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Processing and Characterisation of Nanostructured Zirconia for application in Solid Oxide Fuel Cells

By

Min Nah Tong

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctorate of Philosophy

Loughborough University
October 2011

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Abstract

The fabrication and sintering of yttria-stabilised zirconia with varying yttria concentrations was carried out based on both wet and dry processing routes, utilising conventional single step and two-step sintering techniques. Results show that homogeneous, defect-free, high green density microstructures are essential in producing fully dense sintered samples of a desired grain size. Characterisation on morphology using HRTEM suggests that although there were no indications of impurities or secondary phases in the studies samples, there were signs of yttria segregation present in 3 mol.% YSZ, sintered at 1600°C. This was explained to be due to the increased amount of cubic phase with increased sintering temperature. High yttria ion concentration regions that form within grains undergo phase transformation from tetragonal to cubic, allowing the cubic phase regions to be partitioned. However, the transformation was not detectable based on the techniques used in this study.

The activation energies obtained from AC impedance spectroscopy demonstrated reduced activation energy at higher temperature. This suggests the presence of two different oxygen diffusion mechanisms within the material. These results are backed up by DC 4-probe ionic conductivity measurements. Reduced activation energy reported in nanostructured YSZ was reported to be due to large oxygen-ion vacancies. This phenomenon was also reported at lower yttria concentrations, due to the oxygen vacancies experiencing a binding energy to the dopant atoms caused by a combination of an electrostatic attraction and repulsive lattice relaxation energy.

Overall, the conductivity results based on AC impedance and DC 4-probe showed that the finer grain structured 3 mol.% YSZ at ~100 nm exhibited slightly enhanced conductivity. On the other hand, 8 mol.% YSZ displayed a clear increase in conductivity with increasing grain size based on an intrinsic grain boundary blocking effect. High temperature thermal aging carried out on 3 mol.% YSZ at ~100 nm and ~500 nm was believed to have caused polarisation loss, a time dependent phenomenon.
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Min Nah Tong

Loughborough, United Kingdom

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Chapter 1
Introduction

The solid oxide fuel cell is widely defined as a high temperature electrochemical conversion device that directly converts fuel and oxidant into electrical energy without combustion. Compared to conventional power generation systems, with efficiencies of 30-50%, the electrical efficiency of the solid oxide fuel cell is about 50-60%; in combined heat and power applications, the efficiency can reach up to 90%. At the University of Gottingen, Germany, Walther Nernst and colleagues were the first to propose the solid oxide fuel cell at the end of the 19th century [1]. Work was undertaken using a solid electrolyte made from a ceramic material such as yttria-stabilised zirconia. The solid oxide electrolyte acts as a conductor of oxygen ions at a high temperature between 600°C – 1000°C. Oxygen atoms are reduced at the porous cathode surface by electrons forming oxide ions, which are then transported through the solid oxide electrolyte to the porous anode layer, where the oxide ions react with the fuel, typically hydrogen. However, it was not until the late 1950s when research in this area accelerated. Following the work of researchers at Westinghouse in 1962, attention increasingly focused on fuel cells using zirconium oxide and calcium oxide electrolytes[2]. A typical solid oxide fuel cell system consists mainly of fuel cell stacks, which are made up of individual unit cells. Each unit cell consists of an anode, a solid oxide electrolyte and a cathode.

"A complete conversion to renewable energy by 2050 is possible from a technical and ecological point of view” – Jochen Flasbarth, President of the Federal Environment Agency [3]. In recent years, with the increase in energy prices and advances in materials, the demand for energy generation has increased drastically. In particular, fuel cell technology is considered as one of the most promising and novel approaches towards greener, cleaner and quieter energy generation [4]. Solid oxide fuel cells in particular have gained in popularity due to their high electrical efficiency, low emission of environmentally polluting gases, such as carbon dioxide, nitrogen oxides and sulphur oxides, and their flexibility to use different fuels. The
best applications of this technology utilise both electricity and heat, since both are desirable and useful products of the solid oxide fuel cell operation. For example, a residential solid oxide fuel cell system generates electricity and the heat can be used to produce hot water. Whilst auxiliary power supplies on vehicles can use the heat to keep the occupants warm. Installing solid oxide fuel cell systems in residential applications can significantly reduce carbon dioxide emissions by 50% [4,5].

In the 1980s, there was an expectation that solid oxide fuel cells would compete commercially with other power generation systems, which includes both large centralised power stations and smaller cogeneration units [4]. Over the years, significant advances have been made into this technology with large injections of government funding for solid oxide fuel cell development in the USA, Japan and Europe [6]. Although, a leading company in the development of the technology has successfully operated a 100 kW cogeneration solid oxide fuel cell in the Netherlands. 250 kW and 1 MW systems are being developed [7]. It still remains a challenge to fully commercialise the technology. This has been mainly due to significant cost, power density, reliability, and durability improvements needing to be made [5]. Despite the solid oxide fuel cell advantages of efficiency, modularity and low emissions, they cannot compete with conventional power plants, which can produce electricity for less than US$50 per kWe (Kilowatt electrical). However, electricity produced by SOFCs can cost up to US$10,000 per kWe [8,9].

Yttria-stabilised zirconia remains the most widely used electrolyte for solid oxide fuel cells due to its unique combination of properties in terms of its high chemical and thermal stability, excellent mechanical properties, ease of processing and high ionic conductivity over a wide range of conditions. On the other hand, a major restriction on the application and development of solid oxide fuel cells remains their relatively high operating temperature, about 1000°C, which is necessary to achieve the required ionic conductivity [4,5]. Operating at such a high temperature has led to structural problems, such as electrode sintering, interfacial diffusion between electrolyte and electrodes and thermal expansion mismatch between components. In
addition, there is a need to reduce the electrolyte thickness to reduce ohmic losses during cell operation [5]. These demands explain the motivation to explore the use of nanostructured ceramics in this research.

According to the Oxford English Dictionary, the term ‘nano’ is defined as ‘a factor of one thousand millionth particles’, or ‘extremely small, microscopic particle’. It refers to particles having dimensions on the nanometre (nm) scale (i.e. $10^{-9}$ m).

Nano-technology is often referred to as a general-purpose technology. Once developed, it will play a significant role, with significant impact on many industries and areas of society. It offers the possibility for better-built, longer-lasting, cleaner, safer, and smarter products for the home, communications, medicine, transportation, agriculture, and manufacturing [10].

Nanostructured ceramics are known to require lower sintering temperatures than larger grained ceramics, since nanostructured ceramics possess much larger surface areas, giving increased surface energy, and the main driving force for sintering lies in the surface energy reduction. The greater surface energy provides a larger driving force that allows sintering to occur at lower temperatures [11,12]. This would enable co-sintering with metal components in fuel cell applications and thus reduce both the cost of fabrication and operation [5]. In addition, nanocrystalline ceramics are reported to possess enhanced mechanical properties such as strength, toughness and hardness compared to a microstructured ceramic due to the defect size and crack deflection from grain boundaries [13-15]. It may be possible to produce thinner electrolytes, reducing the ohmic resistance, which will increase the reaction rate such that cell efficiency may be increased whilst reducing the operating temperature. Their magnetic, electronic and optical properties are also highly influenced by grain size [16,17]. These improved properties are assumed to be the effect of increased grain boundaries within the structure compared to conventional microstructured ceramics [18].
The processing of nanostructured ceramics is a great challenge. It is critical to maintain the nanocrystalline structure during and after the sintering process in order to achieve the desired advantages. Hence, the processing route selected and use of sintering conditions are critical. This includes the need to prevent agglomeration, the ability to form homogeneous, dense green nanostructures, and the use of densification techniques that will restrict grain growth. The Nanoceramics Group in the Department of Materials, Loughborough University has developed methods for producing fully dense yttria-stabilised zirconia with grain sizes less than 100 nm via both wet and dry forming routes with a well studied sintering profile [19,20].

The main focus of the present work lies in an investigation into the processing, effect of yttria concentration, (mainly 3 mol.%, 5 mol.% and 8 mol.%) and the influence of grain size on the ionic conductivity of electrolyte material for solid oxide fuel cell applications. Another objective is to establish the effect of sintering conditions on the conductivity and on the nature of the grain boundaries, to ascertain the presence and effect of impurities. The primary objectives are to incorporate nanostructured ceramics in solid oxide fuel cells to reduce operating temperatures whilst improving the mechanical properties, thus enabling the possibility of reducing the electrolyte thickness without compromising the ionic conductivity.
The technology of solid oxide fuel cells (SOFCs) is of major academic and industrial importance, there is a wide range of published literature on subjects ranging from the selection of materials, and fabrication processes to the characterisation techniques of electrolyte materials; which include the potential use of nano-ceramics. The basis of SOFCs; the challenges involved in processing of nanostructured zirconium oxide (ZrO$_2$) stabilised with yttrium oxide (Y$_2$O$_3$), also known as yttria stabilised zirconia (YSZ), and the fundamental properties, viz. mechanical, morphological and electrical, are all reviewed.

2.1 Solid Oxide Fuel Cells (SOFCs)

Solid oxide fuel cells are a solid state electrochemical conversion device that utilise an oxide ion-conducting ceramic material as the electrolyte. The SOFC device allows the direct conversion of chemical to electrical energy through an electrochemical reaction. There has been increased interest in developing SOFCs over the past decades, mainly due to their high-energy conversion efficiency, low pollution emission and high flexibility towards using different fuels.

SOFC technology has come a long way in terms of being used as a practical power generation device since the initial proposal to use zirconia oxide stabilised with yttrium oxide (YSZ) as an electrolyte material. This was proposed by Walther Nernst and his colleagues in Gottingen, Germany at the end of the 1890s. The first patent on a “solid electrolyte fuel cell” was issued to scientists at Westinghouse Electric Corporation in 1962. This was based on the Westinghouse’s cathode-supported tubular SOFCs, which were successfully produced and tested as 5-250 kW power systems during the 1980s [4].
Over the last few years, progress has been made towards achieving materials with desirable characteristics and the present aims of SOFC development are to improve efficiency, enhance long-term stability and reduce the fabrication costs [4,5]. The key to achieving this is to reduce the operating temperature and enhance power density. However, as disadvantages, reducing the operating temperature decreases the thermally activated transport processes, which leads to an increase in ohmic and electrode polarization losses [4,5]. Hence, developing more efficient electrolyte and catalytically effective electrodes are desirable approaches.

2.1.1 Applications

Solid oxide fuel cells offer a wide range of applications, sub-divided mainly into three categories, classified as:

- Central power stations (50 kW – 10 MW) for utility, industrial, commercial and residential use.
- Transportation (auxiliary or drive power units) in intermediate size systems for air, sea and land transportation.
- Portable devices for electronics, military and portable generators.

![Figure 2.02 – A 50 kW atmospheric unit (left) and pressurised 125 kW unit (right)](image)

In a high temperature operating SOFC, the generated electricity and the by-product; heat, can be used in applications ranging from residential combined heat and power (CHP) to auxiliary power supplies for vehicles and stationary central power generators that requires heat for gasification. A residential SOFC system could use the generated heat to produce hot water for a community, which can be achieved with simple heat exchangers whilst in a vehicle, the heat could be used to keep the occupants warm or for luxuries, such as hot drinks.

### 2.1.2 Unit cell components

SOFC systems consist mainly of fuel cell stacks, which are made up of individual unit cells. Each of the latter comprises of two electrodes, the cathode and anode, separated by an electrolyte where the electrochemical reaction takes place. The electrolyte carries electrically charged particles from one electrode to the other, as the catalyst accelerates the reaction at the electrode. The electrodes and electrolyte are then held together by interconnects and sealing materials. These individual fuel cells are stacked in parallel and series to achieve the required energy output [4].
The solid ceramic electrolyte, usually zirconium oxide stabilised with yttrium oxide (YSZ) due to its excellent properties discussed in section 2.2, acts as a conductor of oxygen ions at operating temperatures ranging from 800°C to 1000°C. The electrolyte allows oxygen atoms to be reduced on the porous cathode surface by electrons and converted into oxygen ions, which are then transported through the electrolyte layer to the porous anode surface where the oxide ions react with hydrogen, producing electrons to an external circuit [4].

The key requirement for the solid oxide electrolyte is to possess sufficiently high ionic conductivity, typically greater than $10^{-2}$ S cm$^{-1}$, with low electronic conductivity at the cell operating temperature. Figure 2.04 shows that this is achieved at 700°C for the electrolyte $(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$. In order to minimise ionic resistance, a thinner electrolyte layer, of higher quality and with a more uniform stress distribution, is required to reduce ohmic resistance and increase the reaction rate in the electrodes, which increases cell efficiency. The electrolyte material must also be chemically and physically compatible with other fuel cell components and remain stable in both oxidising and reducing atmospheres during operation. In addition, it needs to be easy to manufacture economically [4,5].
The anode of the SOFC refers to the electrode where oxidation takes place. The most common material is a nickel-YSZ cermet, a mixture of metal and ceramic. The nickel provides electrical conductivity and catalyses the reaction whilst the YSZ provides ionic conductivity, a thermal expansion compatibility with the electrolyte, as well as mechanical strength. The anode has a high porosity (20-40%) so that the mass transport of reactant and product gases is not inhibited. There are ohmic polarisation losses at the interface between the anode and the electrolyte, which causes a large voltage drop at high current densities, where the anode electrolyte interface is starved of fuel or oxidant. This occurs when the gaseous species cannot diffuse through the porous interstices of electrodes fast enough. There is reported literature of bilayer anodes to reduce polarisation loss [5]. Bilayer anodes consist of two layers with different porosities, the bottom layer is more porous than top layer, which is in contact with the electrolyte. The porosity of the layers can be tailored using an immiscible metal oxide, which is removed during sintering. It has been suggested that for anode supported SOFCs, the mass transport of fuel gas, and water vapour through the anodes may hinder the anodic processes. The use of highly porous anodes may help to minimise the resistance to mass transfer. Fuel cells based on bilayer anodes of different porosities have shown promising electrochemical performance, opening up new areas for optimising SOFC efficiency [24].

Figure 2.04 – Specific conductivity versus reciprocal temperature for selected solid oxide electrolytes [5]
The cathode is where reduction takes place, i.e. the process where electrons are added to a species. Strontium-doped lanthanum manganite (LSM) is the most commonly used cathode material. Similar to the anode, the cathode is a porous structure that allows rapid mass transport of reactant and product gases. It is essential for cathode materials to exhibit mixed ionic and electronic conductivity. This is especially important for lower temperature operation, at around 650°C, since the polarisation of the cathode increases significantly as the SOFC temperature is lowered.

### 2.1.2 Electrochemical reactions

Fuel cell operation requires continuous supplies of fuel and oxidant. Since they operate at a finite rate, large reaction surfaces are required to maximise surface-to-volume ratio and for this reason fuel cells are usually made into thin, planar structures. The electrodes are highly porous to further increase the reaction surface area and to ensure efficient delivery of the reactants. One side of the planar structure is supplied with fuel (the anode), whilst the other side is provided with oxidant (the cathode). To keep the two individual half reactions of fuel and oxygen in isolation, the fuel cell membrane consists of a thin, gas impermeable electrolyte, capable of conducting oxygen ions [4].

Figure 2.05 – Schematic drawing of a solid oxide fuel cell [22]
Chapter 2 Literature review

The simplest scenario for operating a fuel cell is where pure hydrogen and oxygen are used as the fuel and oxidant, respectively. In the anode, the hydrogen fuel reacts with oxygen ions to form water and electrons, represented by [4]:

\[
\text{Anode: } 2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-
\]

Eqn. 2.01

The electrons travel from the negatively charged anode, through an external electrical circuit that connects the cathode, creating an electric current. Meanwhile, at the cathode – electrolyte interface, the electrons transfer their charge to the oxygen molecules to form oxygen ions, as given by [4]:

\[
\text{Cathode: } O_2 + 4e^- \rightarrow 2O^{2-}
\]

Eqn. 2.02

For a complete circuit, the oxygen ions diffuse through the electrolyte to the anode - electrolyte interface to combine with hydrogen ions to form molecules of water given by the overall electrochemical reaction [4]:

\[
2H_2 + O_2 \rightarrow 2H_2O
\]

Eqn. 2.03

2.1.3 Polarisation

When there is no current being drawn from the fuel cell, the cell voltage is at a maximum, termed the open circuit voltage (E), which increases with the partial pressures of the fuel and air gases and decreases with increasing temperature, according to the Nernst equation [4].

\[
E = E^o - \frac{RT}{nF} \ln\left(pH_2O/pH_2pO_2^{0.5}\right)
\]

Eqn. 2.04
Hence, it is important to maintain a high fuel cell voltage, even under high current loads, for successful operation of the fuel cell, Eqn. 2.05. However, it is difficult to maintain a high fuel cell voltage under current load. The voltage output of a real fuel cell is less than that of the thermodynamically predicted voltage output due to irreversible polarisation. These polarisations cause a decline in the efficiency of the reversible and real processes of the fuel cell. When the current density increases, the polarisations become greater [5].

Eqn. 2.05

\[ V = JR \]

Where;

- \( V \) = Voltage (V)
- \( J \) = Current density (mA cm\(^{-2}\))
- \( R \) = Area specific resistance (kΩ cm\(^{2}\))

Polarisation is a voltage loss or over potential, which is a function of the current density. It can be broken down into a number of various phenomena that occur when a finite current flows in a cell. The three dominant polarisations are [4]:

- Activation (due to electrochemical reaction)
- Ohmic (due to ionic and electronic conduction)
- Concentration (due to mass transport)

Activation polarisation occurs due to kinetics, which is caused by the delay of the reactions taking place on the surface of the electrodes. A proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons to or from the electrodes [5].

Ohmic polarisation occurs due to a voltage drop from the electrical resistance during transport of electrons through the electrode materials and the various interconnections. The ionic resistance from the flow of oxygen ions through the
electrolyte also contributes towards ohmic polarisation. The voltage drop is linearly proportional to current density, which is also known as ohmic losses, or resistive losses [5].

Figure 2.06 demonstrates that activation polarisation is usually dominant at low current densities, and concentration polarisation is dominant at high current densities, when the mass transport of reactants to the electrolyte – electrode interface becomes a limiting factor for the cell reaction.

![Figure 2.06 – Schematic plot of voltage versus current density on various polarisation effects [5]](image)

The real voltage output for a fuel cell can be written by starting with the thermodynamically predicted voltage output of the fuel cell and subtracting the voltage drops due to the various losses:

\[
V = E_{\text{thermo}} - \text{Activation loss} - \text{Ohmic loss} - \text{Concentration loss}
\]

Eqn. 2.06

Where; \( V \) = real output voltage

\( E_{\text{thermo}} \) = thermodynamically predicted fuel cell voltage output
The internal resistance of the cell could be reduced by the use of electrodes with higher conductivity, suitable design and uses of appropriate materials for bipolar plates or cell interconnects, and reduction in the thickness of the electrolyte layer whilst maintaining a certain level of physical robustness [5].

2.1.4 Advantages & disadvantages

It was over three decades ago when SOFCs were anticipated to compete commercially with conventional power generators, both large centralised power stations and smaller cogeneration units [4]. The driving force behind the use of solid oxide fuel cell technology is the desire for cleaner, greener energy production. The efficiency of power generation is around 33-38%, whilst power generation by high temperature fuel cells, if the by-product heat is utilised, may be as high as 70% or more. However, this has not yet happened; mainly due to the high costs involved in fabrication and other issues. This is despite the very significant Government support in terms of funding for SOFC development in the USA, Japan and Europe [4].

SOFCs possess numerous advantages over conventional power generation technologies. Since they produce electricity directly from a chemical reaction, SOFCs can offer more than 90% chemical-to-electrical conversion efficiencies. SOFCs are all solid state, which means that they have no moving parts and hence avoid mechanical wear and noisy operation. Furthermore, greenhouse gas emissions from conventional power generation technologies such as nitrogen oxide and sulphur oxide particulates are almost negligible from SOFC operation [5].

Other advantages include easy, independent scaling between power, determined by fuel cell size, and capacity, determined by fuel reservoir size, ranging from the 1 W cell phone to the 1 MW power plant. Fuel cells also display fuel flexibility, (hydrogen, methane and gases containing carbon monoxide) as well as cogeneration capabilities, even for small capacities and at part load operation [5]. However, it is only high temperature operating SOFCs, e.g. above 600°C, that offer significant fuel flexibility
and have the ability to reform natural gas directly within their cells. It is possible for high temperature SOFCs to operate using carbon monoxide containing gas or even on ammonia. Hence, high temperature fuel cells offer a higher fuel to power efficiency than the low temperature fuel cells. The electrical efficiency of SOFCs is about 50–60%, in combined heat and power applications, efficiencies can reach 70–90%. Comparing the operation of different power technologies, the efficiencies of gas turbines and diesel engines decrease at part load, whereas the efficiency of the fuel cell based systems will be almost independent of load [5].

Whilst fuel cells offer some intriguing advantages, cost remains a major barrier to large-scale fuel cell commercialisation. Fuel cells are still significantly more costly than conventional power generators that can produce energy for less than US$50 per kWe. Energy produced by fuel cells has been reported to cost around US$10,000 per kWe. Due to the prohibitive costs, fuel cell technology is currently only economically competitive in a few highly specialised applications; such as on board a space station. Power density is another significant limitation; it is the amount of power a fuel cell produces per unit volume or per unit mass. Although there have been dramatic improvements in power density over the years, further progress is required for fuel cells to become commonplace in portable and automotive applications [4].

On the other hand, operating SOFCs at high temperature, e.g. 800°C to 1000°C, may lead to various problems, such as tight restrictions on the choice of materials, electrode sintering, interfacial diffusion between electrode and electrolyte, mechanical stresses due to the mismatch of thermal expansion coefficient of cell components and performance degradation. These disadvantages can be overcome by reduction of the operating temperatures, e.g. 600°C to 800°C. However, as the operational temperature is reduced, it may result in a significant increase in the electrode and electrolyte resistivity, as well as increased polarisation loss and ohmic loss from the electrolyte. In order to counter this effect, thinner electrolyte layers with higher ionic conductivity need to be used [4].
Other limitations include fuel availability and storage. Fuel cells operate best on hydrogen gas, a fuel that is not widely available, that has a low volumetric energy density, and is difficult to store. Alternative fuels, such as gasoline, methanol and formic acid are difficult to use directly and usually require reforming [5].

2.2 Zirconia ceramics

Zirconia has the chemical composition ZrO$_2$, which is the oxide of zirconium, Zr. Zirconium is one of the most abundant materials in the earth’s crust, more common than copper or zinc. Large amounts can be found in Australia, Africa, Asia and America, usually in the form of zirconium silicate, zircon (ZrSiO$_4$). Refining of this raw material is essential in the application of fuel cell systems as SiO$_2$ impurities tend to block the ionic and electron paths during operation. A typical zirconia fuel cell electrolyte should contain less than 0.1 weight percent of silica. Other impurities, such as alumina (Al$_2$O$_3$), titania (TiO$_2$) and hafnia (HfO$_2$) which could be present at very low weight percent would not cause such a problem; especially hafnia since it is an ionic conductor itself.

