous electrolyte. In addition, there are also some undesired elements in the anode side such as 0.2wt.% Al and 0.2wt.% Si. The Si must have been introduced during any stage of fabrication process since Si exists excessively in everywhere while the Al could be coming from either alumina substrate or the alumina rods. Similarly small amount weight percent of Si (0.3wt.%) and Al (0.2wt.%) were detected on cathode side for the same reasons. In addition to this, the 0.6wt.% of Ni was also found on the cathode side. This could be also attributed to the Ni surface diffusion from anode side to the cathode side through porous electrolyte, this impurities are in small percentage but they could still have negative effects on cell’s performance.

Furthermore, Figure 123 depicts the X-Ray Diffraction of cell 1, cell 2 and cell 6. They have similar results with planar anode supported cells mentioned in chapter 5. The expected phases (NiO, CGO and LSCF) were observed and there are no further crystalline phase formations. In addition, EDS analysis of cell 6 shows that there are some impurities in the cell. These impurities as shown in Figure 122 (for instance Al, Pa and Si or diffusion of Sr, Co, and Fe from cathode side to anode side and diffusion of Ni from anode to cathode side, see elemental analysis from Figure 122) could form new phases. However, XRD result of cell 6 show that there is no additional crystalline phase formation. This is due to the limitation of XRD technique to detect phases present in extremely small or miniscule amounts, such as impurities or trace elements. In addition, as per previous sections, each cell possesses the same anode, cathode and electrolyte materials and their fabrication process is the same, only differing in terms of layer thickness. Though these cells are of wavy structure, it is also highly expected to have similar XRD results as their counterpart of planar anode supported cells. The XRD results of each cell depict that, these cells have almost same XRD results.
A) Map Sum Spectrum of cell 6, from anode and cathode sides

B) Map Sum Spectrum of cell 6, from anode side

C) Map Sum Spectrum of cell 6, from cathode side

Figure 122 (A) Map Sum Spectrum of cell 6, (B) A) Map Sum Spectrum of cell 6, from anode side and (C) Map Sum Spectrum of cell 6, from cathode sides
Figure 123 (A) X-Ray Diffraction of cell 1, (B) cell 2 and (C) cell 6
8.3 CELL PERFORMANCE TESTS

Anode supported wavy cells were tested so as to investigate the effect of wavy structure on cells’ performance. In addition, the influence of anode and electrolyte thickness on the performance of the wavy cells was also examined. The gas mixture was sent as a flow through as the planar anode supported cells. Moreover, the nitrogen gas was utilized as diluting agent at different gas mixtures. Figure 124, Figure 125 and Figure 126 depict the open circuit voltages and polarization results of cell 1, cell 2 and cell 6, respectively, at different fuel/oxygen ratio with 200 ml min⁻¹ N₂ while Figure 127 shows the OCV and polarization result of cell 6 at different gas mixture ratios with 100 ml min⁻¹ nitrogen gas.

Figure 124A shows that the OCV results of the cell 1 are generally not stable at fuel/oxygen ratio (R) of 1 and 1.2. This could be mainly attributed to oxygen reduction and reoxidation at oxygen rich mixture. However, a similar result was also observed at a fairly fuel rich gas mixture (R: 1.8). The reason behind this could be explained as follows: the complete reforming of methane occurs at temperature around 700 °C with a fuel/oxygen ratio (R) of 2. Therefore, the working temperature of 600°C and R: 1.8 is not sufficient enough to allow methane to be reformed into syngas. Therefore, possible excessive oxygen could still be at present during performance test and thereby resulting in oxygen reduction and reoxidation reactions on the anode side.

The OCV and power density of the cell 1 generally deteriorates with decreased amount of oxygen gas at all fixed methane gas conditions. This could be as a result of inadequate oxygen partial pressure on the cathode side. Because if there is not sufficient oxygen gas on the cathode side, then the establishment of OCV between anode and cathode become less according to Nernst equation and thus the related power density. However, one should also consider the fact that reforming could also be improved on the anode side due to the fuel/oxygen ratio reaching close to R: 2 and thus resulting in high oxygen partial pressure differences between anode and cathode owing to the less oxygen gas on the anode side and thereby producing an increased OCV for cell 1. However, it seems that the negative effect of decreased amount of oxygen gas is higher than its positive effects, and hence the cell OCV and power density diminished. Furthermore, increased total gas flow rate by simply increasing the amount of methane from 40 ml/min to 50 ml/min and related amount of oxygen gas for the same gas mixture ratio led to the improved OCV and power density of the cell 1 as a consequence of enhanced gas exchange at both electrodes which results in reduction in overpotential relating to gas diffusion at both electrodes. Moreover, the
maximum OCV and power density of cell 1 were measured to be 0.47 V and 16.31 mW cm\(^{-2}\) at gas mixture 4 (CH\(_4\)-O\(_2\)-N\(_2\), 50-50-200 ml min\(^{-1}\), R: 1) (see Figure 124A and B, and Table 17). However, for the same thickness and thickness ratio (400:40:40 µm, 20:2:2, A:E:C), the maximum OCV and power density of the planar cell were greater than these results, and they were measured to be 0.69 V and 27.12 mW cm\(^{-2}\), respectively (see chapter 5, Table 11).

Furthermore, when electrolyte thickness decreased from 40 µm to 20 µm for the same anode and cathode thickness (400 µm and 40 µm, respectively) (cell 2), the maximum OCV and power density decreased substantially at all gas mixture (see Figure 125 and Table 17) though ohmic losses should have decreased with a reduction in electrolyte thickness. This could be attributed to the gas cross over increment due to the thinner electrolyte although electrolyte porosity mitigated with decreased electrolyte thickness. It is because oxygen gas could easily move from the cathode to anode side and syngas such as H\(_2\) and CO could travel from anode side to cathode side and thus leading to (parasitic) chemical reactions with oxygen gas (H\(_2\) + 1/2O\(_2\) = H\(_2\)O or CO + 1/2O\(_2\) = CO\(_2\)) rather than electrochemical reactions with oxygen ions on anode side. In both cases, the establishment of OCV deteriorates; given this is the crucial step in single chamber operation to establish the potential gradient for further power generation, the result is thus a diminished power density. In this case, the fuel is converted only to heat instead of generating electrons via electrochemical reactions, therefore is considered a waste of fuel. Furthermore, similar trends were also observed in the cell 2 in comparison to cell 1, for instance, OCV oscillation, the OCV and power density diminishing with decreasing amount of oxygen gas at all fixed methane gas conditions and the OCV and power density improvement with increased total gas flow rates at the same fuel/oxygen ratios by simply increasing the amount of methane and oxygen gases. In addition, the maximum OCV and power density of cell 2 were obtained at a gas mixture of 60-60-200 ml min\(^{-1}\), CH\(_4\)-O\(_2\)-N\(_2\), R: 1, and were found to be 0.26 V and 6.67 mW cm\(^{-2}\) respectively. However, a planar cell with the same thickness and thickness ratio (A:E:C), the maximum OCV and power density were 0.62 mW cm\(^{-2}\) and 23.64 mW cm\(^{-2}\), respectively, at a gas mixture of 40-40-200 ml min\(^{-1}\), CH\(_4\)-O\(_2\)-N\(_2\), R: 1 (see chapter 5, Table 11).
Figure 124 (A) OCV Measurement and (B) polarization results of cell 1, thickness: 400-400-40 μm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio.
Figure 125 (A) OCV Measurement and (B) polarization results of cell 2, thickness: 400:20:40 µm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio.
In addition, in order to observe the effect of anode thickness on wavy cell structure, the anode thickness increased from 400 µm to 800 µm while the cathode and electrolyte thicknesses was kept constant (40 µm and 20 µm, respectively)(cell 6, thickness 800:20:40 µm, A:E:C). The OCV results at all gas mixture decreased a little while the power density in general improved to some extent in comparison to cell 2 (see Figure 126 and Table 17). The increase in the power density could be attributed the increased capacity for methane reforming as well as improved electrochemical reaction of syngas with oxygen ions due to the increased reaction sites (or TPBs) on anode site. This should have also led to the OCV incrementally improving owing to the increased oxygen partial pressure differences between the anode and the cathode due to the improved oxygen gas consumption on anode site. However, in this wavy cell structure, the OCV was observed to further decrease. Furthermore, it was normally expected to observe an increase in the OCV and the power density substantially by increasing the anode thicknesses as per the planar anode supported cell mentioned in chapter 5. This less-positive effect on cell performance and the negative influence on the OCV of the cell could be as a consequence of wavy structure since the gas flow was perpendicular to the cathode layer. Therefore, the removal of the product gases H₂O and CO₂ due to the chemical reaction of methane with oxygen gases on cathode side may be limited due to the bell type structure, and consequently the reaction zones for oxygen gas reduction might have been blocked by these product gases. Thus the amount of oxygen gas might have decreased because of these undesired product gases on cathode side, and thereby resulting in an OCV reduction. Though increased reforming had positive effect on cell’s power density, the OCV reduction cancelled some of this improvement. Hence, a flow-through gas flow in the chamber could be a useful approach to obtain better OCV and cell performance in such a wavy cell structure by removing the external limitation on gas flow to and from the cell.