Pure zirconia exhibits three well defined polymorphic crystal forms; a monoclinic phase at room temperature, which transforms into a reversible tetragonal phase above 1170°C and remains stable up to 2370°C. Above this temperature the cubic fluorite phase continues to be stable until the melting point at 2680°C. During cooling, phase transformation from tetragonal to monoclinic occurs by a diffusionless shear process, similar to that of the formation of martensite in steels. This transformation is associated with large volume increase, 3 to 5%, and causes extensive shear in the material, resulting in the complete collapse of the ceramic.
However, if the zirconia particles are small enough, about 30 nm, they exist in their metastable tetragonal polymorph [26]. The tetragonal phase can also be stabilised at room temperature with the addition of certain divalent or trivalent oxides, e.g. CaO, MgO, and Y$_2$O$_3$, restraining the volume change, whilst the tetragonal phase is at equilibrium down to room temperature. In general, partially-stabilised zirconia (PSZ) usually consists of cubic and tetragonal phases, with the latter converting into monoclinic. PSZ has remarkable advantages over fully-stabilised cubic zirconia (FSZ) with regards to mechanical properties. In contrast to this fact, the electrical properties of PSZ are rather poor in most cases, compared to those of FSZ. Both PSZ and FSZ will be discussed in more detail in section 2.2.1 below.

Stabilised zirconia possesses a large market, especially as refractory material, pigment coatings and glazes for pottery. Structural ceramic, technical grade zirconia has been developed in engineering applications, such as thermal barrier coatings on gas turbine components, hip, knee and dental implants, cutting tools, oxygen sensors, and fuel cell membranes etc. This is due to zirconia’s excellent properties, including exceptional mechanical strength at elevated temperature, low thermal
expansion compared to metals, good wear resistance, and chemical inertness [13,14].

Zirconia-based compositions are still the most popular SOFC electrolytes at present due to their good stability under both oxidising and reducing atmospheres, low electrical conductivity, and acceptable oxide ion conductivity above 800°C. However, the existing challenge in SOFC development lies in lower temperature operation, as discussed in section 2.1.5.

### 2.2.1 Yttria-stabilised zirconia (YSZ)

The zirconia rich portion of the zirconia-yttria phase diagram is shown in Figure 2.08. At concentrations of 8 mol.% yttria-stabilised zirconia and above a fully stabilised cubic fluorite structure is retained. 8YSZ has a good chemical stability over a wide range of temperatures and it possesses the best ionic conductivity amongst yttria doped ceramics. On the other hand, 8YSZ has poor mechanical properties, which hinder the production of self supported solid electrolytes for use in solid oxide fuel cells [23]. At concentrations of 3–7 mol.% yttria-stabilised zirconia, both the tetragonal and cubic phases, are in situ within the microstructure. Partially stabilised zirconia (PSZ) is formed, consisting of a cubic matrix containing dispersed tetragonal phase precipitates [27]. These tetragonal precipitates give PSZ improved mechanical properties over cubic 8YSZ via the process of transformation toughening [28]. However, due to fewer oxygen vacancies, PSZ has reduced ionic conductivity, compared to fully stabilised 8YSZ [29]. At lower concentrations, of 3 mol.% yttria-stabilised zirconia (3YSZ) and below, tetragonal zirconia polycrystals (TZP) are formed instead of a stabilised cubic structure. The structure consists of two phases, monoclinic and tetragonal. The transformation from tetragonal to monoclinic phase is strain induced, and enhances the mechanical properties of zirconia [28,30].
Oxygen ion conduction occurs based on the fluorite crystal structure of pure zirconia, which forms an anionic lattice consisting of Zr$^{4+}$ ions and O$^{2-}$ ions. With the addition of trivalent oxide; yttrium, Y$^{3+}$ ion exchange occurs and a number of oxide ion sites become vacant as three oxygen ions replace four oxygen ions, as shown in Figure 2.09.

Replacing one atom with another one of different valence is known as aliovalent doping. Each additional aliovalent dopant, Y$^{3+}$ is compensated by the electrical neutrality condition through an appropriate concentration of vacancies on the oxygen ion sublattice; $2[V_o^{-}] = [Y_{Zr}^+]$. 

Figure 2.08 – Phase diagram of ZrO$_2$-Y$_2$O$_3$ system [31]
Since there are more vacancies available as doping concentration increases, then more oxide ions can be transported per unit time, and thus the conductivity is expected to increase. However, there is an upper limit to the amount of doping at about 8 mol.% yttria, see Figure 2.10, beyond which conductivity begins to decrease rather than continue to increase. This is due to the excessive defect concentration of the electrostatic interaction between dopants and vacancies, which eventually impedes the oxide ion and oxide ion vacancy mobility.

Yttria-stabilised zirconia is one of the most widely used high performance ceramic materials. YSZ possesses high ionic conductivity, good thermal stability, and excellent mechanical properties, which are all necessary for high temperature electronic devices, such as, oxygen sensors and electrolyte material for SOFCs [33]. Whilst the ionic conductivity of zirconia increases with yttria concentration, the mechanical strength decreases due to the increase in number of oxygen ion vacancies in the lattice.
Although higher conductivities can be achieved with other systems, YSZ is currently the most common electrolyte material used in SOFCs due to its combined properties; adequate ionic conductivity, good strength and toughness, and ease of processing. In addition, it is stable physically and chemically in both oxidising and reducing environments.

![Figure 2.10](image)

Figure 2.10 – Effect of the concentration of $Y_2O_3$ on ionic conductivity [5]

### 2.3 Nanocrystalline ceramics

‘Nanotechnology’ defines any technology based in the nanometre scale. Hence nanostructured materials are those with an average grain size of less than 100 nm in at least one direction. These materials have been receiving much attention in recent decades and offer new fields of applications. They are used to enhance the properties of commercially available materials in different research fields, such as microtechnology, biotechnology, surface coatings for electronic devices, and also in the area of energy storage and conversion, for example, in the development of SOFCs. These advanced ceramics are also the active materials in underpinning most electronics devices, fuel cells, sensors and biomaterials, as well as magnets, wear and structural parts, cutting tools and substrates. They have “an especially high potential to resolve a wide number of today’s material challenges in process industries, power generation, aerospace, transportation and military applications. Such applications are vital in maintaining global competitiveness, decreasing energy consumption and minimising pollution [34].”
SOFC components produced from nano particles may be advantageous; nanocrystalline thin-film electrolytes in anode-supported cells (ASC) can substantially reduce ohmic losses in comparison to electrolyte-supported cells (ESC). This increases the reaction rate in the electrodes, enhancing cell efficiency. Nanocrystalline thin-film electrolytes potentially improved ionic conductivity due to the high density of interfaces at the nano scale, regarded to lower the grain boundary resistivity by space charge effects. Ionic transport along the grain boundaries is likely to be increased by the large number of displaced atoms and high mobility of oxygen ion vacancies. Further reduction of electrolyte thickness from 10 µm to 1 µm can increase the ionic conductivity of the electrolyte, especially for SOFCs operated in the intermediate temperature range.

Certain nanostructured ceramic compositions can also exhibit very high magneto resistance and super paramagnetic properties, as well as offering controlled band gaps in electronic materials and transparency for usually opaque materials since their grain size is smaller than the wavelength of light. There have also been indications that nanocrystalline ceramics can have extremely low thermal conductivity, whilst Vickers hardness tests suggested that nanocrystalline ceramics are usually softer than larger grained ceramics at room temperature, hence having a lower probability of cracking [19,35,36].

World sales of nano sized powders for these applications were predicted to rise from US$49.5M in the year 2000 to US$900M in 2005 [37]. US sales alone were recorded as US$42.7M in 2003 [38]. All reports predict that further growth will be very extensive. Whilst the total value of the end products is extremely difficult to estimate, the world market for components was greater than US$20B in 2000, with an annual growth rate of 7.2% [39]. Since nanotechnology is a ‘disruptive technology’, it could enhance almost the entirety of the existing global advanced ceramics market; the key barrier to market penetration historically being the inability to produce genuinely nanostructured ceramics via industrially viable manufacturing routes. However, work
in Loughborough appears now to have overcome this barrier, successfully being able to produce nanostructured ceramics with well controlled grain sizes.

The large increase of the interfacial area significantly affects the structural and functional properties of nanostructured materials [40-42]. This facilitates huge atomic interactions within the samples. The massive increase of the disordered regions like grain boundaries provides facile diffusional paths for transport phenomena. The increase of solid solubility in nanostructured materials is a direct effect of increased grain boundaries [43].

2.3.1 Nanocrystalline YSZ

A conventional YSZ based SOFC operates up to 1000°C, this high temperature brings about numerous disadvantages such as sintering of electrodes, diffusion between the cell components, mismatch of thermal expansion coefficients and performance degradation. These problems have adversely affected the commercialisation of SOFCs [36,44]. A new hypothesis is required for the next generation of materials for use in SOFCs in order to achieve high mobility for oxygen in novel structures. There is great interest in nanostructured ceramics and in oxygen mobility along interfaces in engineered and strained electrolyte hetero-structures [45]. Some remarkable claims have been made for these structures [46], which remain to be fully verified, but they are consistent in showing enhancements to the ionic conductivity of electrolyte materials.

Research activities involved with the fabrication of thin film electrolytes for SOFC applications focus on the reduction of the layer thickness, increasing ionic conductivity, minimisation of oxygen and fuel leak rate, and decreasing the electrolyte sintering temperature.
The strength of nanostructured 3 mol.% YSZ has been found to be similar to that of the submicron ceramic at about 1 GPa, shown in Table 2.01. However, the fracture mechanism is different; nanostructured ceramics fail by intergranular fracture mode, whilst transgranular fracture was reported in submicron ceramics [47].

<table>
<thead>
<tr>
<th>3 mol.% YSZ</th>
<th>Flexural strength / MPa</th>
<th>Flexural toughness / MPa m$^{1/2}$</th>
<th>Indentation toughness / MPa m$^{1/2}$</th>
<th>Hardness H$_V$ / GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano</td>
<td>922 ± 155</td>
<td>5.3</td>
<td>3.9</td>
<td>14.1</td>
</tr>
<tr>
<td>Submicron</td>
<td>1040 ± 257</td>
<td>5.2</td>
<td>4.6</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 2.01 – Mechanical values reported for nano and submicron 3 mol.% YSZ

Tuller reported the ability of nanostructured YSZ to display exceptional physical and mechanical properties as a result of the high fraction of atoms residing at grain boundaries and the increased surface area of the active sites for reactions [48].

Nanocrystalline ceramics have been reported to possess the attractive ability to exhibit superplasticity at relatively high strain rates in comparison to microcrystalline ceramics. The above was first reported by Wakai in fine grained tetragonal 3 mol.% yttria-stabilised zirconia (TZP) in 1986 [49]. Winnubst reported an increase in deformation strain rate by a factor of 4 from superplastic deformation by grain boundary sliding [50]. This simultaneously decreases the sintering temperature by 200°C, when compared with standard bulk YSZ [51]. A fine grain size is the key to achieve useful superplasticity, Winnubst reported that the deformation strain rate of nanocrystalline TZP increased by a factor of 4 when the grain size decreased from 200 nm to 100 nm [52]. Nanocrystalline materials also tend to exhibit much reduced ductility, due in part to a low work hardening rate leading to early strain localisation and failure. This is also due to the reduced ability of the materials to accommodate the propagation of cracks by extensive plastic deformation. A ductility study of nanocrystalline zirconia ceramics at low temperature showed that the maximum
elongation of about 60% could be achieved with 10 wt.% addition of yttria and 12 wt.% addition of alumina to form a composite ceramic, sintered at 1250°C [53].

Nanocrystalline YSZ exhibits an increase in electrical conductivity of about 2 to 3 orders of magnitude compared to microcrystalline YSZ [54], whilst Mondal, reported that specific grain boundary conductivity in nanocrystalline YSZ can be enhanced by 1 to 2 orders of magnitude, compared with microcrystalline samples [42]. Nanostructured 8 mol.% YSZ has been reported to have a lower thermal conductivity than the equivalent microstructured ceramic, making it an optional material for thermal barrier coatings [55]. In addition, nanostructured materials may be useful for enhancing the gas tightness of electrolytes for SOFCs [42,56]. Attempts have been made to lower the sintering temperature [57,58], minimise component shrinkage [57-59], and achieve highly sinter-reactive ceramics [60].

Although YSZ is known to be the toughest of all of the advanced ceramic materials, it suffers from one major disadvantage, namely hydrothermal aging, which is catastrophic degradation by moisture, particularly at elevated temperatures. Research by Paul has demonstrated conclusively that nano YSZ can withstand over 3 weeks at about 250°C in steam at 4 bar pressure with no indications of any structural change whilst conventional micro YSZ completely disintegrates in less than 1 hour under the same conditions [18]. Paul demonstrated that nano YSZ can withstand the conditions required for SOFC operation [18]. Nanostructured zirconia demonstrates size-dependent phase stability; research has shown the tetragonal phase to be more stable in nanostructured zirconia.

Nanocrystalline ceramics have lower sintering temperatures, providing fresh opportunities for co-sintering of thin film structures, which should also aid in lowering the production cost [19,35]. Besides the anticipated improvements in properties, the main driving force for using nanostructured ceramics is their lower sintering temperatures. Yoo demonstrated that nanocrystalline tantalum powder with an average particle size of 63 nm, can be rapidly consolidated to high density by plasma pressure compaction at a temperature of 250°C lower than that of coarse
tantalum powder, with an average particle size of 15 μm. This is due to the large intrinsic driving force associated with fine particles [61]. Boulc’h successfully prepared nanostructured tetragonal zirconia ceramics with a particle size of 300 nm containing average primary crystallite size of 70 nm after sintering at 1500°C for 2 hours [62]. Moskovits was able to sinter bimodally distributed 4 mol.% YSZ (10 nm to 430 nm) at a lower temperature of 1200°C due to the enhanced densification rates of nano powders [57]. Work within the Ceramics Group at Loughborough University, UK, has successfully produced nanostructured fully dense YSZ components using a two-step sintering profile [18-20,63].

Zych et al. compared the sintering curves of commercially available submicron zirconia powder (Tosoh Co.) and hydrothermally synthesised nano zirconia powder compacts with the same initial green density [64]. The nanostructured zirconia compacts sintered to about 99% theoretical density whilst the submicron zirconia compacts only achieved about 60% of theoretical density under the same sintering conditions at 1200°C. The sintering curve, Figure 2.11 demonstrates that shrinkage initiates at about 200°C in the nanostructured zirconia compacts whilst it was above 1000°C in the submicron zirconia compacts. At 1200°C, for the submicron zirconia, shrinkage has just initiated, whilst shrinkage has already terminated for the nanostructured zirconia compact. The latter obtained about 99% theoretical density, with an average grain size of less than 150 nm.

![Figure 2.11 – Linear shrinkage of nano and submicron samples during non-isothermal sintering [64]](image-url)
Meyers observed that lower amounts of stabilisers are required for nanostructured zirconia in comparison to submicron zirconia, to achieve equivalent stabilisation [65]. This could result in a differential of properties between nanostructured and submicron ceramics. Based on Garvie, pure zirconia can be stabilised at room temperature in the tetragonal phase without additives, if the grain size is below a critical limit, a value of 30 nm is suggested [26]. It was experimentally demonstrated that the specific surface area of nanocrystalline zirconia is very significantly enhanced below 30 nm, such that the nanocrystallites possess excess energy compared to a single, large crystal. Based on these observations it was proposed that the stabilisation of the metastable tetragonal phase below 30 nm, at room temperature, is due to both enhanced specific surface area and excess energy below this critical size. In a separate report similar to that of Garvie, Shukla concluded that in the case of nanostructured zirconia, the tetragonal phase can be stabilised at room temperature in an isolated, single, strain free nano particle below a critical size of 10 nm [66]. This critical size increases to 33 nm in the case of agglomerated nanostructured powders.

2.3.2 Challenges in processing nano YSZ

Whilst nanostructured ceramics have attracted great interest, processing them involves a number of challenges, in particular the control of agglomeration during fabrication to produce homogeneous, high green density bodies prior to sintering. It is necessary to maximise densification whilst minimising grain growth during the sintering process to obtain a well controlled grain size [19]. Generally, nano particles exhibit a greater tendency to interact due to their high surface areas, leading to the formation of agglomerates. The presence of agglomerates restricts flowability, uniform packing and control of grain size during sintering [11,67].

Agglomeration is a common problem that exists in both wet and dry forming of ceramics. In colloidal nanosuspensions, the surface energy of the individual particles increases as the particle size decreases. Particles start to agglomerate when the magnitude of the zeta potential becomes low. This is due to the high Van der Waals
forces between the individual particles and at zero zeta potential, which is also known as the isoelectric point, particles are highly agglomerated. New repulsion forces are required to keep the particles apart in order to form a well dispersed, homogeneous suspension. This requires a suitable surfactant or dispersant in the suspension to achieve higher zeta potential, away from the isoelectric point. Further discussion on dispersion mechanisms in colloidal suspensions can be found in section 2.4.2.1.

The high surface energy in nano sized powders gives the particles a higher tendency to form agglomerates [68]. This poses flowability problems during die pressing. Furthermore, if these agglomerates are not broken down during green forming, it will not be possible to achieve a uniform density distribution [69]. Zheng reported lower compaction efficiency in finer grained powders and under similar conditions, coarser grained powders demonstrated the ability to achieve higher green densities in comparison to finer grained powders [70]. This is due to the high surface energy of fine particles, which translates into higher inter-particle friction and higher powder to die wall friction coefficients. The presence of hard agglomerates, which do not break down during green forming, also reduce the green density uniformity [71], leading to an inferior sintered density. Green densities of at least 50%, ideally closer to 60%, are preferred to minimise shrinkage, whilst reducing sintering temperature and sintering time. A lower green density requires a higher sintering temperature, and for a longer period of time in order to eliminate all the porosity from the green body, which results in undesirable grain growth. In the absence of a suitable grain growth controlling mechanism during sintering, the finely divided active nano powders can undergo extensive grain growth producing a final microstructure with a grain size in the micron range [12].

In order to retain the unique mechanical, optical, magnetic and electrical properties, the difficulty comes in consolidating nano powders into engineered components with a preserved metastable nanostructure [16], with an average grain sizes below 100 nm [17].
If the agglomerates found in nano powders fail to be crushed during processing, then a non-uniform green density will reside, leading to differential densification during sintering, which has been reported by Yagi [72]. Intra-agglomerate coalescence and excessive grain growth during sintering have also been reported [64]. Laberty-Robert reported that zirconia nano powders with a crystallite size of about 30 nm could be formed and sintered to achieve greater than 98% theoretical density with an average grain size of 500 nm [73]. According to Chen, a two stage sintering process was implemented, where the kinetics of grain boundary diffusion and grain boundary migration were well-controlled, achieving a fully dense ceramic with an average grain size of less than 100 nm [74].

### 2.4 Forming green bodies

In general, green body forming of ceramics from submicron and nano powders is to achieve well-compacted shapes. It is required to form a strong, defect-free green body, with good control over density and microstructure prior to sintering via the chosen forming route. Flaws present in the green body are not eliminated during sintering [12,75].

The forming processes of green bodies can be categorised as; dry forming, wet forming, and plastic-forming. The commonly use processes that fall into these categories are; die pressing, slip casting, and injection moulding, respectively. The selection of a forming technique requires careful consideration, such as; volume of production, capital costs, shape and size of product, quality of internal microstructure, surface finish, as well as the ease and availability of processing operations.

#### 2.4.1 Dry forming

Dry forming is industry’s preferred ceramic processing route for forming simple shapes rapidly. Compaction begins with a prepared ceramic powder, which sometimes consists of pre-mixed dispersants and binders to enhance homogeneity
and to provide additional cohesion. Uniform green density and homogeneity in green compacts is essential in achieving high densification and a well-controlled grain size distribution after sintering [75].

Nanocrystalline powders generically display non-uniform packing due to the extremely high surface energy between nano particles per unit volume, which can cause frictional resistance during compaction. This phenomenon forms strong aggregates, which are not easily broken down under the conventional applied pressing pressures used for a submicron powders. This results in both intra-agglomerate and inter-agglomerate porosity.

The different techniques involved in the production of green bodies via dry forming routes are discussed below.

2.4.1.1 Cold uniaxial pressing

During compaction at room temperature, the loose powder is subjected to uniaxial compressional stress at a relatively high pressure, about 100 MPa up to 250 MPa, in a rigid metal die with an upper and lower punch, see Figure 2.12.

Shaping occurs as the pressure is applied to the loose powder, where particle rearrangement, deformation, and break-down of agglomerates take place, improving particle packing. Density variation can occur despite the high pressure applied to the powders, as there is friction between the powder particles and interactions between powder particles and die walls. Other variables affecting density include particle size variation and the presence of moisture. A higher pressure is usually required to consolidate nanocrystalline powders due to the larger degree of agglomeration present compared to submicron powders [12,75].
2.4.1.2 Cold isostatic pressing

Since cold uniaxial pressing employs single direction compaction, density uniformity varies across the sample.

In order to overcome this limitation, cold isostatic pressing can be used to enhance the uniformity and shape capability of green compacts, usually increasing green density by 2–5% over uniaxial pressing. This involves application of a uniform hydrostatic pressure throughout the green compact, see Figure 2.13 based on wet-bag isopressing, contained in a vacuum sealed, flexible wet-bag immersed in a pressure vessel containing hydraulic fluid. A set pressure is applied in the chamber and held for a given time. After pressing, the bag is removed from the hydraulic fluid.
and the green compact is retrieved from the bag. As the wet-bag takes the shape of the sample, it reduces die-wall friction and enables a more homogeneous density distribution across the sample. This technique allows larger and more complex shapes to be pressed. Another form of cold isostatic pressing, dry-bag isopressing, consists of a fixed mould inside the pressure vessel and is generally used for pressing spark plug insulators [12]. The flowability and crushability of the ceramic powder is of great importance to industry. A specific amount of powder must readily flow into a die, within a fraction of a second. Then this powder must be compacted to a high green density, with no remaining uncrushed powder particles within the body.

![Diagram of isostatic die pressing](image)

**Figure 2.13 – Schematic of isostatic die pressing**

### 2.4.2 Wet forming

Wet forming of ceramics is based on a colloidal system using common casting techniques, such as slip casting, to form a green body by removal of solvent from the colloidal suspension. This technique offers advantages over dry forming mainly due to the ability to form un-agglomerated ceramic particles through colloidal forming [12].
2.4.2.1 Colloidal forming

The steps involved in colloidal formation begin with the powder preparation, the suspension preparation, the consolidation of solids in the suspension to form the desired component shape and the removal of the liquid phase. Densification via sintering is carried out to produce the final required microstructure. In a colloidal system, the contact area of the individual particles in the dispersing medium is large; hence the colloidal stability is determined by the inter-particle forces through careful control of the suspension.