Moreover, the maximum OCV and power density were measured to be 0.25 V and 10.20 mW cm⁻² at a gas mixture of 60-60-200 ml min⁻¹ CH₄-O₂-N₂, R: 1, as cell 2. In addition, decreasing oxygen amount at fixed methane gases had negative effects on both OCV and power density while increased total gas flow rate at the same fuel/oxygen ratios by basically increasing the quantity of methane and oxygen gases resulted in a better cell’s OCV and power density as observed from cell 1 and cell 2. Furthermore, in comparison with planar SC-SOFC which has the same thickness and the thickness ratio, the OCV and power density of the wavy cell (cell 6) is significantly lower (the OCV and power density of the planar
anode supported cell were found to be 0.71 V and 30.69 mW cm$^{-2}$, respectively, at a gas mixture of 40-40-200 ml min$^{-1}$, R: 1) (see chapter 5, Table 11).

![Graph A) OCV Measurement and B) polarization results of cell 6, thickness: 800:20:40 µm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio, 200 ml/min fixed nitrogen gas used as diluting agent](image_url)

\textit{Figure 126} (A) OCV Measurement and (B) polarization results of cell 6, thickness: 800:20:40 µm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio, 200 ml/min fixed nitrogen gas used as diluting agent
Figure 127 (A) OCV Measurement and (B) polarization results of cell 6, thickness: 800:20:40 µm, A:E:C, at different flow rate and gas mixture, R, fuel to oxygen ratio, 100 ml/min fixed nitrogen gas used as diluting agent.
However, when the amount of nitrogen was reduced from 200 ml min\(^{-1}\) to 100 ml min\(^{-1}\), the OCV and the power density of cell 6 improved substantially at all fuel/gas ratios (R) and the maximum OCV and power density were measured to be 0.36 V and 23.45 mW cm\(^{-2}\), respectively at the same fuel/oxygen gas mixture (gas mixture 7, CH\(_4\)-O\(_2\), ml min\(^{-1}\) R: 1) where the maximum OCV and power density of cell 6 were found when 200 ml min\(^{-1}\) nitrogen gas was utilized (see Figure 126, Figure 127, Table 17 and Table 18). Furthermore, increasing the total gas mixture by increasing the amount of methane and oxygen gases even improved the cell performance further at all fuel/oxygen ratios, and the maximum OCV and power density of cell 6 were found to be 0.43 V and 29.70 mW cm\(^{-2}\) at gas mixture 10 (80-80-100 ml min\(^{-1}\) CH\(_4\)-O\(_2\)-N\(_2\), R: 1, see Figure 127 and Table 18). Although the OCV of cell 6 was still lower than that of the counterpart of the planar anode supported cell, the power density almost equalised. This could be as a result of increased amount of methane and oxygen ratio in total gas mixture. Therefore, more methane gas can be reformed on the anode side while more oxygen gas can be reduced on the cathode side. This result shows that finding an optimum amount of gas mixture and gas mixture ratio is vital to achieve a good cell performance, and reintroduces the factor that excessive diluent gas such as N\(_2\) impedes rather than improves performance, by introducing significant mass transport/diffusion penalties and cutting off the access of the reactant gases to the reaction sites on the cell, and that this effect was more pronounced on the wavy cells’ performance.
Table 17 The maximum OCV and power density results of cell 1, cell 2 and cell 6 at different gas mixtures, 200 ml/min fixed nitrogen gas used as diluting agent