The total inter-particle potential energy, \( V_{\text{total}} \) can be expressed as:

\[
V_{\text{total}} = V_{\text{vdw}} + V_{\text{elect}} + V_{\text{steric}} + V_{\text{structural}}
\]

Eqn. 2.07

Where; \( V_{\text{vdw}} \) denotes the attractive potential energy due to Van der Waals forces that exist between the individual particles, \( V_{\text{elect}} \) is the repulsive potential energy from the electrostatic interaction between positive charged particle surfaces, \( V_{\text{steric}} \) is the repulsive potential energy resulting from steric interaction between the particle surfaces coated with an adsorbed polymeric species, and \( V_{\text{structural}} \) is the potential energy resulting from the presence of non-adsorbed species in suspension that may increase or decrease suspension stability [12]. The above mentioned types of stabilisation are shown in Figure 2.14.
Figure 2.14 – Schematic of interaction potential energy for (A) electrostatic, (B) steric and (C) structural contributions, where $k^{-1}$ is the effective double-layer thickness, $\delta$ is the adlayer thickness, and $\sigma$ is the characteristic size of species resulting in ordering within the inter-particle gap [76]

Shojai [77] prepared stable aqueous suspension based on 3 mol.% YSZ powder using both electrostatic and electrosteric stabilisation. Results showed that the zirconia particle surfaces were positively charged at a pH less than that of the isoelectric point (IEP). Electrostatic stabilisation was reported to be efficient at an
acidic pH of less than 4, where zeta potential was above 40 mV. However the stability of the suspension was very sensitive to slight changes in pH, this was caused by the dissolution of yttria in acidic 3 mol.% YSZ. For electrostatic stabilisation an ammonium salt of polymethacrylic acid (PMMA-NH$_3$) was used. Tang [78] also used polymethacrylic acid for the stabilisation of zirconia. Tang et al. have studied the effects of polyethylene imine (PEI) and diammonium citrate (DAC). Wang [79] studied the dispersion stability of 8 mol.% YSZ using polyacrylic acid (PAA) as the dispersing agent, he also analysed the influence of the pH value, solid loading, temperature and the amount and molecular weight of PAA on the dispersion stability. The preparation of 78 and 83 wt.% 8 mol.% YSZ slip using ammonium polyacrylate and its slip casting has also been reported in literature.

The stabilisation of nano zirconia particles in water is more complex due to the small particle size and the resultant large surface area and surface energy. The development of green nanostructured ceramics by wet forming routes requires very strict control of the colloidal forces involved in order to overcome the strong tendency toward agglomeration. The surface properties of nano zirconia particles using PEI as a dispersant have been reported in the literature by Duran [80]. Suspensions were prepared with different amounts of dispersant at different pH values and then slip cast to form green bodies. It was found that the amount of PEI adsorbed onto the surface of particles increased rapidly with increasing pH. Synthesis of nano zirconia powder, dispersion, slip casting and sintering has been reported by Vasylkiv [81]. Ammonium polycarboxylate was used as the dispersant and ultrasonication was used to break up the agglomerates. Suspensions with solid content up to 30 vol.% were prepared and after slip casting, the green density obtained was about 46% of theoretical, which was increased to 52% after cold isostatic pressing. The use of ammonium polyacrylate as a dispersant for nano zirconia has also been reported in literature.

Santacruz [20] developed a multiple ultrasound process involving more than one dispersant to prepare very stable, high solid content, low viscosity nano zirconia
suspensions. Suspensions were prepared up to 28 vol% (70 wt%) with a viscosity less than 0.05 Pa s, they were stable for more than 15 days. A number of systems consisting of different dispersants were studied; including PEI, tetramethyl ammonium hydroxide (TMAH) and ammonium polyacrylate (Dispex A40) and TMAH and TAC. Both Dispex A40 and TAC were found to be effective in the basic pH and the TMAH-TAC system was reported to produce the most well dispersed suspensions.

The destabilisation of TMAH-Dispex A40 system on ultrasonication for long periods of time was suggested to be due to the breaking of the Dispex A40 chains, since they are longer than TAC chains.

### 2.4.2.2 Slip casting

In slip casting of ceramics, consolidation of the particles from consistent slurry is obtained as the liquid flows through a porous medium under a pressure gradient. A choice of different shapes based on the casting techniques can be achieved. Slip casting, Figure 2.15, is a stress-free method used to manufacture both traditional and advanced ceramics.

![Figure 2.15 – Schematic of slip casting](image)

The colloidal suspension, free from agglomerates is poured into a micro-porous mould; which absorbs liquid from the suspension, considered as a low pressure filtration method, leaving behind the particles to consolidate on the surface of the mould, forming a cast. The casting rate decreases exponentially with the thickness of the cast, and the drying process usually takes from a few hours to a few days, depending on the size and theoretical density percentage of the cast. In order to
increase the rate of production, a new technique has been devised. Pressure casting uses porous polymer moulds with an external pressure applied to efficiently and effectively drive the water through the pores. Despite the higher cost of producing a polymer mould, it is compensated for by a longer life mould with little maintenance compared to a plaster of Paris mould [11,12,75].

Slip casting is often carried out at higher solid concentrations, greater than 55%. This is to prevent differential sedimentation from the variation in particle size distribution of the starting powder. Once the majority of the liquid has been removed, a saturated ceramic body is formed. The casts usually shrink away from the mould walls during drying and this enables easy of removal for subsequent drying [12].

Factors that affect the quality of the slip casts include the diffusion process that involves the flow of liquid through the porous mould, the rate of consolidation, capillary suction pressure of the mould, and the colloidal stability of the suspension, which influences the overall microstructure of the green body [11].

2.5 Dispersion mechanisms

A colloidal suspension consisting of particles dispersed in liquid medium can be lyophilic or lyophobic. In lyophilic colloids, there is a strong affinity between the dispersed particles and the liquid medium, as the liquid is strongly adsorbed onto the particles surfaces. This creates an intrinsically stable system due to a reduction in the Gibbs free energy when the particles are well dispersed. In lyophobic colloids, there is no affinity shown between the particles and the liquid medium. The Gibbs free energy increases when the particles are distributed through the medium and flocculation of the particles occurs due to the high attractive forces between the particles as they come into contact. However, this can be overcome if the surfaces of the particles are treated, by the addition of surfactants, to possess a repulsive force between them [11].
Dispersants, or deflocculants, are agents employed to stabilise suspensions of solid particles in liquid systems by reducing the surface tension between individual particles to minimise the formation of agglomerates, or flocculates, and to prevent re-agglomeration. It is critical to achieve a homogeneous dispersion of the particles to prevent the presence of agglomerates, which will result in variations in density and flaws within the microstructure. Although used in small concentrations, usually less than 5 wt.%, the dispersant plays a major role in maximising the particle concentration and forming a homogeneous and dense green body, minimising shrinkage during sintering [11,78,82,83].

Van der Waals forces are the weak electrostatic binding forces that hold the particles together. A dispersant, depending on the mechanism of dispersion (see later) can create a repulsive force between the individual particles as it is adsorbed onto the surface and prohibits particles from coming into physical contact. It can also be applied through ionic charging of the particles through desorption of ions at the surface. The ionic repulsion forces must possess a significantly higher strength than the van der Waals forces in order to stimulate dispersion.

On the other hand, the dispersing force needs to be very short range to allow the dense packing of the particles. This is required to achieve the desired high solid loading. Hence, the right choice of dispersants and dispersion mechanism is vital for suspension preparation. In addition, the dispersing medium is known to influence the inter-particle forces [84]. Thus, a stable colloid may only be produced if the dispersing medium and dispersants are tailored to suit the surface chemistry of the filler particles, in this case, YSZ.

Electrostatic, steric and electrosteric are the three stabilising mechanisms for the dispersion of filler particles. They involve the adsorption of either uncharged polymers onto an electrostatically charged surface, the adsorption of charged polymers, referred to as polyelectrolytes, or a combination of both mechanisms.
Polyelectrolytes possess a charge along the length of the polymer chain [85]. These polymers increase the hydrodynamic volume of the dispersed particles; as a result, they reduce the effective solid volume fraction and thus the maximum filling level. For monodispersed spherical particles, it can be defined by:

\[ \Phi_{\text{eff}} = \Phi (1 + \Delta/r)^3 \]

Where; \( r \) is the radius of particles and \( \Delta \) is the thickness of the repulsive polymer.

The equation reveals the importance of selecting a suitable dispersant for the filler particles. High molecular weight polymers increase the effective particle radius; this will affect the particle interactions when the ‘effective’ radius is achieved as the particles will repel each other in every direction. Thus an elastic ‘network’ is built up and this increases the elastic modulus. Low molecular weight polymers are more desirable, since they allow the free movement of particles. Although it is necessary to create a barrier to prevent agglomeration, on the other hand, it must not significantly reduce the packing factor of the filler [83,84]. Figure 2.16 illustrates the relationship stated in Eqn. 2.08.

![Figure 2.16](image_url) – An illustration of the relationship of a stabilising barrier, thickness \( \Delta \), on the packing of particles [84]
2.5.1 Electrostatic stabilisation

Electrostatic charging is carried out by the adsorption of ions onto the particles surfaces to form electrical double layers, Figure 2.17. The charges on the two approaching particles create repulsion, opposing the attraction from the van der Waals forces, therefore preventing the formation of agglomerates after dispersion [86]. The zeta potential, which characterises the interaction of the filler particles surface charge and its surrounding diffuse layer of net counter-ions, is used to measure the stability of a colloidal suspension [87].

![Figure 2.17 – Electrostatic stabilisation [76]](image)

For electrostatic forces, predicted by the Deryagin-Landau-Verwey-Overbeek (DLVO) theory, dispersions can be rendered to be unstable by either increasing their ionic strength or by changing their pH towards the IEP where the zeta potential is zero [76]. Homogeneous, well dispersed, and controlled viscosity of the suspension is achievable at high zeta potential, away from the isoelectric point. The isoelectric point of non-dispersed yttria-stabilised zirconia usually falls in the range of pH 4–6 [76].

Since the electrostatic repulsion between particles depends on the permittivity of the medium, it is therefore less effective for organic-based solvents than aqueous-based suspension because of the lower ionic concentration and the lower permittivity [83].

For an organic-based suspension with a low permittivity, the charging mechanism involves adsorption of the dispersant, dissociation of the adsorbed molecule via an
acid-base reaction with the surface and a process in which some dissociated dispersant molecules desorb into the solution, leaving charges on the particle surfaces [83].

2.5.2 Steric repulsion

Steric repulsion provides an alternative mechanism for controlling colloidal stability in aqueous and organic-based systems. In this research, adsorbed organic molecules are adopted to induce steric repulsion. In order to be effective, it requires strong attachment of the dispersant molecules to the particle surface and the adsorbed layers need to be of a sufficient thickness and density to prevent the particles from agglomerating at a distance less than 20 nm, see Figure 2.18 [76,83].

Figure 2.18 – Steric repulsion [76]

The steric force is repulsive and some small molecules, such as oleic acid, stearic acid or lauric acid can be effective in stabilising dispersions in organic-based systems despite the fact that they do not possess long molecular chains. Each molecule occupies an excluded volume related to the size and conformation of the molecule. Any attempt to penetrate this excluded volume by another molecule will result in a significant repulsive force. Even though steric repulsion is as effective in aqueous-based systems, it is much more common and important in organic-based suspension since electrostatic stabilisation is hardly possible due to the low permittivity of organic solvents [83].
2.5.3 **Electrosteric stabilisation**

Electrosteric stabilisation involves the combination of both electrostatic and steric dispersion mechanisms, Figure 2.19. Electrosteric forces arise from polyelectrolyte species that contain at least one type of ionisable group (e.g. carboxylic or sulfonic acid groups represented by the red dotes in Figure 2.19), with molecular architectures ranging from homo-polymers, such as poly(acrylic acid), to block copolymers with one or more ionisable segments. Polyelectrolyte adsorption is achieved by the attachment of molecules onto the particle surface, which is strongly influenced by the chemical and physical properties of the particle surfaces and organic solvent [76].

![Electrosteric stabilisation](image)

**Figure 2.19 – Electrosteric stabilisation [76]**

Adsorption is highly favourable when the polyelectrolyte and the particle surfaces carry opposite charges. Particle stabilisation increases with greater polyelectrolyte adsorption due to the long-range repulsive forces from the electrosteric interactions. The adsorption behaviour and conformation of polyelectrolyte can be influenced by a change in pH or ionic strength of the solvent. For an anionic polyelectrolyte, the degree of ionisation increases with increasing pH. The electrosteric mechanism has been more commonly used in aqueous-based systems [76].

### 2.6 Sintering

Ceramic materials are formed into the desired shape via the desired wet or dry processing techniques, (as discussed earlier) which is followed by sintering. There
are several possible types of sintering available; solid-state sintering, liquid phase sintering, and pressure assisted sintering. Only solid-state sintering will be discussed in detail in this report, as this is the most viable route for the production of SOFCs.

Solid state sintering is defined as a heat treatment process where the dried, binder removed green compact is densified to form a useful solid, with the required microstructure, through the application of high temperature, in the absence of liquid and external pressure [88]. The high temperatures required for sintering vary between individual ceramic materials, but usually lie between one half and two-thirds of the material’s absolute melting temperature [75].

Since zirconia has a high melting point of 2680°C, a sintering temperature of about 1450°C is usually required for traditional sintering techniques. The use of finer powders and grinding after the calcination process to remove agglomerates has demonstrated better sinterability [89-91].

Sintering will take place during heating if there is a mechanism to transport material from one area to another, reducing the total energy of the system. The five major transport mechanisms for solid state sintering include:

1. Evaporation-condensation,
2. Surface diffusion
3. Volume diffusion
4. Grain boundary diffusion
5. Viscous flow

In addition to requiring a material transport mechanism, there must also be an energy source to activate it, which is typically the abundant heat energy [12].
With active transport mechanisms, the macroscopic driving force for densification is the reduction of the Gibbs free energy, $\Delta G_T$, associated with the volume $\Delta G_V$, boundaries $\Delta G_b$, and surfaces $\Delta G_S$ of the grains within the compact [75], as shown:

\[
\Delta G_T = \Delta G_V + \Delta G_b + \Delta G_S
\]

Since the majority of the free energy, of a green compact, is associated with its surface energy, the primary driving force for densification is the reduction of the internal surface area. When green compacts are formed using fine particles, the total internal surface area is greater and therefore yields a greater driving force for sintering. Likewise, when larger particles are used the driving force for sintering is reduced due to the lower internal surface area.

Before sintering, the internal surface area of the green compact is at a maximum, since the particles are simply in contact with each other. In order to reduce the total internal surface area during sintering, the particles begin to combine together through the growth of the contact area, which is known as a neck. Also forming at the point of contact is a grain boundary separating the two particles. As the neck lengthens, the grain boundary area between the two particles also increases, see Figures 2.20, 2.21, 2.22.

Neck growth is driven by smoothing of the curvature between the particles and the neck [88]. Atoms on a convex surface are less tightly bound and have a tendency to travel to concave surfaces where there is a high concentration of vacancies to be filled. As the atoms move from the convex surfaces to the concave surface, the difference in surface curvature lessens. If the atoms move from the top surface of the particle to the neck, the neck increases but the particle centres remain the same distance apart. As a result, the particles only changes shape to reduce the surface area, therefore no densification or pore removal has occurred. When surface diffusion is the cause of atoms moving to the neck, the neck grows without densification.
When more material is transported along the grain boundary to the neck, the curvature of the neck decreases. In addition, with less material separating the particles at the grain boundaries, the particle centres move closer together, decreasing the amount of porosity within the compact. Pores between particles will continue to be removed as long as they remain very close to the grain boundary and the energy conditions are favourable [92].

As a result of neck growth, the surface energy decreases but there is also a corresponding increase in grain boundary energy. For densification to continue, the increase in grain boundary energy must be less than the amount of free energy lost due to the reduction in internal surface area [12]. The grain boundary energy, $\gamma_{gb}$, is related to the surface tension, $\gamma_s$, by the following equation:

$$\gamma_{gb} = 2\gamma_s \cos \left( \frac{\phi}{2} \right)$$

Eqn. 2.10

Where; $\phi$ is the dihedral angle representing the angle of intersection of a pore at the pore-grain boundary interface. Neck growth should occur when:

$$\gamma_{gb} < \sqrt{3}\gamma_s$$

Eqn. 2.11

For most oxide systems, $\gamma_{gb} \approx \gamma_s$ resulting in a dihedral angle of $120^\circ$, whilst in metallic systems $\gamma_{gb}$ is approximately 2 to 4 times smaller than $\gamma_s$ [75,88]. If $\gamma_{gb}$ is too high, or $\phi$ is too large, neck growth and thus pore elimination will terminate. This can cause the formation of round thermodynamically stable pores within the interior of a grain that are nearly impossible to remove through further sintering. In certain systems that are more difficult to sinter, a sintering aid may be added to reduce the grain boundary energy, thereby improving densification.

The change in energy associated with neck growth and densification may also be regarded as a “sintering stress”. This sintering stress is proportional to the driving
force for sintering, and when applied to the green compact, it causes densification by forcing the particle centres to move together.

In physical terms, the sintering stress is equivalent to the stress required to compress the initial powder compact into its final fully dense form. Therefore, green compacts created from finer particles have a high internal surface area resulting in a greater sintering driving force and a higher sintering stress.

The densification of a porous polycrystalline system is accompanied by grain growth and pore growth, which leads to coarsening of the microstructure. The effect of coarsening reduces the driving force for densification. Grain growth must be well controlled in order to achieve a high density in the sintered product.

Traditional sintering of submicron YSZ electrolytes usually requires temperatures in the range 1400°C to 1450°C. However, sintering at such high temperatures poses severe problems, such as microstructural coarsening of the cathodes and can also lead to undesirable interfacial reactions between the cathode material and the electrolyte layer, as discussed in section 2.1 [35,93]. It is therefore of great importance to minimise the sintering temperature to improve the quality and the flatness of the bi-layer, saving energy and creating opportunities for co-sintering of the electrolyte with other SOFC components whilst ensuring gas impermeability in the electrolyte layer [35,42,78,94]. This may be achievable through the use of nano sized particles.

Constrained sintering occurs in thick electrolyte layers on pre-sintered substrates. This can retard densification, resulting in residual open porosity, which is detrimental in the SOFC application since the primary requirement is to obtain a highly dense electrolyte, impermeable to the gaseous fuel [95].
Fine particles produce compacts with large surface areas, hence increasing the driving force for densification. When the particle size becomes very fine, the presence of agglomerates becomes more significant, these have a higher local density than the regions between them, meaning that the different regions of the green microstructures are at different stages of densification, leading to areas of excessive grain growth. This in turn yields local regions with poor densification and hence a porous structure, combined with fully dense regions containing very large grains where the agglomerates were located. Hence, the avoidance of hard agglomerates during processing is essential [83].

Significant reduction of the sintering temperatures has been achieved for bulk YSZ materials through reducing the grain size and eliminating hard agglomeration of the starting powders, e.g. the sintering temperature has been reduced to around 1000°C to 1100°C for bulk YSZ materials [96-98].

Renger reported that thinner electrolyte layers are achievable with nanocrystalline YSZ and the sintering temperature is about 300°C to 400°C lower than for submicron YSZ [84]. When conventional sintering processes are used for nanocrystalline zirconia, excessive grain growth leads to loss of the nanostructure. This brings about the need to eliminate or at least minimise grain growth. In order to accomplish this, rapid sintering methods have been widely investigated to sinter nanostructured ceramics; the focus on fast heating and cooling rates with short dwell times leads to minimal time at low temperatures where grain coarsening mechanisms are dominant [94]. More details on grain growth can be found in section 2.4.3.

An increase in the yttria concentration leads to a decrease in the sintering rate due to an increase in the activation energy for diffusion to take place [99,100].
2.6.1 Stages of sintering

In section 2.4, the mechanism and driving force of sintering was discussed and an in-depth understanding of the different stages involved in sintering is further discussed here.

In the initial stage of sintering, any increase in density is slow and gradual and primarily arises from necking. Once sintering reaches the second stage the density increases significantly due to shrinkage, and after reaching a value of 90 to 95% of theoretical, a third stage is reached when the increase in density starts to slow down and eventually ceases. It is in this final stage of sintering where the majority of grain growth occurs [12].

2.6.1.1 Neck formation

During the initial stage of sintering, particles rearrange themselves and join together at the contact points, where neck formation occurs due to transport of matter to the necks by diffusion, which increases the strength of the body. Since surface diffusion has the lowest activation energy, it is most active at the low temperatures during the early stages of sintering. Continuous sintering brings about an increase in the neck diameter and smoothing of the pore surfaces, yielding a three-dimensional network. The microstructures forms an interconnected network of grains entangled with a continuous pore network, with increased contact area between particles. However, the degree of porosity does not significantly change. At this stage, the powder compact only experiences a modest increase in density [11,12].

![Figure 2.20 – Neck formation [12]](image-url)
2.6.1.2 Densification

The densification stage starts after the initial neck growth and ends when the particle compact reaches approximately 90% of the theoretical density. In this stage, necks and grain boundaries continue to grow, particles move closer together, and pores shrink resulting in volumetric shrinkage. The continuous pore network starts to break up into individual, isolated pores and the reduction of porosity continues at a slower rate until densification stops. It is during this stage where the majority of densification takes place [11,12,88,101]. In order to reduce the total grain boundary energy, grain growth is significant, which is why smaller grains are consumed by larger grains. As densification increases, open porosity transforms into smaller spherical pores which are non-continuous, leading to closed porosity.

![Densification Diagram](image)

Figure 2.21 – Densification [12]

2.6.1.3 Grain growth

At this final stage of sintering, full densification can be achieved from careful grain boundary movement as pores are eliminated by the annihilation of vacancies at the grain boundaries. Sintering aids are often added to slow the grain boundary movement and to allow enough time for pore removal. Grain growth becomes more rapid in the later stage of densification when the pores become isolated. Undesirable rapid grain growth may become too overwhelming, separating them from the grain boundaries. Once this occurs, the pores will become impossible to remove even with additional heating [11,12].
Sintered parts undergo dimensional shrinkage as a result of densification. The sintering shrinkage, $\Delta L/L_0$, in the initial stage of sintering can be termed as [75]:

$$\frac{\Delta L}{L_0} = \frac{KD_v \gamma_s V_v t}{k_B T d^n}$$

Where; $D_v$ is the diffusivity of the vacancies with volume $V_v$, $\gamma_s$ is the surface energy, $t$ is time, $k_B$ is the Boltzmann constant, $T$ is temperature, and $d$ is the particle diameter. All particles are assumed to be spherical and of the same dimensions. The constant, $K$, is dependent on the geometry of the system; $n$ is the exponent, commonly close to 3 and $m$ the exponent, commonly around 0.3 to 0.5.

Sintering shrinkage is greatly influenced by composition, temperature (both directly and in terms of diffusivity), particle size and particle packing in the green body, the rate of heating, and the atmosphere in which the sintering process is carried out.

As mentioned in section 2.4, the driving force for sintering is the reduction of the free energy associated with the volume, grain boundary, and surface energy of the particles within a green compact. There are two processes that result in the reduction of the free energy of the system: densification and grain growth. Densification takes place when pores are eliminated due to bulk diffusion mechanisms; grain boundary diffusion and lattice diffusion, which are the dominant material transport mechanisms.
However, if surface diffusion dominates, then grains grow too rapidly, and pores coalesce. The free energy of the compact is reduced but no densification occurs meaning that the microstructure has coarsened. Grain coarsening also takes place when the sintering temperature is too low, the grain boundary energy is too high, or when the pore geometry is thermodynamically stable. In order for the powder compact to become fully dense, coarsening must be suppressed until after the majority of the shrinkage has occurred [88].

Densification can be monitored by measuring the change between green and sintered density or by measuring shrinkage with time using a dilatometer. Since grain growth results in very little shrinkage, the degree of densification can be determined through changes in grain size. Figure 2.23 illustrates grain sizes versus density, and the difference between coarsening and densification. In order to reach full density, grain growth must be suppressed until the latter stages of sintering (curve z). If grain growth dominates, then there will be little densification (curve x). Typically, densification and grain growth occur simultaneously (curve y) [88,102].

![Grain size vs. density plot showing, densification followed by grain growth (curve z), pure grain growth (curve x), and simultaneous densification and grain growth (curve y) [88]](image-url)
2.6.2 Factors affecting sintering

Temperature is the main factor affecting solid state sintering. Since diffusion is temperature dependent, increasing the sintering temperature will greatly enhance sintering kinetics. Rapid heating to a high temperature can minimise surface diffusion whilst enhancing bulk diffusion leading to greater densification.