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>Cell 1 thickness 400:40:40 µm A: E: C</th>
<th>Cell 2 thickness 400:20:40 µm A: E: C</th>
<th>Cell 6 thickness 800:20:40 µm A: E: C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OCV (V)</td>
<td>Power density (mW cm⁻²)</td>
<td>OCV (V)</td>
</tr>
<tr>
<td>Fixed CH₄(40ml/min) And Fixed N₂ (200 ml/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas mixture 1 (R:1)</td>
<td>0.35</td>
<td>6.33</td>
<td>0.23</td>
</tr>
<tr>
<td>gas mixture 2 (R:1.2)</td>
<td>0.42</td>
<td>12.7</td>
<td>0.17</td>
</tr>
<tr>
<td>gas mixture 3 (R:1.8)</td>
<td>0.35</td>
<td>6.54</td>
<td>0.12</td>
</tr>
<tr>
<td>Fixed CH₄(50ml/min) And Fixed N₂ (200 ml/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas mixture 4 (R:1)</td>
<td>0.47</td>
<td>16.31</td>
<td>0.25</td>
</tr>
<tr>
<td>gas mixture 5 (R:1.2)</td>
<td>0.46</td>
<td>18.3</td>
<td>0.21</td>
</tr>
<tr>
<td>gas mixture 6 (R:1.8)</td>
<td>0.40</td>
<td>13.49</td>
<td>0.15</td>
</tr>
<tr>
<td>Fixed CH₄(60ml/min) And Fixed N₂ (200 ml/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas mixture 7 (R:1)</td>
<td>0.41</td>
<td>9.9</td>
<td>0.26</td>
</tr>
<tr>
<td>gas mixture 8 (R:1.2)</td>
<td>0.35</td>
<td>7.1</td>
<td>0.24</td>
</tr>
<tr>
<td>gas mixture 9 (R:1.8)</td>
<td>0.32</td>
<td>2.4</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Table 18: The maximum OCV and power density results of cell 6 at different gas mixtures, 100 ml/min fixed nitrogen gas used as diluting agent

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>OCV (V)</th>
<th>Power Density (mW cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fixed CH(_4) (40 ml/min)</strong> And <strong>Fixed N(_2) (100 ml/min)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas mixture 1 (R:1)</td>
<td>0.32</td>
<td>15.88</td>
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<td>gas mixture 2 (R:1.2)</td>
<td>0.22</td>
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<td>gas mixture 3 (R:1.8)</td>
<td>0.14</td>
<td>3.47</td>
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<td><strong>Fixed CH(_4) (50 ml/min)</strong> And <strong>Fixed N(_2) (100 ml/min)</strong></td>
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<td></td>
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<tr>
<td>gas mixture 4 (R:1)</td>
<td>0.35</td>
<td>18.60</td>
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<tr>
<td>gas mixture 5 (R:1.2)</td>
<td>0.27</td>
<td>12.45</td>
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<tr>
<td>gas mixture 6 (R:1.8)</td>
<td>0.16</td>
<td>5.78</td>
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<tr>
<td><strong>Fixed CH(_4) (60 ml/min)</strong> And <strong>Fixed N(_2) (100 ml/min)</strong></td>
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<tr>
<td>gas mixture 7 (R:1)</td>
<td>0.36</td>
<td>23.45</td>
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<tr>
<td>gas mixture 8 (R:1.2)</td>
<td>0.26</td>
<td>11.96</td>
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<tr>
<td>gas mixture 9 (R:1.8)</td>
<td>0.16</td>
<td>4.81</td>
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<tr>
<td><strong>Fixed CH(_4) (80 ml/min)</strong> And <strong>Fixed N(_2) (100 ml/min)</strong></td>
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<td></td>
</tr>
<tr>
<td>gas mixture 10 (R:1)</td>
<td>0.43</td>
<td>29.70</td>
</tr>
<tr>
<td>gas mixture 11 (R:1.2)</td>
<td>0.36</td>
<td>18.34</td>
</tr>
<tr>
<td>gas mixture 12 (R:1.8)</td>
<td>0.23</td>
<td>9.84</td>
</tr>
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</table>

To conclude, the wavy structure brought about less performance in comparison to its counterpart anode supported planar SC-SOFCs. In addition, the generally low performance of the wavy cells compared to some SC-SOFCs in the literature could be as consequence of common problems mentioned in chapter 5 and chapter 6 such as electrolyte porosity, impurities in anode and cathode layers as shown in the EDS results of cell 6, reactivity of LSCF cathode towards methane reforming, CGO electrolyte reduction at 600°C, which leads electron conductivity between anode and cathode, and so forth.

### 8.4 SUMMARY

Anode supported wavy SC-SOFCs were fabricated via single step co-sintering technique with a novel fabrication method. The results shows that directing curvature
formation occurring during sintering due to the CTE mismatches by the help of alumina rods can give a wavy type cell structure without any cracks and delaminating. Thereafter, they were characterized by using SEM, EDS and XRD techniques so as to examine the microstructure of the wavy cell. In addition, it also demonstrates that curves’ shape such as its peak point and wavelength is highly dependent on the diameters of alumina rods and the mass of the alumina rod placed on the top of the cells. The results show that they had similar microstructures with their respective counterparts of anode supported planar SC-SOFCs, although there were some differences in terms of their percentage. For instance, cathode had a coarse structure and electrolyte was porous. In addition, there were impurities in both electrodes.

The purpose of making wavy cell was to assume to improve the SC-SOFC’s performance by utilizing the its unique structure. However, the results show that using wavy anode supported SC-SOFCs not only caused a reduction in cell performance but also lowered cell strength at the peak sections. The maximum OCV and power density were obtained as being 0.43 V and 29.70 mW cm$^{-2}$ respectively, at a gas mixture of 80-80-100 ml min$^{-1}$, CH$_4$-O$_2$-N$_2$. 
In this study, the anode, electrolyte and cathode supported planar SC-SOFCs and anode supported wavy SC-SOFCs were investigated and manufactured successfully via a single step co-sintering method, where the tape casted anode, cathode and electrolyte green layers were layered upon each other, hot pressed and co-sintered. Moreover, in order to find optimum sintering profile, the TGA, DSC and in-situ shrinkage measurement of layers were examined. Furthermore, the characterisation methods such as SEM, EDS and XRD were later applied to analyse microstructure of the cells and impurities in the cells after sintering. In addition, the residual stress between cathode and electrolyte of anode supported planar cells were measured by applying to the fluorescence spectra technique and a mathematical modelling. Thereafter, sintered cells were tested and the performance of these cells was compared with each other. It is aimed to find a suitable cell structure that can be manufactured via a single step co-sintering, along with high performance. The purpose of single step co-sintering is to decrease fabrication stages of cells, and thereby a decrease in production time, energy consumption and fabrication cost. Additionally, wavy shape of SC-SOFC might help to improve further the performance of SC-SOFC by attempting to increase TPBs.

9.1 CONCLUSIONS

The conclusions garnered from this study are numerous, and expressed as follows:

- The simultaneous TGA-DSC measurements NiO-CGO anode, CGO electrolyte and LSCF-CGO cathode were conducted so as to examine the thermal behaviours of these layers, and these results were explained in details in chapter 4. These results show that:
  - Almost all additives were burnt out up to 400°C and the total weight loss was around 12.5% for the anode and the cathode layers while it was 11.4% for the electrolyte.
  - The cathode had further weight loss at temperature between 800°C and 900°C, making a total weight loss of 12.98%.
Overall process for each layers were endothermic although there was a weak exothermic process for the electrolyte. Besides, three different layers had almost same heating flow.

- In-situ monitoring by a long-focus microscope was applied to find the shrinkage and shrinkage rate of the electrolyte and electrodes as well as to observe their sintering behaviour by visual inspection, and the findings were also mentioned in the same chapter (chapter 4). According to experimental results:
  - The cathode has the higher shrinkage and shrinkage rate (13.25%, 0.029%/°C, respectively) at a temperature of 1200°C and the electrolyte possess the lowest (4.74%, 0.014%/°C, respectively).
  - The main shrinkage occurred at temperature above 900°C for all layers.
  - Cathode layer had the serious issues during debinding process when the heating rate was determined high (5% per minute) for instance, big bubble’s formation on the surface and thus resulting in crack during main densification stages.
- An optimum hot pressing condition was determined for this fabrication process and explained in chapter 4.
  - A temperature of 60°C, a pressure of 5 MPa and 5 minutes we found to be optimum condition for hot pressing so as to obtain a homogeneous cell.
  - The result indicated that sintering cell at 1200°C for 60 minutes with a heating rate of 1°C min⁻¹ up to 500°C for debinding, 2°C min⁻¹ up to 900°C and 1°C min⁻¹ up to 1200°C while the cooling rate is 3°C min⁻¹ could be optimum sintering profile for obtaining a cell via single step co-sintering.
- Single step sintering behaviour of an anode supported planar SC-SOFCs and its performance were introduced profoundly in chapter 5 along with the residual stress measurement between cathode and electrolyte layers. Our study indicates that:
  - Defining optimum thickness and thickness ratio of the cell with determined ideal hot pressing and sintering conditions led to better results of co-sintering, no delamination, cracks but some curvature at the edge of the cells.
  - The study also shows that using an alumina porous cover plate can suppress the curvature formation during sintering. Consequently, an anode supported planar SC-SOFCs, which possess a thickness of 800:20:40 µm and thickness
ratio of 40:1:2, A:E:C, respectively, was obtained successfully by the help of an alumina cover plate placed on the top of the cell.