Longer holding times at the desired sintering temperature will allow more time for diffusion resulting in greater densification and increased grain growth. Generally, rapid heating with a minimal isothermal hold time at the maximum sintering temperature will lead to a fully dense compact with minimal grain growth [75]. Controlled heating and cooling is necessary to avoid an uneven temperature distribution and residual stresses.

The size of the particles is another important consideration, since finer particles produce a compact with a larger surface area, hence increasing the driving force for densification. However, too fine particles may cause agglomeration, where the fine particles quickly sinter together to form larger particles. These larger agglomerated particles lead to a decrease in densification and the creation of large pores between the particles.

Larger particles can also lead to exaggerated grain growth, whereby a few grains grow quickly into very large grains contributing to poor densification. This can be avoided by making the green compact from particles with a narrow particle size distribution. On the other hand, uniformly packing particles with a narrow size distribution is more difficult, which can lead to large pore formations that are difficult to remove [12,88].
The green density and microstructure also affect the resultant sintered microstructure. The densification of a compact is related to both the starting density and linear sintering shrinkage as follows:

\[
\rho_s = \frac{\rho_g}{(1 - \frac{\Delta L}{L_0})^3} = \frac{\rho_g}{(1 - \frac{\Delta V}{V_0})}
\]

Eqn. 2.13

Where; \(\rho_s\) is the sintered sample density, \(\rho_g\) is the green density, \(\Delta L/L_0\) is the linear shrinkage and \(\Delta V/V_0\) is the volumetric shrinkage [103]. A higher green density would result in a higher sintered density due to less pore volume to remove during sintering. A more uniform and homogeneous green microstructure also means that there are fewer agglomerates that can adversely affect the sintered microstructure and cause non-uniform densification.

Sintering may be improved with sintering aids in order to enhance diffusion or suppress grain growth. Additives concentrated at the grain boundary can also enhance sintering by reducing the grain boundary energy or by slowing grain boundary movement. By slowing down the movement of grain boundaries, more time is available for pore elimination which leads to better densification.

2.6.3 Two-step sintering

Conventional sintering consists of heating the green sample to an elevated temperature, which is held for several hours before cooling takes place. The term ‘two-step sintering’ is a pressureless sintering technique successfully used to suppress the accelerated grain growth of nano-powders during the final stages of sintering [104]. In addition, two-step sintering has been reported to produce a higher sintered density, a smaller deviation of grain size, and a smaller average grain size. This is explained as the reduction in the effects of differential densification,
which results from the pinning of grain boundaries by immobile triple-junctions to effectively produce finer structured ceramics.

The concept of ‘two-step sintering’ changed the work for the sintering of nanostructured yttria-stabilised zirconia [74]. In the study, the green compacts are initially heated to a higher temperature, known as T1, for a very short period of time and then cooled down rapidly to a lower temperature, T2, which is held until full densification is achieved, which typically takes around 20 hours. The key attribute to the process is that no grain growth is reported during the temperature held at T2, providing that a sufficiently high-density, e.g. greater than 70% for nano YSZ, is obtained during the first step. Studies on free bodies made from nanostructured powders have demonstrated that it is possible to achieve densification without significant grain growth based on two-step sintering [63,105,106]. This is explained by the lack of grain growth, or ‘frozen microstructure’ during the second step, whilst densification continues. It is argued to be consistent with a grain boundary network pinned by triple-point junctions that have higher activation energy for migration than the grain boundaries. Thus the feasibility of densification without grain growth is thought to rely on the suppression of grain-boundary migration whilst keeping grain-boundary diffusion active [13,55].

A two-stage sintering profile was first used for microstructure refinement of alumina [107]. Alumina green compacts were initially heated to 800°C for 50 hours in a pre-coarsening step, and then the temperature was then increased to 1450°C for final sintering. Results were compared with samples that had undergone the pre-coarsening step, and it was reported that the microstructures of the pre-coarsened compacts were more uniform and for the equivalent density, the amount of closed porosity was lower in the case of the pre-coarsened alumina.
A kinetic window for the second stage sintering of YSZ, Figure 2.25, has been reported by Wang, and it extends over a wide range of temperatures, ranging from 1000°C to 1300°C with the effect of suppressing grain growth. The solid symbols within the kinetic window in Figure 2.25 denote full densification of ceramic compacts with minimised grain growth. At temperatures above the kinetic window, grain growth occurs, for which the driving force for densification diminishes as the grain size increases. However, fully dense samples do not resist grain growth indefinitely at T2; the grain size was found to increase after a long 'incubation period’. The symbols below the kinetic window, Figure 2.25, represent samples that fail to achieve full densification due to the use of low temperature.
Two-step sintering is an economical and effective technique to prepare fully dense YSZ and other ceramic components, once suitable sintering temperatures have been identified, based on the kinetic window. Two-step sintering provides better control over densification and grain growth. The Ceramics Group at Loughborough University has been able to produce fully dense genuinely nanostructured YSZ bulk samples, based on single and two-step sintering profiles, using conventional, microwave and hybrid furnaces [19,63].

### 2.7 Properties of YSZ

Yttria-stabilised zirconia ceramics have been used for a wide variety of structural and functional applications because of their excellent mechanical, electrical, thermal, and optical properties. Many of these outstanding properties are largely controlled by defects in the sublattice, phase relationships and crystal structure, which are optimised by modifying the fabrication techniques. Hence, a good knowledge of
these factors is essential to improve the properties and prevent detrimental effects occurring in the material.

For the application of SOFCs, the electrolyte layer is expected to exhibit good phase stability in order to maintain the required ionic conductivity over a long period of time, operating under adverse conditions.

Morphological effects, such as phase transformations, grain growth, the effect of ageing and impurities on ionic conductivity, hydrothermal ageing and mechanical properties will be discussed below.

2.7.1 Morphology

Although 8 mol.% YSZ provides full stabilisation of the cubic high-temperature phase at room temperature and yields the highest ionic conductivity amongst YSZ ceramics [108], it is reported that the conductivity of 8 mol.% YSZ decreases after a long period [109,110] under SOFC operating conditions, this was interpreted as phase precipitation. Despite the hindrance that degradation imposes on the commercialisation of SOFCs, experimental verification of the effect ageing has on the microstructure combined with electrical measurements is relatively limited. Studies have shown that the various phenomena that occur due to aging at relatively low temperatures are caused by short range ordering of oxygen ion vacancies, due to precipitation of tetragonal zirconia from cubic matrix and the further decrease to the ordering in the cubic phase. The microstructural changes associated with increasing dopant concentration is responsible for the decrease in ionic conductivity caused by short range ordering of oxygen ion vacancies [111]. However, in the work carried out by Paul, a comparison was undertaken between commercially available sub-micrometer 3 mol.% YSZ and nanostructured 3 mol.% YSZ. They were both subjected to the same aging treatment and characterisation. The nanostructured 3 mol.% YSZ samples, with an average grain size less than 100 nm, did not exhibit degradation within the study period of 14 days at 245°C, whereas the sub-
micrometer 3 mol.% YSZ samples underwent severe degradation [18]. The nanostructured samples were proven to possess excellent hydrothermal ageing resistance, which is an essential property in the application of SOFCs. Several possible causes of ageing are discussed further in section 2.7.3.3.

2.7.1.1 Segregation & impurities

It has been observed that yttria segregation at grain boundaries leads to charging of the grain boundaries. Primarily using extended X-ray absorption fine structure measurements of x-ray absorption coefficient of a material as a function of energy, it was concluded that an increase of the short-range order of oxygen vacancies around zirconia ions occurs, which reduces the concentration of mobile oxygen vacancies [112].

The presence of impurity phases plays a key role in determining the overall properties, especially the ionic conductivity of YSZ. Grain boundaries are a sink for structural defects, pores and impurities. Control over segregation at the grain boundaries to maximise ionic conduction is crucial in improving the SOFC electrolyte performance [113].

During sample preparation, even the purest commercially available powders still contain impurities at a level of 50 to 100 ppm. Typical detectable impurities are silica, alumina, iron oxide, sodium oxide and hafnium oxide. As a result, even very pure YSZ electrolytes contain at least the above mentioned levels of impurities. High silica content is often responsible for the presence of a secondary insulating siliceous phase in the ceramics, which is usually accompanied by a high grain boundary ionic resistance. The triple points, which are filled by glass pockets, and grain boundaries, which are more or less continuously wetted by glass films, constitute a blocking layer for oxygen ion conduction [114]. Based on the literature, an intrinsic grain boundary blocking effect is suggested [98]; it is supported by electrochemical measurements,
however, no evidence for such an effect has been found by direct microstructural observations.

2.7.1.2 Phase transformation

Morphological properties, which include phase transformation and grain growth in yttria-stabilised TZP, have been studied by many researchers [115-117]. The most important aspect of the relationship between phase transformation and grain growth is that the latter in the tetragonal and cubic dual-phase is slower than in the tetragonal or cubic phases alone. The grain growth behaviour of 4 mol.% YSZ has been explained in terms of the pinning effect of cubic phase grains dispersed in TZP [117]. On the other hand, investigation into the microstructure of TZP, by high-resolution transmission electron microscopy (HRTEM) and energy-dispersed X-ray spectroscopy (EDS), found that yttria cations are segregated over a width of 4–6 nm across the grain boundaries in TZP [118]. In a more recent study, investigation was carried out on the detailed microstructural changes during the sintering process of TZP and it was found that the formation of the cubic phase from the grain boundary is due to the yttria cation's segregation, which grows into the grain interior [119,120]. This transformation from tetragonal to cubic phase was termed 'grain boundary segregation-induced phase transformation' (GBSIPT) [121]. In this, a cubic and tetragonal inter-phase boundary is formed in the TZP grains. The lattice parameter ratio was slightly different between the tetragonal and the cubic phase, and a less-than-1% lattice mismatch was reported. Therefore, it is possible that the inter-phase boundary is a coherent or semi coherent boundary. In the case of the latter, the excess strain interface energy is released introducing a misfit dislocation. This study by Matsui focuses on investigating the presence of tetragonal and cubic inter-phase boundaries formed in YSZ sintered over a range of temperatures, where a tetragonal to cubic transformation takes place in a GBSIPT manner. The yttria cation distribution across the tetragonal and cubic inter-phase boundary has also been measured using EDS with a probe size of less than 1 nm, based on these results, no amorphous phase was present, however, the amount of yttria ion segregation in 8 mol.% YSZ was significantly lesser than in 3 mol.% YSZ.
The thermal ageing process of stabilised zirconia was first investigated by Carter for a calcium oxide-zirconia dioxide system, and it was concluded that a defect ordering process was taking place [122]. Moghadam has reported the influence of annealing on the ionic conductivity of 4.5 mol.% YSZ at 1000°C. The initial decrease in ionic conductivity has been attributed to precipitation of tetragonal zirconia in a cubic matrix. Further decreases have been attributed to the ordering in the cubic phase. However, even after annealing for 1000 hours, when the cubic phase should be stable, relative XRD intensity changes were detected.

At a high temperature of 1000°C, 8 mol.% YSZ appears in the two-phase region on the equilibrium phase diagram [31], which indicates that the cubic symmetry observed in samples of this composition prepared at temperatures in the single phase region, greater than 1200°C, correspond to a metastable phase. When annealing at 1000°C, a two-phase mixture of cubic and tetragonal phase is produced [109].

The ionic conductivity of YSZ materials with an yttria content of more than 9 mol.% decreases during ageing at 1000°C [123-128]. Conductivity degradation of 8 mol.% YSZ by more than 50% after annealing, for 1000 hours at 1000°C, has been observed many times [123-128], but has been interpreted differently. A possible reason for this phenomenon is the partial transformation to the tetragonal phase during ageing [123,124], or the formation of micro-domains [126,127]. However, it is not caused by the diffusion of yttria into the grain boundaries, or by the formation of ordered phase [125].

\section{Mechanical properties}

A SOFC electrolyte material is required to possess mechanical properties that are sufficient to withstand the stress levels encountered during fabrication and normal operating environments, such as;
1. Fabrication handling
2. Thermal expansion
3. Vibration forces
4. Impact shock

Thermal expansion stresses build up between layers in the fuel cell stacks due to varying coefficients of thermal expansion between electrodes, electrolytes, seals and interconnects during high temperature fuel cell operation. This is especially important when the electrolyte is used to support the SOFC mechanically or when it is being used in mobile applications. In terms of mechanical requirements, for a ceramic, high Young’s modulus, low hardness and high fracture toughness are essential in providing the mechanical performance of the thin electrolyte layer, which needs to be strong and not brittle [129,130].

In general, ceramic materials exhibit high yield strengths, but low toughness against crack propagation. This is due to the nature of the ionic and covalent molecular bonding, having the ability to resist atom movement. The strength of a bond is directly proportional to the electronegativity of the atoms and distance between them. Ceramic atoms with a higher electronegativity have the tendency to form ionic bonds, which are typically highly symmetric and isotropic. Covalent bonds are the strongest type of bonds; with two ions sharing valence electrons and neither of the atoms have a tendency to give up an electron completely. The overlapping of the outer valence shells results in a highly ordered and directional covalent bond.

In terms of strength, the maximum value reported for nanostructured 3 mol.% YSZ at different grain sizes was between 1000 to 1100 MPa, with the highest value at an average grain size of 1.4 \( \mu \)m. An increase in grain size to 2.2 \( \mu \)m brings about a decrease in fracture strength, which corresponds to the critical grain size when transformation occurs during cooling. When grain size is less than 1 \( \mu \)m, the fracture strength decreases significantly when changing the stabiliser concentration from 2 to
3 mol.% YSZ. The relationship between yttria concentration and fracture strength are hence dependent on the grain size of the material [131].

In the literature on hardness of microstructured YSZ, a hardness value of 12 GPa for PSZ was reported [132], whilst the hardness of nanostructured 3 mol.% YSZ with theoretical densities ranging from around 90% to 99%, and with grain sizes between 55 nm to 160 nm, demonstrated an increase in hardness with density [133], reporting the maximum hardness to be similar to that reported by Medvedovski. There was no observation of a grain size dependency on hardness. However, this result is supported by data obtained in the study on the effect of grain sizes on hardness in nanostructured 3 mol.% YSZ, with grain size ranging from 23 to 130 nm [134]. For 3 mol.% YSZ of about 99.8% theoretical density and an average grain size of 112 nm, it was reported to possess the highest value of hardness, reaching 11.7 GPa [81].

The mechanical properties of YSZ are dependent on its microstructure behaviour. The grain boundaries are a sink for structural defects, pores and secondary phases. Any impurities within the material segregate to the grain boundaries, further decreasing the mechanical properties. There are two distinct modes of failure in sintered ceramics:

(i) Transgranular fracture
(ii) Intergranular fracture

In transgranular fracture, it is due to cracks propagating through the grain boundaries. Intergranular fracture is crack propagation that occurs through the grains rather than the grain boundaries. Since dislocations slide along slip planes and adjacent grains are not aligned, the dislocation cannot simply transfer from grain to grain. The grain boundaries provide an added resistance to dislocation movement, forcing the dislocations to nucleate in the grain to travel in a new direction. As a crack propagates through a grain boundary in an indirect path, the crack can run
into a grain perpendicularly. This will stop the crack until the energy is increased to a level higher than the intergranular resistance. Therefore a material’s toughness can be increased by engineering the phase and grain size.

Based on the ZrO$_2$-Y$_2$O$_3$ phase diagram, at stabiliser concentrations between 3–7 mol.\% YSZ, both cubic and tetragonal phases can be retained in the microstructure. The latter consists of a cubic phase in which tetragonal phase is dispersed. This YSZ solid solution is termed partially stabilised zirconia (PSZ). When a significant volume fraction of metastable tetragonal phase is present, the tetragonal precipitates provide good mechanical properties, in terms of strength and toughness, to the ceramic. This process is known as transformation toughening [12,28].

The transformation toughening effect in zirconia is dependent on grain size [26,135-140], and is especially evident in nanocrystalline 3 mol.\% YSZ [133], which is found to exhibit low values of fracture toughness of between 2–5 MPa m$^{1/2}$. The low values of fracture toughness are due to over stabilisation of the tetragonal phase by the finer grain size, such that it cannot transform to the monoclinic phase upon introduction of a crack. The stability of a tetragonal zirconia grain inside a tetragonal matrix is controlled by three factors; the grain size, the matrix constraint, and the amount of stabilising dopant, in this case yttria [141,142]. If the material remains nanostructured, and the matrix constraint remains constant, in solid form, then in order to lower the stability of the tetragonal phase and regain transformation toughening, the amount of yttria needs to be reduced.

Ceramics exhibit a linear elastic stress strain curve, followed by little or no plastic deformation before a permanent brittle failure. The linear elastic behaviour enables the bonds to stretch and recover completely when loading is removed. Plastic deformation is caused by two rows of atoms slipping under stress and dislocating to the next available position [143]. Ceramics do not permit line dislocations due to the directional nature of covalent bonds. Plastic deformation is not significant at low temperatures in most ceramic materials, except for MgO by grain boundary
softening, but as the temperature increases the material becomes more ductile. Dislocations start as a defect within the microstructure. The two types of defects are:

(i) Point defects
(ii) Line defects

Point defects are caused by vacancies in the crystal structure or by impurities. In YSZ, the presence of oxygen vacancies within the material is due to the replacement of zirconia (based on Zr$^{4+}$) lattice sites with yttria (based on Y$^{3+}$). With the increase of yttria concentration, the number oxygen vacancies increase to maintain charge neutrality, bringing about a reduction in overall strength of YSZ. Typically, 3 mol.% YSZ is 4 times stronger than 8 mol.% YSZ. Line defects, which are also known as dislocations, are detrimental to the material allowing deformation to occur at a much lower stress state, as compared to a perfect crystal. As a dislocation moves through the lattice it progressively breaks bonds. When too many bonds are broken from dislocation motion and plastic deformation reaches its maximum value, the ceramic material will fail.

Brittle failure is found in ceramics, since they possess high yield strength and do not allow plastic deformation. A small, sharp crack starts in a material at a line defect and propagates along a slip plane within the lattice structure. As the dislocation crack propagates, it spreads between the atomic planes yielding an atomically smooth surface. The maximum stress applied to the material occurs at a 45° angle from the force vector. The material will fracture at the slip plane oriented closest to the 45° angle. The area of material at the crack tip can absorb the energy of the propagating crack by plastically deforming and work hardening the area. When the strength exceeds the energy of the crack [144], then it will be stopped. Ceramics are not conducive to plastic deformation, prohibiting the absorption of crack tip energy and causing brittle failure in tensile loading.

In the study on toughness of 3 mol.% YSZ, the toughness value was reported to be 5 MPa m$^{1/2}$ [144], whilst in another report, it demonstrated a much higher indentation toughness of 9–10 MPa m$^{1/2}$ for a PSZ [132,145]. The measured
indentation toughness of nanostructured 3 mol.% YSZ, carried out by Cottom, was found to be independent of grain size, and values were found to be in the range of 2.25 to 4.25 MPa m$^{1/2}$. These values are lower than the micron grain size value of 8.2 MPa m$^{1/2}$ reported by the same author. The toughness of fully stabilised cubic zirconia ranges between 2 to 3 MPa m$^{1/2}$ [145]. The reported literature suggests that 3 mol.% YSZ is over stabilised, and that 1.5 mol.% YSZ is required to achieve high toughness values in nanostructured YSZ.

2.7.3 Electrical properties

Electrical conductivity is a measure of how well a material conducts an electrical current. A good electrical conductor possesses many highly mobile electrons [146]. The mobility of electrons through a material is very much dependent on its atomic bonding, the number of crystal lattice imperfections, and the microstructure of the material. Metals, such as nickel, are good electrical conductors whilst insulating materials, such as YSZ are not. The electrical conductivity of nickel is 146,200 S cm$^{-1}$, whilst the electrical conductivity of YSZ is 0.006 S cm$^{-1}$ at 25°C [147].

The resistance to current flow through a conductor is denoted by Ohm’s Law:

$$R = \frac{V}{I} \quad \text{Eqn. 2.14}$$

Where; $R$ is the resistance of the sample (Ohms, $\Omega$), $V$ is the potential difference measured across the conductor (Volts, V), and $I$ is the current through the conductor (amperes, A). It is also a function of the size, shape and properties of the materials within the circuit, given by [148]:

$$\sigma = \frac{l}{RA} \quad \text{Eqn. 2.15}$$

Where; $\sigma$ is the electric conductivity (S cm$^{-1}$), $l$ is the length of the sample, and $A$ is the cross-sectional area of the sample.
The bulk ionic conductivity of a material can be derived from [148]:

\[
\sigma = \frac{Il}{VA}
\]

Eqn. 2.16

Electrical resistivity (Ω cm) is a reciprocal of electrical conductivity, another term commonly used to describe electrical conductivity. A good conductor has lower electrical resistivity whilst poor conductor has higher electrical resistivity.

SOFCs operate at high temperatures, about 1000°C, in order to obtain a sufficiently high ionic conductivity, but studies have shown that operating at such high temperatures over a prolonged period result in a degradation effect; predominately a reduction in ionic conductivity [112]. As SOFC performance is mainly dominated by the ohmic loss of the electrolyte, it is important to optimise the electrical properties of the sintered electrolytes.

YSZ is an important solid electrolyte with applications in SOFCs and oxygen separators, mainly due to its good electrical and mechanical properties [149-151]. It is known that the ionic conductivity of YSZ occurs due to a vacancy mechanism. The substitution of \( Y^{3+} \) for \( Zr^{4+} \) results in the formation of oxygen vacancies as compensating defects [152,153].

\[
Y_2O_3 \rightarrow 2Y^{2+} + V_o^- + 3O_0^\bar{c}
\]

Eqn. 2.17

At higher amounts of yttria, the concentration of oxygen vacancies \( V_o^- \) and \( Y^{3+} \) ions at zirconia sites is high enough for the formation of dopant vacancy associates, which serve as vacancy trapping centres:

\[
2Y_{Zr}^\prime + V_o^- \rightarrow (Y_{Zr}^\prime V_o^- Y_{Zr}^\prime)^x
\]

Eqn. 2.18

\[
Y_{Zr}^\prime + V_o^- \rightarrow (Y_{Zr}^\prime V_o^-)^x
\]

Eqn. 2.19
The expected random distribution of $Y'_{Zr}$ suggests the occurrence of the charged defect. As a result, only a small fraction of the oxygen vacancies take active part in the conductivity process.

The ionic conductivity of stabilised zirconia increases with the addition of stabilising oxides. The high electrical conductivity in YSZ at elevated temperature is due to the mobile oxygen ion vacancies created in the oxygen sub-lattice, when the lower valent dopant, yttria is substituted for zirconia. Ionic conductivity is found to show a maximum at around 8 mol.% YSZ [154-156]. It has long been suggested that the ionic conductivity decreases with further increase of vacancy concentration, this is due to defect ordering, vacancy clustering, and, or electrostatic interaction, reducing their mobility and thus the oxygen ion conductivity [157]. This phenomenon can also be explained by some of the oxygen vacancies forming a complex with yttria by Coulombic forces, and this prevents those oxygen vacancies from contributing to ionic conduction [158-160]. On the contrary, there has not yet been any experimental verification from the viewpoint of crystallography. There is literature reporting that oxygen vacancies do not exist preferentially as the first nearest neighbour of yttria, even in a sample containing more dopant than the critical amount, when ionic conductivity reaches its maximum [161]. Although higher conductivities are possible with other oxide additions, YSZ is currently the most commonly used electrolyte material used in the SOFC application, mainly for its availability and cost. It possesses an adequate ionic conductivity over the required operating range of oxygen partial pressures and it is stable physically and chemically in both reducing and oxidizing environments.