- Sintered planar cell has a porous electrolyte (16.01%), coarse cathode structure and some impurities in electrodes (Si, Al etc) but no third phase formations.

- The maximum voltage and power density of the final cell were obtained as 0.71 V and 30.69 mW cm\(^{-2}\), respectively, at a fuel to oxygen ratio of 1 (40 mL min\(^{-1}\) of CH\(_4\), 40 mL min\(^{-1}\) of O\(_2\) and 200 mL min\(^{-1}\) N\(_2\), R:1).

- Moreover, total mean residual stress between cathode and electrolyte layers along x direction of a cell which had a thickness of 200:40:40 \(\mu\)m, A:E:C, was found to range from -1675.45 MPa to -1214.32 MPa. When the anode thickness increased 800 \(\mu\)m and electrolyte layer reduced to 20 \(\mu\)m (the final obtained planar curvature free cell, thickness: 800:20:40 \(\mu\)m, A:E:C, respectively) in order to mitigate the curvature formation, the total mean residual stresses along x direction decreased and they range from -488.688 MPa to -270.781 MPa.

- The mean residual stress because of CTE mismatch during cooling was found to be -200 MPa for the thinner cell (thickness: 400:40:40 \(\mu\)m, A:E:C, respectively) and -170 MPa for the thicker cell (thickness: 800:20:40 \(\mu\)m, A:E:C, respectively). As it is observed, the main residual stress contribution is from the stress developed during heating up for the thinner cell but it can sometimes arise from stress developed during cooling due to the CTE mismatch for the thicker cell.

- A cathode supported planar cell for single chamber condition was also successfully obtained via single step co-sintering using the similar techniques mentioned for anode supported planar SC-SOFC. The fabrication processes of this cell with its performance results were explained in detail in chapter 6. According to our study:
  - The optimum thickness and thickness ratio for achieving a planar cathode supported cell with the help of the cover plate were found to be 60:20:800 \(\mu\)m and 3:1:40 (A:E:C), respectively.
  - Three porous alumina cover plate with a 75 mm × 75 mm W×L and mass of 49.35 g were used to suppress curvature formation in order to obtain final curvature free cathode supported planar SC-SOFC. It can be seen that the total
mass of porous cover plate for the curvature suppression is much higher than that of cover plate used to suppress curvature evolution of the final anode supported planar cell (7.31 g).

- The cell has the similar micro structure with anode supported planar cell such as coarse cathode layer, porous electrolyte, no unwanted phase formation etc.

- The EDS result shows that the anode and cathode have some impurities in their structure either introduced from the outside during fabrication stages (Al, Si, and so forth) or from each other, for instance, Ni was found on the cathode side and Co was detected on the anode side.

- The porosity of final curvature free cathode supported cell was measured to be 12.43%, which is less than final anode supported planar SC-SOFC (16.01%).

- The maximum voltage and power density of the final cathode supported planar cell were found to be 0.2 V and 1.71 mW cm\(^{-2}\), respectively, at a gas mixture of 50 mL min\(^{-1}\) of CH\(_4\), 31 mL min\(^{-1}\) of O\(_2\) and 100 mL min\(^{-1}\) N\(_2\), R: 1.6, which are much less than that of the final anode supported planar cell (0.71 V and 30.69 mW cm\(^{-2}\), respectively).