In general, 8 mol.% YSZ is reported to exhibit an ionic conductivity of 0.1 S cm$^{-1}$ at about 1000°C [162], whilst the electronic conductivity is less than 10$^{-4}$ S cm$^{-1}$ [163]. The ionic conductivity is very much dependent on the sintering conditions of the electrolyte since they determine the electrolyte microstructure, relative density, grain size and inter-granular phases. The ability to interpret microstructural influence on the ionic conductivity of the electrolyte can help to optimise the sintering conditions and further improve the electrical properties of the electrolyte [164].
Ceria (CeO$_2$) is another potential electrolyte material, having a higher ionic conductivity than YSZ, but it is reported to be less stable under the reducing conditions at the anode [165,166]. Under reducing conditions at high temperatures, CeO$_2$ develops a higher electrical conductivity, which diminishes the fuel cell potential and energy conversion efficiency. Hence, ceria is used primarily for SOFC applications that operate at lower temperatures, e.g. about 500°C.

YSZ is a polycrystalline ceramic, whose oxygen ion conductivity comprises of bulk and grain boundary contributions. Whilst bulk conductivity seems to be a direct function of the level of heterovalent dopant, and the associated oxygen vacancy concentration [4], literature data on grain boundary conductivity reveals a broad scattering that cannot be easily explained [114,167]. In addition, the grain boundary resistance is usually two or three orders of magnitude higher than the intragranular resistance. Other studies have demonstrated that the total ionic conductivity in the zirconia system is influenced by grain boundaries [168,169] and that they act as barriers to oxygen ion conductivity [170-172].

The oxygen ion bulk conductivity in fully stabilised cubic zirconia is a factor of two times higher than that of tetragonal 3 mol.% YSZ [114,167]. However, with the use of nanostructured 3 mol.% YSZ, with a tetragonal structure, it demonstrates a higher electrical conductivity than 8 mol.% YSZ at lower temperatures, typically below 550°C [30].

Alternating current impedance spectroscopy is a powerful technique devised to characterise the electrical properties of ceramic ionic conductors [173]. It has been reported that for a zirconia-based electrolyte coated with platinum electrodes, the individual polarisation of bulk material, grain boundaries, and electrode reaction interfaces can be measured [174,175]. Through analysing the impedance spectra obtained from YSZ, the ionic conductivity of grains and grain boundaries can be
correlated to the microstructure of the material prepared by different sintering conditions.

The technique of complex impedance analysis was first introduced to investigate the conducting mechanisms of ionic materials [174]. This provided a dielectric means of examining the conductivity of ion-conducting materials. The principle underlying this technique is that free charge carriers behave like dipoles in dielectric materials under the influence of a high frequency field and also cause dielectric relaxation.

The conductivity behaviour is easily observable at lower temperatures, e.g. below 500°C, whilst the electrode reaction is measured better at higher temperatures [173,174]. The impedance measured above 500°C is affected by the parasitic inductance of the wiring and the cell [152], which complicates the impedance analysis.

Polycrystalline materials with a uniform composition of the grains and grain boundaries show only one bulk and one grain boundary effect, regardless of whether the grains and grain boundaries are of uniform thickness or not. In impedance spectroscopy, the electrochemical reaction arc, obtained from the grain and grain boundary effect which are observed at higher temperatures in the KHz – MHz range, is usually strongly depressed [173,174].

The ionic conductivity of phase stabilised zirconia is very often found to depend on various factors, such as composition, grain size, microstructure, crystal phase, porosity and the purity of the sample [164,170,176-178], which will be discussed in the following sections.
2.7.3.1 Effect of nanostructure

In recent years, there has been an increase of interest in nanostructured ceramics, particularly the physical properties [96,179]. This is mainly due to the key role played by the increased number of grain boundaries.

Studies have shown that the electrical properties of dense oxides depend upon their microstructures, in particular when the average grain size is in the nanometre range [180-182]. This is said to be due to the increased interfacial area, which enhances the electrical conductivity and reaction kinetics, crucial for electrochemical application [182]. Others have explained it by means of the high diffusion coefficient of the system, which result in a greater conduction coefficient achieved. It seems, therefore, that an increase in the number of atoms located on grain boundaries, i.e. finer grains, will enhance ionic conductivity [169], whilst others have observed that the high density of interfaces at the nano range will reduce the grain boundary resistivity due to space-charge effects [183-185]. Ionic transport along the grain boundaries is likely to be enhanced due to the large number of displaced atoms and a high mobility [48,186].

Han reported on the effect of grain size on the electrical conductivity in an YSZ electrolyte. It was demonstrated that as YSZ grain size decreases, the thickness of the intergranular region reduces significantly [41]. Since there are only a few atom layers in the intergranular region, solute-segregation, or impurities that form blocking layers preventing oxygen ion conduction become negligible. As such, the oxygen-vacancy concentration at the grain boundaries for oxygen ion conduction is further enhanced with decrease of grain size. It is worth noting that most nanostructured thin film yielded results different from the bulk material. A higher total conductivity was observed in nanocrystalline YSZ thin films compared to micron-sized bulk YSZ [187,188]; this is explained by the possibility of an interfacial contribution [189,190]. Compared with nanostructured 8YSZ films, with thicknesses of 12 nm and 25 nm, the ionic conductivity of microcrystalline bulk 8YSZ is greater.
by around a factor of 4, which is down to the higher grain boundary conductivity and the higher bulk conductivity [191].

In a report on the influence of the microstructure on electrical transport, a direct comparison was achieved between the electrical conductivity of single crystal, micron, and nanocrystalline YSZ in relation to the microstructure. Results have shown that at the nanocrystalline level, YSZ possesses enhanced electrical conductivity, which is attributed to grain boundary and interfacial effects [182]. Mondal [42] explained that the bulk and grain boundary conductivities of nanostructured tetragonal 1.7 mol.% and 2.9 mol.% YSZ, with 25–50 nm in grain sizes were equivalent to microstructured YSZ [42]. However, specific grain boundary conductivity was increased by 1 to 2 orders of magnitude in the nanostructured samples. Similarly, Guo demonstrated an increase in the specific grain boundary conductivity and a slight decrease in the bulk conductivity as the grain size decreased from 1.33 µm to 120 nm in tetragonal 3 mol.% YSZ [192].

In contrast, the confined passage of the conducting oxygen ions within the nanosized grains was reported as the reason for the lower conductivity in nanostructured electrolytes compared to the microstructured electrolytes [169].

Li showed that the activation energy for ionic migration in nanocrystalline samples with an average grain size of 20–30 nm is about 10% higher than that of micron-sized YSZ [193]. The activation energy for microstructured YSZ is about 1.3 eV, whereas this reduces to about 0.9 eV for nanocrystalline YSZ [54].

Studies have also shown that the grain size is independent from grain boundary activation energies, and oxygen vacancy concentrations, based on calculated activation energies and conductivities in TZP, with grain sizes ranging from 90 nm to 200 nm [194]. Mondal reported that when the total conductivities are in the same
range as the microcrystalline samples, then the specific grain boundary conductivities are 1 to 2 orders of magnitude higher in the nanocrystalline samples [42]. Clearly there are many inconsistent results for the electrical property of nanocrystalline YSZ. The main problem for the results is the densification of the sample. The use of conventional single-step sintering at high temperatures would inevitably result in undesirable grain growth and causes the sintered samples to lose the characteristics of nanostructured materials. To avoid this the sintering cycle is often cut short, producing samples of rather low theoretical densities, around 80%. Such low densities will compromise the electrical properties of the samples.

Hence, it remains a mystery as to whether or not the ionic conductivity of YSZ will further be enhanced by reducing of the grain size. Whilst there are clearly some discrepancies in the reported grain size dependence on electrical properties, there does seem to be some evidence in support of increasing specific grain boundary conductivity with decreasing grain size.

For a conclusive evaluation of the grain-size effects in YSZ, the analysis of chemical homogeneous high-purity samples with a broad variation of the grain size from nm to μm is essential.

2.7.3.2 Effect of impurities

Zirconia grain boundaries are known to exhibit a blocking effect with regard to ionic transport across them [149,155,170,172,195-197]. The specific grain boundary resistivity is often several orders of magnitude higher than the bulk resistivity. In YSZ of usual purities, the blocking effect has been largely attributed to the siliceous phase present along the grain boundaries. However, even in higher purity materials, where a siliceous phase was not observed by TEM [170,172,198], the specific grain boundary resistivity was still found to be two orders of magnitude higher than that of the bulk, which explains the intrinsic grain boundary blocking effect.
The grain boundary blocking effect is known to occur due to increased resistance to ionic transport across the grain boundaries, relative to the bulk. Impurities at grain boundaries contribute to grain boundary blocking, yet even in very pure 8 mol.% YSZ, the grain boundary specific conductivity is more than two orders of magnitude less conductive than the bulk. This then explains that the higher the volume fraction of grain boundaries in a sample, the lower the total conductivity. X. Guo [199] explained that this intrinsic grain boundary resistance in high purity materials may be due to space charge oxygen vacancy depletion rather than the presence of impurities. Since the grain boundaries can be considered to consist of two space charge layers separated by a grain boundary core, oxygen vacancy depletion in the space charge layer could be the cause of this grain boundary blocking effect [170,199-201].

Mondal [42] found that the electrical conductivity of the grain boundaries of 1.7 and 2.9 mol.% YSZ is 2 to 3 orders of magnitude lower than that of the crystallite volume. Similar suggestions were made for oxygen-transport blocking at the grain boundaries as a result of experiments undertaken using 3 mol.% YSZ [202] and 4.5 mol.% YSZ [203]. Several other suggestions have been made to explain the observed blocking of ionic transport by the grain boundaries such as;

(i) Different levels of yttrium segregation [204].
(ii) Poor crystallinity [205].
(iii) Intergranular silicate phases [172,206,207].
(iv) A depletion of oxygen vacancies in the space-charge layers [192,200,208,209].

Ikuhara [210] conducted detailed HRTEM observations and nanoprobe EDS measurements on tetragonal YSZ and has reported that no amorphous phase exists along the grain boundaries and from the measurements of yttria ion distribution across the grain boundaries in tetragonal YSZ. Yttria segregation was found at grain boundaries, however only a narrow range of widths, 4–6 nm, were analysed.
For the grain boundary structure in cubic YSZ, Tekili [211] reported that there was no evidence of preferential segregation of the yttria at the grain boundaries in 8 mol.% YSZ. The concentration of yttria near the grain boundary region in 8 mol.% YSZ was found to be much lower than in 3YSZ.

Winnubst [52] attributed the grain growth in tetragonal YSZ to the decrease in grain boundary mobility through the impurity drag mechanism which occurs under the presence of a segregation layer of impurities or yttrium atoms at the grain boundaries.

The controversy between the reported results can originate from the processing routes. Reduced ionic conductivity of the grain boundaries are also reported to be due to presence of impurity phases [193]. Silica is generally considered as an impurity in YSZ used as an electrolyte in SOFC application, as it is believed to reduce the grain boundary ionic conductivity [170,172]. There has been much discussion over whether the siliceous glassy phase [212], which segregates to the grain boundary covers, the grains completely, partially or not at all [172,213]. HRTEM analysis showed that it was silicon ions which were found to be segregated at three and four point grain junctions but not the silica layer along the grain boundaries [210].

Mondal [42] has reported enhanced specific grain boundary conductivity in nanocrystalline YSZ. This has been attributed to the very low silica content of the nanocrystalline samples and the grain-size dependent segregation of silica. This is assumed that silica segregation at the grain boundaries leads to an even lower silica concentration at the grain boundaries of the nanocrystalline samples compared with similar microcrystalline sample;

(i) In their review of grain boundary properties of bulk nanocrystalline doped zirconium oxide and cerium oxide, Guo explained that the increase in specific grain boundary conductivity with decreasing grain size could be due to two
reasons [214]; in samples with high impurity concentrations, such as silica, impurities at the grain boundaries become diluted as the grain boundary volume fraction increases with decreasing grain size, allowing for a higher local grain boundary conductivity.

(ii) In highly pure samples, grain boundary space charge effects should dominate. In space charge models of YSZ, the grain boundary core has a positive potential and the positively-charged oxygen vacancies are depleted in the adjacent space charge regions.

As the grain size decreases, the grain boundary potential decreases and, with this, the associated oxygen vacancy concentration along the grain boundaries increases, improving the local ionic conductivity.

2.7.3.3 Effect of aging

The ageing process for stabilised zirconia was first investigated for a calcium oxide-stabilised zirconium system and it was established that a defect ordering process was taking place [122]. In the study on the influence of annealing on the electrical conductivity of 4.5 mol.% YSZ at 1000°C [215], it showed that the initial decrease of electrical conductivity was due to transformation of tetragonal zirconia from a cubic matrix and the further decreases were due to ordering in the cubic phase.

Considering the previous studies carried out, the effect of aging on YSZ was due to the short range ordering of oxide ion vacancies around zirconium ions, as a result of the relaxation of the lattice distortion. This causes a decrease in ionic conductivity [111,112,216]. Such an ageing effect decreases with increase of yttria concentration and disappears in the case of 10 mol.% YSZ. As a practical use of YSZ us as an electrolyte, the stability in conductivity as well as the value itself is an important factor, in order to maintain the performance of the SOFCs [112].
The decrease in conductivity due to ageing, which occurs particularly in calcium oxide and yttria-stabilised zirconia, have been studied and explained by numerous researchers as;

(i) Phase transformation toward the phases with a lower symmetrical crystal structure [111,112,215,217].

(ii) Precipitation of long-range ordered phases, such as, yttrium zirconate, following complex formation of oxygen ion vacancies and yttria by the Coulombic forces [111,112].

(iii) An increase in grain boundary resistivity caused by the grain boundary segregation of a glassy phase [109,111,217].

(iv) Trapping of oxygen ion vacancies towards yttria with time due to Coulombic force, in other words, long-range ordering [111,112].

However, there is yet to be experimental verification of each of these explanations.
3.1 Processing flow chart

The processing flow chart in Figure 3.01 illustrates the fabrication route and characterisation techniques implemented in this study.

![Processing flowchart of YSZ](image)

Figure 3.01 – Processing flowchart of YSZ
3.2 YSZ characterisation

3.2.1 Materials

The zirconia nanosuspension containing different amounts of yttria, viz. 3 mol.%, 5 mol.% and 8 mol.% used in this study were provided by MEL Chemicals (Manchester, UK). Benchmark 3 mol.%, 5 mol.% and 8 mol.% yttria-stabilised zirconia powders were obtained from Tosoh Corporation (Tosoh Europe, Amsterdam, Netherlands), which were used to compare the processing, sinterability and properties to those of the nanosuspensions. Table 3.01 indicates the material codes given to the materials used in this study.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Material codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEL 3 mol.% nanosuspension</td>
<td>M3</td>
</tr>
<tr>
<td>MEL 5 mol.% nanosuspension</td>
<td>M5</td>
</tr>
<tr>
<td>MEL 8 mol.% nanosuspension</td>
<td>M8</td>
</tr>
<tr>
<td>Tosoh 3 mol.% powders</td>
<td>T3</td>
</tr>
<tr>
<td>Tosoh 5 mol.% powders</td>
<td>T5</td>
</tr>
<tr>
<td>Tosoh 8 mol.% powders</td>
<td>T8</td>
</tr>
</tbody>
</table>

Table 3.01 – Material codes used to denote the materials used in this study

The chemicals used include tetramethylammonium hydroxide (TMAH) 97%, and tri-ammonium citrate (TAC) 98%, both procured from Fisher Scientific UK Ltd. (Loughborough, UK). All other chemicals were procured from Fisher Scientific, which includes; ethanol 99.99%, acetone 99%, methanol 99%, stearic acid 96%, Freon 99.5%, hydrochloride acid 1M and sodium hydroxide 1M.
3.2.2 X-ray diffraction analysis

X-ray diffraction was carried out to identify the crystallite phases of the zirconia powders and sintered samples using an X-ray diffractometer (D8 model, Bruker AXS GmbH, Karlsruhe, Germany). Measurements were carried out using CuKα with radiation of wavelength 1.5406 Å and at scanning increments of 0.02° with a scan speed of 1° per second in the range of 20° to 80°.

The lattice spacing, d, was calculated using Bragg’s law [218]:

Eqn. 3.01

\[ n\lambda = 2d \sin \theta_\beta \]

Where n is an integer, \( \lambda \) is the wavelength of the X-ray source and \( \theta_\beta \) is the angle between the incident ray and scattering plane.

Crystallite size can be calculated using X-ray broadening, assuming that the crystals were free of strain or fault, based on the Scherrer formula [219]:

Eqn. 3.02

\[ L = \frac{0.9 \lambda}{\theta \cos \theta_\beta} \]

Where L is the crystallite domain size (nm), \( \lambda \) is the wavelength of the X-ray source (nm), \( \theta \) is the full width at half maximum (rad) and \( \theta_\beta \) is the diffraction angle (degrees).

High temperature X-ray diffraction was also carried out on the YSZ powders to establish the phases present within the range of 20° to 80° at temperatures from 500°C to 1200°C.
3.2.3 Micro-Raman spectroscopy

Characterisation was performed to identify the crystallite phase of YSZ powders and sintered samples using a micro-Raman spectrometer (Raman LabramHR spectrometer, Horiba Jobin Yvon SAS, Villeneuve d’Ascq, France). The equipment consists of a liquid nitrogen cooled charge-coupled device (CCD) detector and two objective lenses of ×10 and ×50 magnification. The optical microscope of the micro-Raman device is connected to a video monitor that allows a focused selection of specific areas on the sample surface to record the Raman spectrum. The movement of the sample stage is controlled using a joy stick connected to the computer. The spectroscopy is equipped with an argon laser tuneable to a wavelength of 488 nm or 514 nm, and a helium-neon laser with a wavelength of 632.8 nm, with a resolution range between 450 nm and 850 nm, and wavenumber accuracy of +/- 1 cm\(^{-1}\). Under normal conditions of temperature stability (+/- 1°C), the repeatability is within 1 pixel with a standard CCD (1024 x 256 pixels of 26 microns). The signal-to-noise ratio is 3000:1.

The YSZ samples were placed under the microscope and focused by a computer controlled stepping motor in the Z direction. The helium-neon laser was used in this study with a laser power of 20 mW, micro-Raman spectra of the samples were recorded from a wavenumber 100 cm\(^{-1}\) to 800 cm\(^{-1}\) for 60 seconds at an integration time of 15 seconds. At least two spectra were collected for each analysis to ensure reliability of results and to eradicate cosmic ray spikes. The spot size of this equipment was less than 1 µm.

3.2.4 Solid content determination

The solid content of the as-received suspension is the weight percentage of solid (YSZ) present. This was carried out by firstly weighing out a small crucible, then accurately measuring out 1 – 2g of suspension into the crucible. The latter was placed in a Carbolite HST 12/400 tube furnace, Carbolite Ltd., UK, including a Eurotherm controller, and heated at 700°C for 2 hours using heating and cooling
rates of 5°C min⁻¹. This enabled all moisture and organics to be removed from the suspension, leaving behind the YSZ solids. The crucible was retrieved from the tube furnace once it had cooled down to room temperature. The dried powders obtained were used for the XRD, micro-Raman and TEM analysis.

The mass of crucible with remaining solids were measured and the solid content (%) was calculated based on:

\[ \text{Solid Content (\%)} = \frac{\text{Mass (final)}}{\text{Mass (initial)}} \times 100\% \]

Where; mass (final) denotes the final mass of YSZ measured after heating whilst mass (initial) denotes the initial mass of suspension taken before heating. The measurements were made to the nearest 0.001 g

### 3.2.5 Zeta potential measurements

Zeta potential measurements were carried out on suspensions using an AcoustoSizer II (Colloidal Dynamics, Florida, USA) based on fully automated titration. The equipment measures over a pH range from 1 to 13 with a measuring range of 1 to 20 MHz. The vessel can contain a sample volume of 150 ml flowing or 20 ml static. It directly measures zeta potential of suspension with 5 wt.% YSZ over a wide range of pH values, from pH 2 to pH 13. The range of pH values was achieved using either 0.1 M dilute hydrochloric acid (HCl) or dilute sodium hydroxide (NaOH) solutions. An equilibrium time of three minutes was used to ensure that the pH modifier was homogeneously dispersed throughout the suspension before each zeta potential measurement was made at a particular pH value. The first measurement was made at the nearest upper or lower limit of pH value to the suspension, and the remaining measurements were made by taking the pH towards the other limit.
3.2.6 Transmission electron microscopy

Particle size analysis of the YSZ material was carried out using a transmission electron microscope (JEOL JEM 2000FX, JEOL Ltd. Tokyo, Japan). It identified the primary particle size, shape and any presence of agglomerates in the suspensions and powders.

Transmission electron microscopy (TEM) was also used to obtain diffraction patterns of both starting material and sintered samples. The micrographs obtained from analysis of thin samples were prepared by FEI Dual Beam Nova 600 nanolab focussed ion beam (FIB) (FEI, Hillsboro, OR, U.S.A) milling using a lift-out technique, where grain size, presence of impurities, amorphous phase and segregation were analysed.

3.2.7 Viscosity measurements

The viscosities of the suspensions, both as-received and concentrated were analysed using a rheometer, an Anton Paar Rheolab QC viscometer (Anton Paar GmbH, Austria), with a viscosity range from 1 to $10^9$ mPas. Measurements were performed using shear rates from 1 s$^{-1}$ to 1000 s$^{-1}$ and held at 1000 s$^{-1}$ for one minute before the shear rate was reduced back down to 1 s$^{-1}$. All measurements were carried out at room temperature.

3.3 Processing of YSZ green bodies

3.3.1 Wet forming

The as-received 3 mol.% YSZ suspension was concentrated up to 57 wt.% solid content using a patented process developed at Loughborough University. The pH of as-received suspension was adjusted to the alkaline region, yielding a high zeta potential of below -50 mV, using tetramethylammonia hydroxide (TMAH). During the addition of TMAH, the suspension was mechanically agitated to ensure homogeneity before the addition of 3 wt.% tri-ammonium citrate (TAC) dispersant. During
concentration at 60°C in water bath, the suspension underwent gradual loss of water to evaporation, which would cause agglomeration of particles if not controlled. Agglomeration was broken down with the use of a Soniprep 150 ultrasonicator (MSE scientific instruments, Manchester, UK) during the concentration process; however, this does not work in highly agglomerated suspensions. Hence, in order to produce a homogeneous suspension with the required solid content, the following has to be well controlled; amount of organics in the suspension, the viscosity of suspension, drying and humidity condition, thickness of sample and mould quality. Drying at controlled humidity can slow down the rate of drying, which prevents rapid removal of moisture from the sample helping to avoid cracks. However, this further prolongs the duration of sample preparation, up to 14 days, which is not ideal for industrial scale production.

The as-received 5 mol.% YSZ suspension was concentrated up to 45 wt.% solid content and no concentration was carried out on the 8 mol.% YSZ as-received suspensions due to the high viscosity.

These concentrated suspensions were slip cast and or spray freeze dried to obtain green samples.

3.3.2 Spray freeze drying

Before granulation, 2 vol% Freon was added to the concentrated suspension to aid the crushability of the granules. Once the Freon had been added, the suspension was left stirring for around two hours and the beaker was covered to minimise evaporation of the Freon. The concentrated nanosuspension was sprayed into liquid nitrogen using a Soniprep 150 ultrasonic rod. The suspension was slowly placed on the ultrasonic rod using a plastic pipette as a delivery method. The frequency of the rod was 23 kHz and the amplitude was set at 12 µm. The ultrasonic vibrations broke down the suspension into tiny droplets, which were sprayed off into the liquid nitrogen at -196°C. The droplets rapidly froze into small granules. After all of the
The suspension had been sprayed into the liquid nitrogen, it was left to allow excess nitrogen to evaporate. Once most of the liquid nitrogen had evaporated off, freeze drying was carried out using a benchtop freeze dryer (Virtis Benchtop SLC, New York, USA), which used a Leybold D2.5B double stage oil-sealed rotary vane vacuum pump (Leybold vacuum GmbH, Germany). The borosilicate flask containing the frozen granules connected to the freeze dryer and evacuated. The condenser was set at -60 °C the vacuum was set below 100 mTorr. The granules were then left for about two days for all of the water to evaporate off via sublimation.

### 3.3.3 Dry forming

Dry forming of green samples through uniaxial die pressing was carried out using a Beckman bench top hydraulic press. Powders were fed into a 10 mm diameter hardened steel die which was thoroughly cleaned with acetone before each use.

Amounts of about 0.5 g and 1 g of powder were weighed out for each sample to be pressed. A mass of 2000 kg to 2500 kg was used for the compaction, giving pressures of ~250 MPa to ~312 MPa, and was held for 60 seconds.

\[
\text{Uniaxial Pressure} = \frac{\text{Mass} \times 9.81}{\pi \times \text{die radius}^2}
\]

Isostatic pressing (Stansted Fluid Power Ltd Iso-Lab Isostatic System) was carried out after uniaxial pressing to enhance the green density and homogeneous compaction throughout the sample. Samples were vacuumed and sealed in a flexible bag to be isostatically pressed. The pressure of 250 MPa was applied and held for 60 seconds.

\[
\text{Isostatic Pressure} = \frac{\text{Mass} \times 9.81}{0.01^2}
\]
When the time was up, the pressure was slowly released and the samples were removed from the isopress machine.

### 3.3.4 Binder removal

The organics present in the green samples mainly consist of TMAH and TAC which are added during the concentration process and are required to be removed by thermal decomposition before sintering. This process is known as binder removal. A slow and careful heating cycle was used to ensure complete removal of moisture and organics using a Carbolite RHF 1800 Furnace (Carbolite Limited, Derbyshire, UK).

The ramp rate needed to be slow to prevent rapid burning of organics, which would have resulted in charring of the samples. Hence, the binder removal cycle was optimised to involve heating and cooling rates of 0.5°C min\(^{-1}\) with 30 minute holds at 100°C, 200°C, 300°C and 400°C en route to a final temperature of 700°C where the samples were held for 120 minutes before being brought back down to room temperature.

### 3.4 Characterisation of green bodies

#### 3.4.1 Green density measurements

The green density of the die pressed samples was analysed via the geometrical method. Calculations were based on the mass of the sample (measured to the nearest 0.001 g) and the dimensions (measured to the nearest 0.01 mm). A mean value of the measured dimensions was used to determine the green density (prior to binder removal):

\[
p = \frac{M}{V}
\]

Eqn. 3.06
Where; $\rho$ is the density (g cm$^{-3}$), $M$ is the mass of the sample (g) and $V$ is the geometrical volume of the sample (cm$^3$).

Green density was also measured after binder removal via the Archimedes principle in mercury:

$$\rho = \frac{M_s \times \rho_{Hg}}{M_s + M_{Hg}}$$

Eqn. 3.07

Where $M_s$ is the mass of the sample in air, $M_{Hg}$ is the mass of sample in mercury and $\rho_{Hg}$ is the specific gravity of mercury at the measurement temperature. Measurements were made to the nearest 0.0001 g.

The theoretical density of the samples was calculated based on the theoretical densities provided by MEL Chemicals; 3 mol.% YSZ is $\sim$6.1 g cm$^{-3}$, 5 mol.% YSZ is $\sim$6.0 g cm$^{-3}$ and 8 mol.% YSZ is $\sim$5.9 g cm$^{-3}$ using:

$$TD \text{ (\%)} = \frac{\text{Measured density (g cm}^{-3})}{\text{Theoretical density (g cm}^{-3})} \times 100\%$$

Eqn. 3.08

Where; TD (%) is the measured percentage of theoretical density of the sample.

### 3.4.2 Optical microscopy

Fracture surface analysis of die pressed green samples was carried out using an optical microscope (Reichert Jung MeF3, Wein, Austria). In the bright field mode, it enabled identification of the presence of agglomerates, uncrushed granules and surface flaws under $\times$10 and $\times$20 magnifications in the green samples after pressing.
3.4.3 **Field emission gun scanning electron microscopy**

Granules, agglomerates, microstructures, and the morphology of the zirconia starting powders were examined using the field emission gun scanning electron microscope (FEGSEM) (Leo 1530VP FEGSEM, LEO Elektronenskopie GmbH, Oberkochen, Germany) at higher magnifications. The powders were dispersed onto carbon pads, mounted on aluminium stubs. The fracture surfaces of green samples were analysed to verify the absence of agglomerates or uncrushed granules. The microstructures of sintered samples were observed on polished, etched surfaces.

Field emission gun scanning electron microscope samples were sputter coated with gold using an EMITECH SC7640 sputter coater (Quorum Technologies, Ashford, Kent, UK) to create a conductive path, preventing charge build up during analysis.

Micrographs were taken using an in-lens detector with an aperture size of 30 µm, accelerating electron voltage of 5 kV and working distance of 5 mm.

3.5 **Sintering**

Conventional sintering was carried out on all the YSZ samples used in this project. The conventional box type furnace (Carbolite Ltd. UK) consisted of SiC heating elements with a Eurotherm 902 temperature controller (Eurotherm Ltd., UK) and a K-type thermocouple.

A series of sintering profiles based on single and two step sintering were used to achieve variations in grain size, from the nano to micron range, with densities above 98% theoretical density.
3.5.1 Single-step sintering
Single step sintering involved a slow heating rate of 3°C min\(^{-1}\) to the required temperature where each sample was held for a given amount of time, from 60 minutes to 300 minutes, depending on the material. 3 mol.% YSZ required lower sintering temperatures compared to 5 mol.% YSZ and 8 mol.% YSZ to achieve a density of above 98% theoretical density. Single-step sintering will be discussed in more detail in section 4.4.

3.5.2 Two-step sintering
Two-step sintering involved a faster heating rate of 10°C min\(^{-1}\) to the first temperature, known as T1, which was held for a short period of time, usually 0.1 minutes to 0.5 minutes. The temperature was then decreased to T2 and held for a longer period of time of 600 minutes. A cooling rate of 10°C min\(^{-1}\) was used to bring the furnace back down to room temperature. In two-step sintering, lower temperature profiles were used to sinter 3 mol.% YSZ to produce fully dense sintered samples, as opposed to 5 mol.% YSZ and 8 mol.% YSZ. Two-step sintering will be discussed in more detail in section 4.4.

3.6 Characterisation of sintered bodies
3.6.1 Sintered density measurements
Analysis of the sintered density of YSZ samples was carried out via the geometrical method and or using the Archimedes principle. In the geometrical method, calculations were based on the mass of the sample (measured to the nearest 0.0001 g) and the dimensions (measured to the nearest 0.01 mm). A mean value on the measured dimensions was used,

\[ \rho = \frac{M}{V} \]

Eqn. 3.09
Where; \( \rho \) is the density \((g \text{ cm}^{-3})\), \( M \) is the mass of the sample \((g)\) and \( V \) is the geometrical volume of the sample \((\text{cm}^3)\).

The sintered density calculated based on the Archimedes principle in de-ionised water:

\[
\rho = \frac{M_s \times \rho_l}{M_s - M_l}
\]

Eqn. 3.10

Where; \( M_s \) is the mass of the sample in air, \( M_l \) is the mass of sample in de-ionised water and \( \rho_l \) is the specific gravity of de-ionised water at the measurement temperature. Measurements were made to the nearest 0.0001 g.

The theoretical density of the measured samples can be calculated based on the theoretical densities given for 3 mol.% YSZ as \(~6.1 \text{ g cm}^{-3}\), 5 mol.% YSZ is \(~6.0 \text{ g cm}^{-3}\) and 8 mol.% YSZ \(~5.9 \text{ g cm}^{-3}\) using,

\[
TD (\%) = \frac{\text{Measured density (g cm}^{-3}\)}{\text{Theoretical density (g cm}^{-3}\)} \times 100\%
\]

Eqn. 3.11

Where; \( TD (\%) \) is the measured percentage of theoretical density of the sample, measured density is the actual density of the sample and theoretical density is the literature value of densities for the various samples.

3.7 Morphology

3.7.1 Sample preparation

In the preparation of samples for viewing microstructures and taking grain size measurements, samples required polishing and thermal etching. In order to ensure a
smooth flat polished surface was achieved, samples were mounted in epoxy using a Struers EpoFix kit (Struers Ltd., Rotherham, UK) with 15 ml of epoxy resin and 3 ml of hardener. The samples embedded in epoxy were allowed to cure for at least 24 hours.

The mounted samples were polished using a semi-automatic polishing machine, Struers TegraPol-25 (Struers Ltd., Rotherham, UK) with an automatic feeding system for the polishing suspension, TegraDoser-5, (Struers Ltd., Rotherham, UK) and a TegraForce-5 (Struers Ltd., Rotherham, UK) rotating sample holder. In a typical polishing cycle, MD-Piano polishing discs of 220, 600 and 1200 grit were used, respectively. Finally, an MD-DAC polishing disc was used with an MD-DAC 3 µm diamond suspension. Samples were cleaned with methanol after polishing to remove contamination and remains of polishing media.

Samples were subsequently removed from the epoxy by heating in an oven at 150°C for about 10 minutes. This softened the epoxy, enabling the samples to be retrieved.

Thermal etching was carried out on polished sintered samples. A thermal etching cycle at a temperature of 100°C lower than the sintered temperature was used to enhance the original grains without unnecessary grain growth. Samples were held at the required temperature for one hour, using heating and cooling rates of 10°C min⁻¹.

These sintered samples underwent gold coating (refer to FEGSEM) before analysis.

In the preparation of TEM samples, an FEI Nova 600 Nanolab dual-beam focused ion beam (FIB) / field emission gun scanning electron microscope (FEGSEM) (FEI, Eindhoven, the Netherlands), with a Pegasus combined EDAX electron backscatter diffraction (EBSD) and energy dispersive spectroscopy (EDS) system (EDAX, Mahwah, NJ, USA) was used. The FIB uses a liquid gallium source, and a 30 kV accelerating voltage was used throughout, producing a typical sample thickness of <100 nm.
A 500 nm thick platinum layer was deposited on the surface of the section to be analysed using the ion beam to help homogenise the cut surfaces. The initial stage for this involved moving the sample to the ion beam milling position. The gallium ion beam current of 3 nA was used for milling the slices. Parameters such as focus, stigmation, contrast and brightness required for slice milling and initial mill box position were set. Other parameters that control the number of slices, slice thickness and depth of cut were also input. Once the slice was made, it was lifted onto a TEM copper grid by platinum deposition using a micromanipulator. Final thinning was carried out to the required thickness of less than 100 nm for HRTEM analysis.

### 3.7.2 Morphological measurements

Microstructures were analysed and grain size measurements were carried out on polished and etched samples using the FEGSEM. Micrographs were taken using an in-lens detector with an aperture size of 30 µm, accelerating electron voltage of 5 kV and working distance of 5 mm.

The grain size of sintered samples was calculated based on the linear intercept method (ASTM E 112-96),

$$D = \frac{L \times A_1}{M \times N}$$

Where; $D$ is the equivalent mean grain size (m), $L$ is the length of the superimposed lines (m), $A_1$ is the shape correction factor (1.56), $M$ is the magnification used in the micrographs (dimensionless) and $N$ is the number of intercepts obtained.

Phase determination was carried out using XRD (refer to XRD) and micro-Raman spectroscopy (refer to micro-Raman spectroscopy) using similar testing parameters.
A Philips Tecnai F 20 HRTEM microscope (Birmingham University, UK) was used to record the HRTEM images, study the grain boundary segregations, presence of impurities and lattice parameters of the samples.

### 3.8 Electrical properties

#### 3.8.1 Impedance spectroscopy sample preparation

In the preparation of samples for AC impedance measurements, samples were required to be cut to the required size, allowing them to fit between the platinum electrode meshes. The fully dense sintered samples of M3, M5, M8, T3, T5 and T8 with varying grain sizes were cut into rectangular sections of about 0.5 mm × 0.3 mm using a diamond cutting blade.

Platinum paint (Johnson Mattey, London, UK) was used as the electrodes, being applied to the top and bottom surfaces of the sample and after drying, sintered at 850°C for 60 minutes.

#### 3.8.2 Impedance spectroscopy measurements

The bulk and grain boundary resistivity of the sintered samples were determined by alternating current (AC) impedance spectroscopy, measurements carried out in a protective alumina tube within a tubular furnace.

The AC ionic conductivity measurements were carried out on the sintered samples using a Solartron SI 1260 impedance/gain phase analyser in atmospheric air with amplitude of 100 mV in the frequency range 1 Hz to 1 MHz. The temperature was varied from 200°C to 500°C at 20°C intervals, and one hour was allowed for equilibration at each new temperature measurement. 19 points per decade of frequency were measured whilst scanning from the highest to the lowest frequency. The bulk, grain boundary and contact contributions to the impedance were fitted by
an equivalent circuit comprising a parallel resistor and constant phase element for each observed arc.

![Equivalent Circuit Diagram]

Figure 3.02 – A typical equivalent circuit. Q is the constant phase element

Constant phase elements were used in the modelling instead of simple capacitors since they better describe the real system with its depressed arcs, via the program ZView (Version 3.3a, Scribner Associates, Inc., North Carolina, United States of America).

![Impedance Spectroscopy Setup Diagram]

Figure 3.03 – Schematic of setup for impedance spectroscopy

3.8.3 DC four-probe sample preparation

In the preparation of samples for DC four probe measurements, samples were required to be cut to allow the platinum wire connections to be wrapped around the samples. The sintered samples of M3, M5, M8, T3, T5 and T8 with full density and a variety of grain sizes were cut into rectangular cuboids of about 20 mm × 0.5 mm × 0.3 mm using a diamond cutting blade.

Platinum wires (Johnson Mattey, London, UK) were tied around the samples, which were connected to the power supply, ammeter and voltmeter, measuring voltage
and current. Platinum paint was applied on the samples along the wires to ensure a good connection. The platinum was sintered at 850°C for 60 minutes before measurements were carried out.

### 3.8.4 DC four-probe measurements

The total electrical conductivity from bulk and grain boundary of the sintered samples was measured in atmospheric air within a temperature range of 250°C to 950°C at 50°C intervals, one hour was allowed for equilibration at each new temperature measurement. The four-probe measurement technique was based on a TTi QL355TP (TTi, Cambridge, UK) power supply and two Blackstar 4503 intelligent multimeters (TTi, Cambridge, UK), which were used to apply a current and to measure the voltage drop, respectively.

![Figure 3.04 – Schematic of the setup for DC four-probe measurements](image)

The power supply controlled the applied current, whilst the voltage across the sample dimension is measured. Based on the measured current and voltage, the resistance was calculated. The resistance of each sample varies with temperature.

\[
R = \frac{V}{I}
\]

Where; \( R \) is the resistance (\( \Omega \)), \( V \) is the potential difference (V), and \( I \) is the current (A).
4.1 Characterisation of materials

The as-received YSZ suspensions and powders used in this study were characterised using the following methods to obtain a good understanding of the materials before processing.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Material codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEL 3 mol.% suspension</td>
<td>M3</td>
</tr>
<tr>
<td>MEL 5 mol.% suspension</td>
<td>M5</td>
</tr>
<tr>
<td>MEL 8 mol.% suspension</td>
<td>M8</td>
</tr>
<tr>
<td>Tosoh 3 mol.% powder</td>
<td>T3</td>
</tr>
<tr>
<td>Tosoh 5 mol.% powder</td>
<td>T5</td>
</tr>
<tr>
<td>Tosoh 8 mol.% powder</td>
<td>T8</td>
</tr>
</tbody>
</table>

Table 4.01 – Material codes used to denote the materials used in this study

One of the materials, M3 was prepared via both wet and dry forming routes to demonstrate that the chosen processing route does not significantly change the primary properties of the material.

4.1.1 X-ray diffraction spectroscopy

Powder samples of M3, T3, M5, T5, M8 and T8 were analysed at room temperature and the diffraction patterns obtained are compared with the standards from the Joint Committee on Powder Diffraction Standards (JCPDS), shown in Figure 4.01, 4.02 and 4.03 respectively.
In Figure 4.01, the nano M3 powder displays a tetragonal phase whilst the submicron T3 powder contains a partial monoclinic phase in the structure, identified by 'm'. At a low yttria content of 3 mol.% YSZ, the presence of monoclinic phase can be expected. However, the presence of the tetragonal phase is attributed to the self-stabilisation of the zirconia, a result of the ultrafine particle size.

Figure 4.02 – XRD spectra of tetragonal, M5 and T5 powders
In Figure 4.02, the nano M5 powder displays a tetragonal phase, without any sign of monoclinic phase, whilst the submicron T5 demonstrates a small amount of monoclinic phase, less than that of T3 in Figure 4.01.

Figure 4.03 compares M8 and T8 with the benchmark cubic pattern. Both materials were shown to possess a stabilised cubic phase, which could be well explained as 8 mol.% YSZ should be fully stabilised. There is no indication of monoclinic or tetragonal phases present based on the diffraction spectra shown below.

![XRD spectra of cubic, M8 and T8 powders](image)

Based on the X-ray diffraction patterns measured at room temperature, it was observed that T3 and T5 exhibit a monoclinic phase, which was further investigated using high temperature X-ray diffraction, shown in Figure 4.04 and 4.05, and Micro-Raman spectroscopy shown in Figure 4.06 and 4.07.
In Figure 4.04, monoclinic peaks are observed at room temperature, at 1400°C a tetragonal pattern is displayed, with no suggestion of a monoclinic phase present. Based on the high temperature XRD results, when T3 is heated to above 500°C, monoclinic phase can no longer be detected with the detection limit of 5%. The amount of monoclinic phase decreases with increasing temperature, which is expected due to crystallisation. The same is shown for T5 in Figure 4.05.
Note that the results are accurate in detecting the monoclinic phase when there is more than 5% by volume present.

4.1.2 Micro-Raman spectra

The micro-Raman spectra of the as-received materials are shown in Figure 4.06 to Figure 4.07. A comparison was carried out on samples from different sources containing the same amount of yttria. Tetragonal peaks are denoted by ‘+’ whilst the unmarked peaks correspond to monoclinic zirconia. The major peaks that represent tetragonal phase in zirconia are at 148 cm\(^{-1}\) and 264 cm\(^{-1}\) whilst the monoclinic doublet is at 181 cm\(^{-1}\) to 192 cm\(^{-1}\). The peak at 476 cm\(^{-1}\) is a common peak found in both monoclinic and tetragonal phases. For a fluorite structure of zirconia in the cubic phase, a well-defined Raman active frequency should be expected near 617 cm\(^{-1}\) [220].

![Raman spectra](image)

**Figure 4.06 – Raman spectra of powder made from M3 suspension and T3 powder showing the presence of tetragonal and monoclinic peaks**

In Figure 4.06 for M3 and T3, there is an indication of monoclinic phase combined with tetragonal phase. This coincides with the results from XRD, which was able to detect the presence of monoclinic phase better than micro-Raman. The signal in
XRD is collected from a thin layer on the surface of the sample whilst the laser beam in micro-Raman can penetrate deeper into the sample. The micro-Raman penetration depth is dependent on the optics used, for 3 mol.% YSZ it may vary from 5 µm to 40 µm depending on the laser power and the pinhole aperture, when used in the confocal configuration [221]. Hence, Raman scattered signals were collected from surrounding areas of the sample. The surfaces of the prepared zirconia samples are less constrained during sintering and subsequent sample preparation, hence it is more likely that the surface layer will transform into monoclinic phase, especially for samples with a low yttria concentration. This explains the increase in intensity of the monoclinic peaks found using XRD spectroscopy and the decrease in intensity found using micro-Raman spectroscopy.

Figure 4.07 – Raman spectra of powder made from M5 suspension and T5 powder showing the presence of monoclinic peaks in T5 and tetragonal peaks in M5

In Figure 4.07, the presence of monoclinic still persists in T5, which matches with the XRD results. The intensity of the monoclinic peaks found in the range of 181 cm$^{-1}$ to 192 cm$^{-1}$ in T5 are lower than that of those found in T3 and M3, however the intensity is still relatively large due to the monoclinic phase absorbing around 30 times stronger than the tetragonal phase [222]. This increases the intensity of
monoclinic peaks and inevitably shadows the tetragonal peaks. M5 displayed a purely tetragonal phase at 264 cm\(^{-1}\).

Although both M8 and T8 exhibit strong cubic peaks at 617 cm\(^{-1}\) in Figure 4.08, T8 demonstrated a significant indication of a tetragonal peak at 264 cm\(^{-1}\), which is not found by XRD as tetragonal and cubic peaks are very similar. The M8 spectrum shows cubic peaks only.

![Raman spectra](image)

Figure 4.08 – Raman spectra of powder made from M8 suspension and T8 powder showing the presence of cubic peaks only

The factors affecting Raman intensity in the results could be due to the refractive index, colour and temperature of the samples.

### 4.1.3 Solid content determination

The solid contents of the as-received aqueous suspensions, M3, M5 and M8 were measured and tabulated in Table 4.02.
Material (MEL Chemicals)  | Yttria content / mol.% | Solid content / wt.%
--- | --- | ---
M3  | 3  | 27 ± 0.2
M5  | 5  | 21 ± 0.2
M8  | 8  | 34 ± 0.2

Table 4.02 – Solid content of as-received suspensions of M3, M5 and M8

Results were determined experimentally and measured using a three decimal place balance. The information on yttria concentration was provided by supplier.

4.1.4 Zeta potential measurements

The zeta potential of as-received nanosuspensions, M3, M5 and M8 were measured and are presented in Figure 4.09, along with the for a pure zirconia powder from MEL.

Figure 4.09 – Zeta potential of as-received nanosuspensions of M3, M5 and M8
0 mol.% YSZ was included in the figure to demonstrate a gradual change in iso-electric point (IEP) with the increase in yttria concentration, from 0 to 8 mol.% yttria. The IEP for 0 mol.% YSZ was at pH 8.5 and it increases to pH 9.0, pH 9.6 and pH 10.4 for M3, M5 and M8 respectively. Since at the IEP, at 0 mV where the particles are held together by the very high van der Waals forces with zero net repulsion between the particles, the suspension is flocculated. In order to retain homogeneity, it is essential to carry out concentration of the suspension at high zeta potential, away from the IEP. Even though a higher zeta potential is achievable in the acidic region, which matches with the starting pH of the as-received suspensions, the pH of as-received suspensions was adjusted to the alkaline region before concentration was carried out. This was implemented to prevent yttria dissolution under acidic conditions [77]. Also, no suitable cationic dispersant had been found for the acidic region. TAC is an anionic dispersant, and operates in the alkali region for zirconia based suspensions.