- Much higher OCV and power density were obtained from a thinner cathode supported cell (cell 1, thickness: 60:40:400 µm, A:E:C), and they were found to be 0.56 V and 24.79 mW cm\(^{-2}\) at a gas mixture of 40 mL min\(^{-1}\) of CH\(_4\), 17 mL min\(^{-1}\) of O\(_2\) and 100 mL min\(^{-1}\) N\(_2\), R: 2.4 (still less than the OCV and power density of the final anode supported planar cell). However, this time, curvature formation and cell strength became an issue and thus obtaining a curvature free cathode supported planar cell become restricted.

- The fabrication of an electrolyte supported planar curvature free cell for single chamber condition via single step co-sintering and its performance results were comprehensively presented in chapter 7. Our study depicts that:

  - For the planar electrolyte supported cell, the mass of alumina cover plate required to suppress curvature formation was found to be 49.35 g as the cathode supported cell.

  - A thickness of 60:300:40 µm and thickness ratio of 3:15:2, A:E:C, were determined to be optimum in order to achieve a curvature free electrolyte supported cell with the help of alumina cover plate.

  - Likewise the anode and cathode supported cells, the electrolyte supported cell has coarse cathode structure and porous electrolyte.
The porosity of electrolyte was measured to be 18.48%.

The electrolyte supported cell possesses similar impurities in its electrodes as the cathode supported cell such as Al and Si on both electrodes, and La and Sr on anode electrode.

The maximum OCV and power density of the final electrolyte supported SC-SOFC at the highest cell performance were measured to be 0.55 V and 29.39 mW cm\(^{-2}\) at a gas mixture of 100 mL min\(^{-1}\) of CH\(_4\), 38 mL min\(^{-1}\) of O\(_2\) and 100 mL min\(^{-1}\) N\(_2\), R: 2.6, (less than that of final anode supported planar cell but higher than that of final cathode supported planar cell).

- A wavy anode supported cell was investigated in chapter 8 in terms of its fabrication method and its performance. The aim of making wavy structure cell is to improve the cell performance due to its unique shape. The study shows that:
  - Reasonable wavy anode supported cells can be fabricated successfully via previously suggested single step co-sintering technique.
  - The microstructure of the wavy cells possess similar microstructure with its counterpart planar cells such as porous electrolyte and course cathode structure, however, they differs from each other in terms of mean particle and pores sizes or pore percentage.
  - The maximum OCV and power density were obtained as being 0.47 V and 16.31 mW cm\(^{-2}\) at a gas mixture of 50 mL min\(^{-1}\) of CH\(_4\), 50 mL min\(^{-1}\) of O\(_2\) and 100 mL min\(^{-1}\) N\(_2\), R: 1 from an anode supported wavy cell possessing a thickness of 400:40:40 µm, A:E:C. These results are less than that of its counterpart anode supported planar cell which has the same thickness and thickness ratio (OCV: 0.69 V and power density: 27.12 mW cm\(^{-2}\)).
  - For the final anode supported wavy cell, which has a thickness of 800:20:40 µm and thickness ratio of 40:1:2, A:E:C, the performance result is even worse in comparison to its counterpart anode supported planar cell. The maximum OCV and power density of the final wavy cell were found to be 0.25 V and 10.20 mW cm\(^{-2}\), respectively at a gas mixture of 60 mL min\(^{-1}\) of CH\(_4\), 60 mL min\(^{-1}\) of O\(_2\) and 200 mL min\(^{-1}\) N\(_2\), R: 1.
  - When the amount of diluted nitrogen gas was reduced from 200 mL min\(^{-1}\) to 100 mL min\(^{-1}\), the performance of the wavy cell was improved and the OCV and power density of the final wavy cell reached from 0.25 V to 0.43 V and
from 10.20 mW cm\(^{-2}\) to 29.70 mW cm\(^{-2}\) at the same amount of methane and oxygen gases (still less than its counterpart planar cell).

➢ To conclude, the wavy structure cell led to the lower performance results in comparison to its counterpart planar anode supported cell.

9.1 FUTURE WORKS

A single step co-sintering technique was successfully applied to obtain a curvature free anode, cathode and electrolyte supported planar cells as well as an anode supported wavy cell for single chamber condition using NiO-CGO anode, CGO electrolyte and LSCF-CGO cathode. However, the study shows that all type of cells possess a porous electrolyte and coarse cathode structure when they were sintered at 1200°C. Though these imperfections are tolerated in SC-SOFCs, they still cause severe performance degradation. In addition, when a cell with CGO electrolyte is tested at 600°C, the Ce\(^{4+}\) is reduced to Ce\(^{3+}\) and thus ceria electrolyte based cells become conductive. This causes the cell to short circuit and thereby lowers performance results.

Therefore, the next step of this study will be to focus on:

• Fabrication of the similar cells with dense CGO electrolyte and reasonable LSCF-CGO composite cathode microstructure utilizing the same single step co-sintering technique.

• Achieving or obtaining favourite cathode microstructure, the sintering temperature of the cells will be reduced further to 1100 °C. However, decreasing sintering temperature will cause the electrolyte become more porous. Therefore, CGO electrolyte sintering temperature (over 1400°C) will be lowered close to the cathode sintering temperature either by adding some sintering aids such as CoO [245] and LiO [246] or reducing electrolyte particle size.

• The cells will be tested with different hydrocarbon-based fuels possessing lower reforming temperature, for instance propane, butane etc. in order to avoid ceria reduction problem. This will allow one to test the cells at a temperature lower than 600°C.

• The cell will not only be tested under single chamber conditions but also that of dual chamber conditions when the cells are made successfully with a dense electrolyte, and their performance results will be compared with this study as well as with each other.
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Figure S1 Heating profile during sintering of 9 anode supported cells hot pressed in different experimental conditions
Table S1 Hot pressing results for 9 anode supported cells, thickness ratio: 10:2:2 (A:E:C), thickness: 200:40:400 µm, at different pressure and temperature

<table>
<thead>
<tr>
<th>Cells</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Time (minutes)</th>
<th>After Hot Pressing (cell 50 mm x 50mm)</th>
<th>After Sintering (cell 40 mm x 40mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 1</td>
<td>1</td>
<td>50</td>
<td>5</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 2</td>
<td>2</td>
<td>50</td>
<td>5</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 3</td>
<td>3</td>
<td>50</td>
<td>5</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 4</td>
<td>1</td>
<td>60</td>
<td>5</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 5</td>
<td>2</td>
<td>60</td>
<td>5</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 6</td>
<td>3</td>
<td>60</td>
<td>5</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 7</td>
<td>1</td>
<td>70</td>
<td>5</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 8</td>
<td>2</td>
<td>70</td>
<td>5</td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
</tr>
<tr>
<td>Cell 9</td>
<td>3</td>
<td>70</td>
<td>5</td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Figure S2 (A) dimensional changes in anode-supported planar SC-SOFC after hot pressing on W and L directions, and (B) on T and D directions.
Figure S3 (A) the value of W and L, and (B) T and D of the cell after sintering
Figure S4 Four different anode supported cell for the same cathode and electrolyte thickness with their curvature height after sintering. Hot pressing and sintering conditions are the same with the cells mentioned in Chapter 5.
Figure S5 Fluorescence spectra R1 shift of Cell 4, Cell 5 and Cell 6
Cell 7 (ASC, thickness ratio: 40:1:2 (A:E:C), thickness: 800:20:40 µm)

Cell 11 (ASC, thickness ratio: 40:1:2 (A:E:C), thickness: 800:20:40 µm), sintered with a porous alumina cover plate

*Figure S6 Fluorescence spectra R1 shift of cell 7 and cell 11*
A) EDS Maps of cell 8

B) Map Sum Spectrum cell 8

Figure S7(A) EDS Maps of cell 8, and (B) Map Sum Spectrum of cell when the EDS of cathode and anode were taken together, the cell possess a thickness of 60:20:800 µm, A:E:C, sintered with three 75 mm x 75 mm alumina porous cover plate.
**Cell 1 40 mm x 40 mm WxL, thickness ratio: 3:10:2 (A:E:C), thickness: 60:200:40 µm**

A) From anode side  
B) From cathode side

**Cell 2 40 mm x 40 mm WxL, thickness ratio: 3:15:2 (A:E:C), thickness: 60:300:40 µm**

**Cell 6 40 mm x 40 mm WxL, thickness ratio: 3:15:2 (A:E:C), thickness: 60:300:40 µm, sintered with three 75 mm x 75 mm LxW porous alumina cover plate on the top of the cell**

Figure S8 Backscatter electron (BSE) SEM image of polished Cell 1, Cell 2 and Cell 6: (A) from anode side and (B) from cathode side