The amount of dispersant within the suspension can alter the IEP and modify the zeta potential, as shown in Figure 4.10. Based on the results, the IEP of the as-received M3 nanosuspension is at pH 8.8, however, with the addition of 1 wt.%, 2 wt.% and 3 wt.% of TAC, the IEP shifts from pH 7.9, to pH 6.5 and then pH 4.3, respectively. This means that with the addition of 3 wt.% dispersant during suspension concentration, which was undertaken at about pH 9.5, the zeta potential had a high value and the suspension was well dispersed.
4.1.5 Transmission electron microscopy

The TEM micrographs of the materials used in this study are shown in Figure 4.11. M3, M5 and M8 displayed a narrow particle size between 10 and 15 nm and appear to be very well dispersed whilst T3, T5 and T8 consist of particles of a wide range between 100 and 200 nm and they form agglomerates of about 600 nm in size. T5 presented a larger particle size compared with the rest, possibly due to the fact that it is not commercially available and it was obtained by request. T3, T5 and T8 also appear to be slightly agglomerated based on the figure shown. Only dry samples can be looked at in the TEM, therefore the suspension preparation and drying methods are likely to be important when examining the state of dispersion in the original suspensions.
4.1.6 **Viscosity measurements**

Viscosity measurements were carried out on all of the as-received suspensions, M3, M5, M8, as well as concentrated M3 and M5. M3 represents 3YSZ as-received (~27 wt.%) suspension with a solid content of about 27 wt.%, it displayed low viscosity, similar to M5 as-received at solid content of about 21 wt.%. M3 concentrated to 57 wt.% is the benchmark in terms of viscosity, commonly used to form green bodies at a later stage. Since it exhibits adequate rheology, it enables the concentrated suspension to flow during the slip casting and spray freeze drying processes. This is crucial as poor rheological properties in concentrated suspension contribute towards the agglomeration of particles in the suspension, which will worsen during forming of green bodies.
Chapter 4 Results & Discussion

Viscosity inevitably increases during the concentration process, as demonstrated by Figure 4.12. The role of dispersant, triammonium citrate (TAC) aids in keeping the suspension homogeneous and the particles well dispersed. Whilst the dispersant benefits the viscosity, it also increases the amount of organics within the suspension, which can cause problems during binder removal. As Figure 4.12 shows, when the amount of TAC was increased from 3 to 4 wt.% in the concentrated 5YSZ suspension of 45 wt.%, the viscosity reduced dramatically. Even though the M5 suspension was concentrated to 45 wt.% with additional amounts of dispersant at 4 wt.%, the viscosity is still higher than that of the benchmark M3 suspension. This is because the IEP of M5 suspension is at a higher pH value than that of the M3 suspension, resulting in a reduced zeta potential at the working pH, giving higher van der Waals forces. This suggests that M5 consists of more agglomerated particles within the suspension and a different dispersant may be required to reduce the viscosity further, allowing a higher solid content to be achieved. The figure also
shows the viscosity of M8 as-received suspension, at a solid content of 34 wt.%. This is the highest viscosity amongst the as-received and concentrated suspensions. No further concentration of M8 was carried out since higher viscosities could not be tolerated during subsequent processing.

4.2 Forming of green samples

In the formation of green samples, the primary aim is to produce defect-free, homogeneous, high green density samples, regardless of the route used in the preparation. This was one of the biggest challenges in this study, especially in the preparation of M3, M5 and M8 to produce nanostructured ceramics after sintering.

The best green samples produced from M3 were obtained using a 57 wt.% concentrated suspension, further increase of solid content resulted in cracking of the samples during drying. The slip casting technique for use with nanosuspensions, particularly for M3, has been well studied and developed by the Ceramics Group at Loughborough University [19,20]. In a separate report, cracking of nano zirconia prepared at a high solid content for slip casting has also been observed. An optimum solid content of about 60 wt.%, was derived from the study [81].

Even though the preparation of M3 via slip casting has been well developed, the same method does not work for M5 and M8. This is mainly due to the poor control over viscosity during concentration to a solid content above 50 wt.%. As demonstrated in section 4.1.7, even with the addition of 4 wt.% TAC to M5, the viscosity remained high. Similarly for M8, the starting viscosity was much higher than the benchmark M3 at 57 wt.%, which made it difficult to bring down the viscosity whilst increasing the solid content. Hence, alternative methods were used in the preparation of M5 and M8. Processing of M5 and M8 was based on the dry forming route, spray freeze drying, to obtain granules that were subsequently die pressed. M5 was concentrated to about 45 wt.% solid content with the addition of 4 wt.% TAC and 2 vol.% Freon before being spray freeze dried. M8 was sprayed
freeze dried with the addition of 2 vol.% Freon without any further concentration. The vacuum dried granules were uni-axially die pressed at a relatively high pressure of 320 MPa, a much higher pressure compared to the norm for industry, which is in the range of 150–200 MPa. The compacts were further densified with the aid of an isostatic press at 250 MPa, which gave a more uniform density across the sample. This increased the green density from about 52% theoretical density to 54-57%. However, the high pressure required for die pressing M5 and M8, limited the size of samples that could be produced.

As for the commercially available submicron powders, T3, T5 and T8, they underwent uni-axial pressing at about 150 MPa, which resulted in green densities of about 55% of theoretical density. The compacts were also further densified using the isostatic press at a pressure of 250 MPa, density increments between 2 to 5% were observed. These pressures are comparable to those used in industry.

### 4.3 Characterisation of green samples

These samples were characterised based on their morphology, green density after binder removal and fracture surface analysis. The green samples prepared by slip casting and die pressing were characterised before sintering. The characterisation was based on the green density and fracture surface of die pressed samples. This determined the presence of low green density, defects and uncrushed agglomerates within the green sample. Hence, with all the green samples, density was measured and found to be between 55 to 60% of theoretical density. The density within the range was dependent on the particle size, the technique used in preparing samples, and the method used to carry out the measurements, i.e. geometrical, or Archimedes principle.

Generally, finer particles exhibit a higher surface energy, which increases the attractive forces between particles. The ability to form hard agglomerates is higher in nano sized particles compared with submicron sized particles and this affects the
green density of the sample. The use of the geometrical density measurement technique usually presents a lower value of theoretical green density compared with the Archimedes method. The geometrical method measures the size of samples using Vernier Callipers to calculate the volume. This often results in inaccurate measurements, due to the presence of surface defects on the sample whilst the measurements taken from the Archimedes method enables more precision and control through the sample’s mass in air and mercury.

4.3.1 Nano & submicron 3 mol.% YSZ

Figure 4.13 shows the FEGSEM micrographs of M3 granules after spray freeze drying. At low magnification it shows many spherical spray freeze dried granules, with a narrow size distribution. On the micrograph that shows the individual granule, it can be seen that there are surface flaws present on the granules, this is the effect of adding Freon. Freon has been demonstrated to create surface flaws during spray freeze drying, which weakens granules, thus enhancing the crushability during compaction [223]. In the high magnification image, the surface flaws that aid in the crushability during compaction can be seen in detail, these are key to achieving a high green density with nanoparticles.
Micrographs of the fracture surfaces of green compacts made from 57 wt.% solid content M3 nanosuspensions are shown in Figure 4.14, which displayed a uniform microstructure. This was aided by the good dispersion of nanoparticles in the original nanosuspensions and there are no signs of hard uncrushed agglomerates.
Figure 4.15 show the micrographs of T3 as-received powders. As compared to M3 in Figure 4.13, T3 exhibits a smaller granule size, spherical in shape with a smoother surface finish, which also aids flowability into the die for compaction. The size distribution of the granules is seen to be similar to that of M3 in Figure 4.13.

![Micrographs of T3 powders](image)

**Figure 4.15 – FEGSEM images of Tosoh 3 mol.% YSZ submicron powders**

The fracture surface of T3, shown in Figure 4.16 demonstrates a rougher microstructure compared to M3, seen in Figure 4.14, which may suggest the presence of hard uncrushed agglomerates or granules. Hard agglomerates are often accompanied by cracks and the formation of obvious spherical shapes, which are shown as below.
Figure 4.16 – FEGSEM images of green compacts made from Tosoh 3 mol.% YSZ submicron powders

4.3.2 Nano & submicron 5 mol.% YSZ

The granules formed from as-received M5 suspension, spray freeze dried without the addition of dispersant or Freon are illustrated in Figure 4.17. The granule may be close to spherical in shape but it can be seen that the surface layer is covered by flakes; this hinders flowability into the die for compaction. At just 21 wt.% solid loading, it is difficult to ensure good crushability and achieve a high green density greater than 50%.

Figure 4.17 – FEGSEM images of spray freeze dried granules made from 21 wt.% solid content M5 nanosuspensions

Figure 4.18 illustrates the spray freeze dried granules of concentrated M5 at 45 wt.%, without the use of dispersant or Freon. It produced spherical shape granules, with rough surface finish, which not only caused flowability problems, but also a lack
of crushability. Hard granules are often represented by a continuous surface without flaws; this would oppose compaction and prevent the break down granules into their primary particles, in the nano range.

Figure 4.18 – FEGSEM images of spray freeze dried granules made from 45 wt.% solid content M5 nanosuspensions

In Figure 4.19, M5 was concentrated to 45 wt.% and with the addition of 3 wt.% TAC and 2 vol.% Freon. At higher magnification, flaws can be seen on the surface of the granules, which indicate ease of crushability during compaction. However, the shape of the granules needs to be optimised for flowability. This could be carried out with the addition of more dispersant, say 4 wt.%.

Figure 4.19 – FEGSEM images of spray freeze dried granules made from 45 wt.% solid content M5 nanosuspensions with 3 wt.% TAC
Hence, in Figure 4.20 where 4 wt.% TAC was added, it demonstrates better dispersion, producing more spherical granules. The surface flaws visible are similar to those found benchmark M3, see Figure 4.13.

Figure 4.20 – FEGSEM images of spray freeze dried granules made from 45 wt.% solid content M5 nanosuspensions with 4 wt.% TAC

The fracture surface of M5 (45 wt.% with 4 wt.% TAC) shown in Figure 4.21 displays a relatively smooth surface, without the indication of hard agglomerates. The dark specks seen on the micrographs are gold flakes from the sputter coater during sample preparation, commonly found on coated samples as it exist in the range of 10 to 20 nm. This was supported by EDX analysis.

Figure 4.21 – FEGSEM images of green compacts made from spray freeze dried granules made from 45 wt.% solid content M5 nanosuspensions
Figure 4.22 illustrates T5 as-received powders with a wide distribution of granule sizes and rough surfaces, which exhibits poor flowability into the die for compaction due to the flakes around the granules. Compared to M5 from Figure 4.20, T5 possess smaller granules with rougher surfaces, which would not possibly produce good green microstructures.

Figure 4.22 – FEGSEM images of Tosoh 5 mol.% YSZ submicron powders

Figure 4.23 consists of contours on the fractured surface from T5. These features, very similar to those shown in Figure 4.16, suggest the presence of hard agglomerates. However, based on Figure 4.23, the rough surface contours may be due to an inhomogeneous green density.

Figure 4.23 – FEGSEM images of green compacts made from Tosoh 5 mol.% YSZ submicron powders
4.3.3 Nano & submicron 8 mol.% YSZ

In Figure 4.24, M8 as-received suspension at 33 wt.% solid content was spray freeze dried with the addition of 2 vol.% Freon. As shown in Figure 4.12, the viscosity for M8 at 33 wt.% solids is much higher, compared to the as-received suspensions of M3 and M5. This hinders the possibility of further concentration whilst reducing the viscosity of the suspension and simultaneously keeping it well dispersed and homogeneous. Since the intention was to obtain granules that were able to crush down to their primary particle sizes, it was important to maintain a low viscosity that was suitable for spray freeze drying.

Figure 4.24 – FEGSEM images of spray freeze dried granules made from 33 wt.% solid content M8 nanosuspensions

In Figure 4.25, the fracture surface of M8 after compaction was shown. Based on Figure 4.24, the granule sizes ranges between 50 µm to 200 µm. Uncrushed granules would be seen under low magnification, which is not evident in either micrograph, Figure 4.25. The green microstructures appeared to be uniform and homogeneous.
Figure 4.25 – FEGSEM images of green compacts made from spray freeze dried granules made from 33 wt.% solid content M8 nanosuspensions

The spray dried T8 granules, shown in Figure 4.26 consists of a wide distribution of sizes. The surface finish is very different compared to the granules produced from M8 suspension, seen in Figure 4.24; however it is very similar to that of T3.

Figure 4.26 – FEGSEM images of Tosoh 8 mol.% YSZ submicron powders

The fracture surface seen in Figure 4.27 resembles that of the T3 fracture surface seen in Figure 4.16. These green microstructures are not as uniform as the ones from M8 granules, in Figure 4.25. This could be due to the larger particle sizes of T8 compared to the nanoparticles found in M8.
In the green forming of YSZ, the selection of and the amount of dispersant play an important role in controlling the viscosity of suspension. Flocculation of particles is the main cause of high viscosity, which leads to the formation of inhomogeneous green bodies. This is often accompanied by uncrushed granules in the green body, however, 2 vol.% Freon acted as a foaming agent and created surface flaws to the spray freeze dried granules, enabling a higher and more uniform green density to be achieved during compaction. A minimum green density of 50% was essential to achieve fully dense samples with well-controlled grain sizes. Any uncrushed granules in the green samples resulted in regions of excessive grain growth with poor sintered density.

4.4 Single-step & two-step sintering

Sintering of slip cast and die pressed samples was based on single and two-step methods. Different sintering profiles were used to achieve samples with a high sintered density and a variety of grain sizes.

In the following tables, single-step and two-step sintering are denoted by SS and TS respectively. The dwelling time used is in minutes (min) and the heating and cooling rates are in °C min⁻¹. In order to minimise the variables between samples, the heating and cooling rates for all single-step sintered was maintained at 3°C min⁻¹,
whilst the heating and cooling rates for all two-step sintered samples was maintained at 10°C min\(^{-1}\). Temperature and dwelling time plays an effect on the sintered density and final grain sizes; all of these will be discussed in this section.

### 4.4.1 3 mol.% YSZ nano & submicron sintered samples

Sintering of nano 3 mol.% YSZ(M3) has been studied to a great extent by the Ceramics Group at Loughborough University to achieve variations in grain size without compromising the sintered density. A bi-modal pore size distribution for nano zirconia green samples prepared via the dry forming route was reported by Zych, whilst a mono-modal was observed for samples formed via the wet route with equivalent green densities [224]. The large pores found in the die-pressed samples corresponded to the inter-agglomeration porosity, and the smaller ones to the intra-agglomerated pores. The presence of open porosity was reported to persist even at a density above 97% theoretical density. A low green density reduces the amount of contact points between the particles, hence reduces the number of matter transport paths, and as a result decreases the degree of densification. In a study conducted by Gao, it was found that a decrease in green density of 12% in nano TZP would cause the number of transport paths to be reduced by a massive 50% [98]. In a report by Maca, the compaction of nano zirconia at high pressure of 1000 MPa reduced the maximum pore size to 4.5 nm, compared to 9 nm at 300 MPa, and the green densities were measured to be 57% and 42% respectively [225].

The densities and grain sizes of 3 mol.% YSZ samples sintered using both single and two-step profiles are summarised in Table 4.02 and Table 4.03 respectively. It can be observed that during single-step sintering, the density increased with temperature until it reached a maximum, then any further increase of temperature caused a detrimental effect on density. This reduction in density is known as de-sintering or bloating, due to oversintering and has been reported in nano ceramics. [104,226,227]
In the study by carried out by Paul, a single-step sintering profile used with a maximum temperature of 1100°C and a dwell time of 30 hours brings about a reduction of density from 99.7% to 99.1% compared to a dwell time of 10 hours. This also increased grain growth by about 13 nm. A series of sintering studies were also carried out using short dwell times of 0.1 min in the temperature range of 1050°C to 1150°C, and the results showed that densities were below 95.6%, however, the grain sizes were kept at below 80 nm.

Hence, the sintering temperatures and dwell times used in this study were selected based on previous studies to achieve above 98.5% theoretical density with a variation of grain sizes.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>T1 / °C</th>
<th>Time / min</th>
<th>Density / % theoretical</th>
<th>Mean grain size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3SS-1050-600</td>
<td>1050</td>
<td>600</td>
<td>98.7</td>
<td>105</td>
</tr>
<tr>
<td>M3SS-1050-1200</td>
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<td>1200</td>
<td>98.5</td>
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<td>600</td>
<td>99.4</td>
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<td>195</td>
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<td>T3SS-1350-120</td>
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<td>120</td>
<td>99.2</td>
<td>280</td>
</tr>
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<td>T3SS-1350-300</td>
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<td>300</td>
<td>98.5</td>
<td>300</td>
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<tr>
<td>T3SS-1350-600</td>
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<td>600</td>
<td>89.5</td>
<td>380</td>
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<td>T3SS-1350-1200</td>
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<td>1200</td>
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<td>T3SS-1400-600</td>
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<td>600</td>
<td>88.2</td>
<td>350</td>
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</tbody>
</table>

Table 4.03 – Single-step sintering of 3 mol.% YSZ
Figure 4.28 – FEGSEM micrographs of 3 mol.% YSZ samples using single-step conventional sintering a) M3SS-1050-600 b) M3SS-1050-1200 c) M3SS-1100-600 d) M3SS-1300-600 e) T3SS-1350-120 f) T3SS-1350-300 g) T3SS-1350-600 h) T3SS-1400-600
Representative micrographs of the samples after single-step sintering are shown in Figure 4.28.

Based on the micrographs in Figure 4.28, a comparison was carried out on the effect of temperature and time on the density and grain size. Sintering of T3 to achieve above 98.5% theoretical density required a much higher temperature of 1350°C compared to M3 at 1050°C. Grain sizes are in the range of 100-250 nm for M3 compared to about 250-400 nm for T3. In general, with increasing temperature the mean grain size also increased, however in the ‘oversintered’ samples, the density started to decrease again. This occurred for grain sizes above about 150 nm for the M3-based samples, and above about 250 nm for the T3-based samples. Therefore a balance has to be found when trying to minimise grain growth whilst maximising densification.

The data for the two-step sintering used on the 3 mol.% YSZ samples is tabulated in Table 4.03. These profiles were selected based on previous studies carried out to achieve full densification with variation in grain sizes.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>T1 / °C</th>
<th>Time / min</th>
<th>T2 / °C</th>
<th>Time / min</th>
<th>Density / % theoretical</th>
<th>Mean grain size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3TS-1100</td>
<td>1100</td>
<td>0.1</td>
<td>1050</td>
<td>600</td>
<td>96.4</td>
<td>70</td>
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<td>0.1</td>
<td>1050</td>
<td>600</td>
<td>99.5</td>
<td>90</td>
</tr>
<tr>
<td>M3TS-1150-2</td>
<td>1150</td>
<td>0.1</td>
<td>1100</td>
<td>600</td>
<td>99.7</td>
<td>170</td>
</tr>
<tr>
<td>M3TS-1550</td>
<td>1550</td>
<td>0.1</td>
<td>1100</td>
<td>600</td>
<td>99.0</td>
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<td>M3TS-1600</td>
<td>1600</td>
<td>0.1</td>
<td>1150</td>
<td>600</td>
<td>98.7</td>
<td>500</td>
</tr>
<tr>
<td>M3TS-1650</td>
<td>1650</td>
<td>0.1</td>
<td>1200</td>
<td>600</td>
<td>98.2</td>
<td>550</td>
</tr>
</tbody>
</table>

Table 4.04 – Two-step sintering of 3 mol.% YSZ
The theoretical density and mean grain sizes at T1, 1100°C for 0.1 minute were given at 89.9% and 66 nm respectively. Sintering M3 at 1100°C for 0.1 minute and 1050°C for 600 minutes resulted in a very fine mean grain size of 70 nm, but also low densification was obtained. In a report by Chen, he explained that a density of about 75% after the first step sintering would be sufficient to achieve nanostructured yttria samples with full densification during the second step, providing that the temperature used in the second step is reasonably high [74]. However, this was not proven to be the same for the use of YSZ in this study. Despite the achievement of above 89% theoretical density during the first step, it was not sufficient to produce sintered samples of above 98.5%, considering the high temperatures used in the second step. Hence, a higher temperature was required for the first step, so this is why 1150°C was used. At 1150°C of 0.1 minute and 1050°C for 600 minutes, samples were able to attain a density of about 99.5% theoretical density and a fine grain size of 90 nm. Grain growth started to occur as T2 was
increased above 1100°C and further increment of T1 and T2 gave a gradual decrease in sintered density, whilst grain growth increased significantly. As the purpose of this study was to obtain samples with above 98.5% theoretical density, there were no further attempts made after density decreased to 98.2% for sample sintered at 1650°C for 0.5 minute and 1200°C for 600 minutes.

According to the two-step sintering studies carried out, samples should achieve more than 95% theoretical density after the first step in order for M3 to attain above 99% density and a grain size below 100 nm. Graaf reported that grain growth in yttria-stabilised zirconia accelerates exponentially above 95% density during single-step sintering [60]. Hence, to limit the unnecessary grain growth, the density after first-step should be kept close to 95%. A report also showed that a T1 temperature between 1100°C to 1200°C demonstrates abnormal grain growth for nano zirconia and a minimal dwell time should be used at the T1 temperature in order to maximise density and minimise grain growth.

Figure 4.30 – Density vs. grain size of 3 mol.% YSZ for single-step (SS) and two-step (TS) sintering
Figure 4.30 shows a comparison between single-step and two-step sintering of 3 mol.% YSZ. Based on the results, the best sintering profiles used for M3 to produce a maximum density with minimal grain growth were found to be 1075°C for 600 minutes using a single-step sintering profile, and 1150°C for 0.1 minute, 1050°C for 600 minutes using a two-step sintering profile, both achieved sintered theoretical density of 99.5%.

4.4.2 5 mol.% YSZ nano & submicron sintered samples

As densification of 5 mol.% YSZ requires a higher temperature compared to 3 mol.% YSZ, the sintering profiles used were based on Table 4.04 and 4.05.

Single-step sintering was carried out on 5 mol.% YSZ with a temperature range from 1200°C to 1500°C. In the sintering temperatures used for M5, it was observed that closed porosity was not obtained at a density below 93%, sintered at 1300°C. Based on the micrographs in Figure 4.31, the grain size distribution was relatively narrow; however, grain sizes should not only be obtained at high magnification, 50,000×. At a lower magnification of 1000× or less, an overview microstructure of the sintered samples was displayed, which enables any defects, agglomerates or uncrushed granules to be shown. In the earlier section 4.31, on the powder characterisation of M5, numerous problems have been displayed in achieving spherical granules with surface flaws necessary to aid crushability during compaction. The compacts obtained using the better M5 powder (45 wt.% with 4 wt.% TAC) did not seem to sinter well under the conditions studied, as shown in Figure 4.32, which is based on M5SS-1300-600. A similar phenomenon was observed at the other sintering conditions used.


<table>
<thead>
<tr>
<th>Sample code</th>
<th>T1 / °C</th>
<th>Time / min</th>
<th>Density / % theoretical</th>
<th>Mean grain size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>M5SS-1200-600</td>
<td>1200</td>
<td>600</td>
<td>89.7</td>
<td>90</td>
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<tr>
<td>M5SS-1300-600</td>
<td>1300</td>
<td>600</td>
<td>93.0</td>
<td>140</td>
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<tr>
<td>M5SS-1400-600</td>
<td>1400</td>
<td>600</td>
<td>91.4</td>
<td>250</td>
</tr>
<tr>
<td>M5SS-1450-60</td>
<td>1450</td>
<td>60</td>
<td>90.2</td>
<td>380</td>
</tr>
<tr>
<td>T5SS-1450-60</td>
<td>1450</td>
<td>60</td>
<td>95.4</td>
<td>500</td>
</tr>
<tr>
<td>T5SS-1450-120</td>
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<td>120</td>
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<td>970</td>
</tr>
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<td>T5SS-1500-60</td>
<td>1500</td>
<td>60</td>
<td>98.5</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 4.05 – Single-step sintering of 5 mol.% YSZ

For sintering T5, the suggested temperature by Tosoh Corporation to fully density compacts is about 1450°C, which actually yielded a relatively low sintered density in this study. As seen in Figure 4.31 c) and d), the density was significantly higher when sintered at 1500°C compared to 1450°C, but the mean grain size also doubled as a result. However, the density needs to be further improved in order to achieve above 98.5%.
Figure 4.31 – FEGSEM micrographs of 5 mol.% YSZ samples using single-step conventional sintering a) M5SS-1200-600 b) M5SS-1300-600 c) T5SS-1450-60 d) T5SS-1500-60

At a low magnification of 1000×, Figure 4.32 displays the cracks formed in the microstructure of M5SS-1300-600. These cracks are clearly caused by hard agglomerates that were not crushed during compaction, resulting in defects within
the samples, which hindered densification during sintering. It was therefore critical to achieve a well dispersed, homogeneous and uniform microstructure before sintering. In general, this was not observed when the fracture surface of the sample was examined using FEGSEM.

Two-step sintering was performed on 5 mol.% YSZ, using a higher sintering temperature compared to 3 mol.% YSZ. Studies by Vasylkiv demonstrated that a higher temperature is required to sintering samples with higher yttria concentration, for the case of 2 mol.% and 3 mol.% nano YSZ [81]. As shown in single-step sintering of 5 mol.% YSZ in Table 4.04, higher temperatures were necessary to obtain densification of the samples. However, this is however, accompanied by the assumption that good green microstructures were achieved.

The temperatures used in the two-step sintering ranged from 1200°C to 1250°C for T1 and 1050°C to 1100°C for T2. The dwelling time ranged from 60 minutes to 600 minutes.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>T1 / °C</th>
<th>Time / min</th>
<th>T2 / °C</th>
<th>Time / min</th>
<th>Density / % theoretical</th>
<th>Mean grain size / nm</th>
</tr>
</thead>
<tbody>
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<td>M5TS-1200</td>
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<td>0.1</td>
<td>1050</td>
<td>600</td>
<td>75.4</td>
<td>150</td>
</tr>
<tr>
<td>M5TS-1200-3</td>
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<td>0.1</td>
<td>1100</td>
<td>60</td>
<td>98.7</td>
<td>100</td>
</tr>
<tr>
<td>M5TS-1200-2</td>
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<td>1100</td>
<td>600</td>
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<td>0.1</td>
<td>1050</td>
<td>600</td>
<td>97.1</td>
<td>3000</td>
</tr>
<tr>
<td>M5TS-1250-2</td>
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<td>0.1</td>
<td>1100</td>
<td>600</td>
<td>98.4</td>
<td>2500</td>
</tr>
</tbody>
</table>

Table 4.06 – Two-step sintering of 5 mol.% YSZ

Based on results tabulated in Table 4.05, M5TS-1200 sintered at 1050°C for T2, which was insufficient to achieve full densification. Whilst an increment of 50°C to 1100°C in M5TS-1200-2 provided better densification of the sample, which inevitably
increased the grain size, shown in Figure 4.33. Hence, a shorter dwell time of 60 minutes was used in the preparation of M5TS-1200-3, which minimised grain growth, resulting in a smaller grain size.

![Figure 4.33 – FEGSEM micrographs of 5 mol.% YSZ samples using two-step conventional sintering a) M5TS-1200-2 b) M5TS-1200-3](image)

M5TS-1200-2 was studied at low magnification as shown in Figure 4.34. Defects could still be seen, even though not as significant as the one shown in Figure 4.32.

![Figure 4.34 – FEGSEM micrographs of M5TS-1200-2 at low magnification of 1000x](image)

Figure 4.35 shows a comparison between single-step and two-step sintering of 5 mol.% YSZ.
Based on the results, the best sintering profiles used for M5 in producing the maximum density with minimal grain growth were found to be 1300°C for 600 minutes for single-step sintering and 1200°C for 0.1 minute, 1100°C for 60 minutes for two-step sintering, however, the sintered theoretical densities achieved were only 93% and 98.7% respectively.

### 4.4.3 8 mol.% YSZ nano & submicron sintered samples

As the yttria content increases to 8 mol.%, an even higher sintering temperature was required to produce a fully dense sample. Based on the sintering temperatures used for 5 mol.% YSZ and the supplier’s recommended sintering temperature, Table 4.06 tabulates the single-step sintering cycle used.
Table 4.07 – Single-step sintering of 8 mol.% YSZ

Among the cycles used for M8 and T8, sintered density reached its maximum at 98.6% and 99.2% respectively, with temperature ranging between 1400°C to 1500°C. The range of sintering temperatures was observed to be relatively narrow as a further increase to 1450°C for M8 brought about the decrease in density by about 1.5%. On the other hand, T8SS-1500-300 and T8SS-1500-600 demonstrate that although a longer dwelling time may present an increase in grain size, density seems to decrease.

Similarly to the results shown from 3 mol.% and 5 mol.% YSZ, the grain size increased with temperature and caused a decrease in density, shown in Figure 4.36. In both T8SS-1500-60 and T8SS-1500-300, analysis was carried out at low magnification and visible porosity can be observed.
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Figure 4.36 – FEGSEM micrographs of 8 mol.% YSZ samples using single-step conventional sintering a) M8SS-1300-600 b) M8SS-1400-60 c) M8SS-1450-60 d) T8SS-1450-60 e) T8SS-1500-60 f) T8SS-1500-300

Two-step sintering of M8 samples was performed over a range of temperature, shown in Table 4.07.
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<table>
<thead>
<tr>
<th>Sample code</th>
<th>T1 / °C</th>
<th>Time / min</th>
<th>T2 / °C</th>
<th>Time / min</th>
<th>Density / % theoretical</th>
<th>Mean grain size / nm</th>
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</thead>
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<tr>
<td>M8TS-1200</td>
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<td>0.1</td>
<td>1100</td>
<td>600</td>
<td>85.4</td>
<td>110</td>
</tr>
<tr>
<td>M8TS-1200-2</td>
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<td>0.1</td>
<td>1150</td>
<td>600</td>
<td>87.1</td>
<td>180</td>
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<tr>
<td>M8TS-1250</td>
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<td>0.1</td>
<td>1150</td>
<td>600</td>
<td>97.2</td>
<td>250</td>
</tr>
<tr>
<td>M8TS-1250-2</td>
<td>1250</td>
<td>0.1</td>
<td>1200</td>
<td>600</td>
<td>98.7</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 4.08 – Two-step sintering of 8 mol.% YSZ

It was observed, as expected for M8 to require a higher sintering temperature and as temperature T2 increased in both M8TS-1200-2 and M8TS-1250-2, density increased with grain sizes. This indicates that a higher sintering temperature is required to density the samples. The temperature used for T2 was between 50°C to 100°C lower than temperature used for T1.

Density reached its maximum for M8TS-1250-2 and achieved a mean grain size of 500 nm, further densification could take place if the temperature and or dwelling time is altered, however further densification was not achieved in this study.

Figure 4.37 displayed the micrographs obtained from the samples sintered at the conditions used in Table 4.07. Very fine microstructures were shown amongst the samples, but it can be observed from the sintering studies that 5 and 8 mol.% YSZ are generally more difficult to sinter when compared to 3 mol.% YSZ.

The presence of agglomerates or uncrushed granules, reported to exist in 5 mol.% YSZ, can be detrimental to densification. They prevent the samples from achieving maximum density and they are a cause of abnormal grain growth and non-uniform samples. However, this was not observed in 3 mol.% YSZ and 8 mol.% YSZ.
Based on the results, the best sintering profiles used to produce M8 with a maximum density with minimal grain growth were found to be 1400°C for 60 minutes in a single-step sintering and 1250°C for 0.1 minute, 1200°C for 600 minutes in a two-step sintering, both achieved sintered theoretical density of 98.5%.

Figure 4.38 shows a comparison between single-step and two-step sintering of 5 mol.% YSZ.
Density variations were observed to occur at different yttria concentrations. 3 mol.% YSZ samples were relatively easy to sinter and were able to achieve a high density with a well controlled grain size. The effect of decreased density with increasing yttria concentration was studied and reported by Matsui. It has been observed that in the sintering of fine zirconia powders containing 3 mol.% and 8 mol.% yttria, the shrinkage temperature for 3 mol.% YSZ was about 930°C, whilst shrinkage started to occur for 8 mol.% YSZ at a higher temperature of about 950°C. This was explained by the increase in activation energy during the initial first-step of sintering [100]. Another study by Luo reported that a higher sintering temperature is required for a higher yttria concentration [228].

The optimised sintering condition for 3 mol.%, 5 mol.% and 8 mol.% YSZ were summarised and tabulated in Table 4.08.
Table 4.09 – Optimised conditions for SS and TS sintering of various yttria concentrations

<table>
<thead>
<tr>
<th>Sample</th>
<th>T1 / °C</th>
<th>Time / minutes</th>
<th>T2 / °C</th>
<th>Time / minutes</th>
<th>Density / % theoretical</th>
<th>Mean grain size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mol.%</td>
<td>1075</td>
<td>600</td>
<td>-</td>
<td>-</td>
<td>99.5</td>
<td>109</td>
</tr>
<tr>
<td>5 mol.%</td>
<td>1300</td>
<td>600</td>
<td>-</td>
<td>-</td>
<td>93.0</td>
<td>140</td>
</tr>
<tr>
<td>8 mol.%</td>
<td>1400</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>98.6</td>
<td>230</td>
</tr>
<tr>
<td>3 mol.%</td>
<td>1150</td>
<td>0.1</td>
<td>1050</td>
<td>600</td>
<td>99.5</td>
<td>90</td>
</tr>
<tr>
<td>5 mol.%</td>
<td>1200</td>
<td>0.1</td>
<td>1100</td>
<td>60</td>
<td>98.7</td>
<td>100</td>
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<tr>
<td>8 mol.%</td>
<td>1250</td>
<td>0.1</td>
<td>1200</td>
<td>600</td>
<td>98.7</td>
<td>400</td>
</tr>
</tbody>
</table>

The success of two-step sintering depends on the separation of grain boundary migration and grain boundary diffusion. The activation energy for grain boundary diffusion is lower than that of grain boundary migration; hence careful selection of T2 would keep grain boundary diffusion active whilst suppressing grain boundary migration. In the report by Chen [74], densification rate during second-step of sintering can be calculated based on Herring’s scaling law [229,230];

\[
\frac{dp}{\rho \, dt} = F(\rho) \frac{3\gamma \Omega \delta D}{kT G^3}
\]

Where;
- \( \rho \) = relative density
- \( t \) = time
- \( \gamma \) = surface energy
- \( \Omega \) = atomic volume
- \( \delta \) = width of the grain boundary and
- \( D \) = grain boundary diffusivity
- \( F(\rho) \) = an unspecified function of density
- \( k \) = Boltzmann constant
- \( T \) = absolute temperature
- \( G \) = mean grain diameter

Eqn. 4.01
During the second-step of sintering, density is the only parameter that undergoes changes, assuming that grain growth is suppressed. Hence, at this stage, it is the $F(\rho)$ that determines the densification rate. Typically, when $\rho$ is greater than 0.7, $F(\rho)$ is a gradually decreases function of $\rho$. This decrease in $F(\rho)$ is assigned to an increase in diffusion distance at higher density.

The isothermal grain growth behaviour can be illustrated with kinetic growth equation,

$$G^n - G_0^n = kt$$

Where; $G =$ actual grain size  
$k =$ kinetic constant  
$G_0 =$ starting grain size  
$t =$ time  
$n =$ constant

This equation is applicable for two-step sintering and under isothermal conditions. Hence, the grain size at the end of first-step is critical in determining the final grain size at the end of the second-step. $G_0$ should be kept as low as possible in order to attain a fine microstructure. Therefore, minimisation of grain size could be aided by maximising green density, which will enable the first-step to be carried out at lower temperature, preventing unnecessary grain growth, and resulting in finer grain structure.

### 4.5 Characterisation of 3 & 8 mol.% YSZ sintered samples

The characterisation of sintered samples involved measurements of sintered density, and mean grain size, which are discussed in section 4.4. Based on the results, further characterisation was made on 3 mol.% and 8 mol.% YSZ, which includes phase determination, morphology analysis, electrical and mechanical testing, using XRD, micro-Raman, TEM, HRTEM, EIS and 4-probe techniques.
4.5.1 X-ray diffraction determination

The sintered samples of 3 mol.% YSZ (M3 and T3) and 8 mol.% YSZ (M8 and T8) were analysed at room temperature and the spectrum obtained are shown in Figures 4.39 and 4.40 respectively, compared to the benchmark tetragonal and cubic patterns.

The spectra in Figure 4.39 show that both sintered samples of M3 and T3 exhibit a tetragonal phase, and there is no indication of monoclinic peaks. The broadening of the peaks seen in M3 is due to the finer grain size compared to T3.

![XRD spectra](image)

Figure 4.39 – XRD of 3 mol.% YSZ after sintering showing only tetragonal peaks

In Figure 4.40, both M8 and T8 are shown to possess a stabilised cubic phase and a broader peak can once again been seen in M8, due to its finer grain size. There is no indication of secondary phase present based on the XRD results.
Ageing of M3 samples with an average grain size of around 100 nm was carried out at 1000°C for 1000 hours. This test was performed to better understand the effect of ageing on ionic conductivity and phase stability, found in section 4.5.4. The results shown in Figure 4.41 demonstrate a pure tetragonal phase for both the standard and aged M3 samples; no indication of a deviation from the benchmark tetragonal pattern can be seen.
4.5.2 Micro-Raman spectroscopy

The micro-Raman spectra for sintered 3 mol.% and 8 mol.% YSZ are shown in Figures 4.42 and 4.43 respectively. The sintered samples of different grain sizes with similar yttria contents and theoretical densities above 98.5% were compared. Tetragonal peaks are denoted by a ‘+', as explained in section 4.1.2. Based on the results, there is no indication of a monoclinic phase present in the sintered 3 mol.% YSZ samples, corresponding with the XRD results shown in Figure 4.39.

![Raman spectra of M3 and T3 sintered samples showing only tetragonal peaks](image)

Figure 4.42 – Raman spectra of M3 and T3 sintered samples showing only tetragonal peaks

The micro-Raman spectra of 8 mol.% YSZ is shown in Figure 4.43, both M8 and T8 exhibit a strong cubic peak at 617 cm\(^{-1}\) and there is no indication of other phases present, as for the XRD results.
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Figure 4.43 – Raman spectra of M8 and T8 sintered samples showing only cubic peaks

4.5.3 Transmission electron microscopy (High resolution)

TEM and HRTEM analysis was performed to observe any changes in the internal structure. Two samples of both 3 mol.% and 8 mol.% YSZ with grain sizes in the nano and submicron range were analysed. Samples were prepared via focused ion beam milling and a sample thickness of about 100 nm was obtained.

Figure 4.44 presents a typical TEM micrograph of M3TS-1150-1 sintered at 1150°C for 0.1 minute and 1050°C for 600 minutes, with a mean grain size of 100 nm (left image). M3TS-1600 was sintered at 1600°C for 0.1 minute and 1150°C for 600 minutes with a mean grain size of 500 nm (right image). In M3TS-1150-1, there were no visible defects or pores found in the sample and the grain size was found to be evenly distributed with the individual grains packed closely, indicating excellent densification. This was achieved through careful processing to ensure homogeneity and elimination of agglomerates within the samples. The darker shade of some grains is due to a high level of diffraction, depending on the orientation of the grains to the electron beam.
M3TS-1600 exhibits a larger grain size of about 500 nm and a slightly lower density compared to M3TS-1150-1. Although visible pores could be seen in the microstructure at triple point grain boundaries, a uniform grain size distribution was observed.

![Figure 4.44](image)

**Figure 4.44** – STEM images of (a) M3TS-1150-1 and (b) M3TS-1600

Element-mapping nanoprobe EDS was carried out on the same samples, which is shown in Figures 4.45 and 4.46. The white lines indicate the grain boundaries present in the microstructure. Figure 4.45, demonstrates a homogeneous distribution of Zr$^{4+}$ and Y$^{3+}$ ions providing qualitative evidence for a lack of yttria segregation in nanostructured YSZ. In addition, the spectra obtained by EDS did not detect any unusual elements at a spatial resolution of 4 nm other than small amounts of carbon, which could be present due to handling.
In Figure 4.46, M3TS-1600 displayed possible segregation of $Y^{3+}$ within the grain interior. When the sample was sintered at 1600°C–1150°C, regions with high $Y^{3+}$ ion concentrations were formed within the grains. According to K. Matsui, the amount of cubic phase increases with increasing sintering temperature, seen in Figure 4.47. Based on Matsui’s results, high $Y^{3+}$ ion concentration regions that form within grains undergo a phase transformation from tetragonal to cubic, allowing the cubic phase regions to be partitioned as the sintering temperature increases. It is presumed that this tetragonal to cubic phase transformation occurs by redistribution of $Y^{3+}$ ions within the grain interiors and the redistribution process is related to the grain boundary.
Figure 4.46 – STEM-EDS element mapping images of M3TS-1600. The white lines in the mapping images indicate the grain boundaries. Bright parts in the images correspond to regions with high ion concentration.

Figure 4.47 – Effect of sintering temperature to the fractions of cubic and tetragonal phases in Y-TZPs (O) and (□) indicate 3YE and 3Y respectively [231]

The line scan map shown in Figure 4.48 provides a typical Zr$^{4+}$, Y$^{3+}$ and O$^{2-}$ distribution profiles across grain boundaries in the samples. In M3TS-1150-1, the increased intensity of the darker grain is due to the diffraction condition. When the crystal structure orientates plane or perpendicular to the electron beam, the increase in intensity could be due to the level of diffraction, rather than segregation. For the sample sintered at 1600°C-1150°C, there was an increase in Y$_2$O$_3$ concentration at
the grain boundary by about 51.5% compared with the grain interior. This segregation behaviour revealed a similarity with the studies reported by Matsui [232] and the results in Figures 4.45 and 4.46.

According to Matsui, during the initial stage of sintering the distribution of $Y^{3+}$ ions in the particle interiors is homogeneous. In the grain boundary regions formed at the neck, particles join together directly without an amorphous or secondary phase. When the grain boundary starts to form with neck growth, $Y^{3+}$ ions present within the vicinity diffuse and start to segregate at the grain boundary. As a result, a segregation profile of $Y^{3+}$ ions is formed at the grain boundary, as shown in Figure 4.50. Subsequently, at the intermediate sintering stage, neck growth between particles completes and then grain formation and growth occur.

![Figure 4.48](image_url)  
Figure 4.48 - Line scan map of (a) M3TS-1150-1 and (b) M3TS-1600 showing distribution profiles of $Zr^{4+}$, $Y^{3+}$ and $O_2^-$ across the grain boundary
Figure 4.49 – Line scan profile of M3TS-1150-1 showing elements distribution from Figure 4.48 (a)

A closer look at Figures 4.49 and 4.50 reveals the typical lines scan profiles across the grains for M3TS-1150-1 and M3TS-1600 in more detail. Even though there was no significant indication of increased intensity along the grain boundary or in the grain interior, the result shown in Figure 4.50 suggests a simultaneous decrease of Zr$^{4+}$ and an increase in Y$^{3+}$ at the grain boundary, indicated on Figure 4.49 and 4.50 by GB.
To analyse the formation behaviour of $Y^{3+}$ ion segregation at the grain boundaries further, with increasing sintering temperature, the grain boundary structures and compositions were examined using HRTEM and nanoprobe EDS techniques, which are very effective at analysing a localised region. The HRTEM micrographs of grain boundaries of samples M3TS-1150-1 and M3TS-1600 are shown in Figure 4.51 and 4.53, which were analysed over an area of 20 to 30 nm. Both samples exhibited very clear grain boundaries, with no indication of segregation or an amorphous phase along the grain boundary. This observation agrees with reported literature by Ikuhara and Matsui [118,232,233].

The characterisation of the grain boundaries is particularly relevant regarding the study of grain size effects. The HRTEM micrographs were taken with the boundary at the edge-on condition to observe directly the grain-boundary structure. In both samples, no amorphous or secondary phase was observed along the grain boundary. Electron-diffraction patterns showed that both grains were in the tetragonal phase in the analysed region. EDS analysis, performed at several grain boundary and triple-point regions did not give any indication of segregation of impurities or yttrium ions.
within the detection limit of 0.1 to 1 at.%. The results on phase analysis obtained by XRD, micro-Raman and HRTEM studies have shown that 3 mol.% YSZ with a grain size of 100 nm demonstrates purely tetragonal phase. When the sample prepared was thicker than the grain, it displayed an interface with higher fringes, shown on the bottom right corner in the left image of Figure 4.52.

Figure 4.51 – HRTEM micrograph of grain boundary region in M3TS-1150-1

Figure 4.52 – HRTEM micrograph of grain boundary region in M3TS-1600
Figure 4.53 presents a typical TEM micrographs of M8TS-1250-2 sintered at 1250°C for 0.1 minute and 1200°C for 600 minutes with a mean grain size of 500 nm and T8SS-1450-60 sintered at 1500°C for 60 minutes with a mean grain size of 2500 nm. In both samples, visible porosity could be found in the grain interior and at triple points and grain sizes were found to be bi-modally distributed with the presence of larger grains among finer ones. The density achieved for both samples was above 98.5% and they were selected based on their density and grain size variation. Similarly, as explained earlier in this section, the darker shades of some grains are due to the high diffraction of grains, in plane or parallel to the electron beam.

Element-mapping nanoprobe EDS was carried out on the samples, Figures 4.54 and 4.56. In both samples, a high concentration of Y³⁺ was observed due to the higher amount of Y³⁺ present in 8 mol.% YSZ compared to 3 mol.% YSZ. Homogeneous distribution of Zr⁴⁺ and Y³⁺ ions are almost the same in both samples, with no presence of other elements detected. No additional peaks were detected in the spectra obtained by EDS.
Figure 4.54 – STEM-EDS element mapping images of M8TS-1250-2. The white lines in the mapping images indicate the grain boundaries. Bright parts in the images correspond to regions with high ion concentration.

Figure 4.55 – STEM-EDS element mapping images of T8SS-1450-60. The white lines in the mapping images indicate the grain boundaries. Bright parts in the images correspond to regions with high ion concentration.

In Figure 4.56, line mapping was performed on both samples and there is no indication of yttria segregation within the grain interior or along the boundary. In T8SS-1450-60, a step increase in intensity was observed for the detected elements, Zr$^{4+}$, Y$^{3+}$ and O$^{2-}$ in the grain with higher diffraction. This phenomenon was explained earlier to be due to the orientation of crystal grain when in plane or parallel caused by the diffraction contrast. Figures 4.57 and 4.58 display the line scan profiles across the grains in more detail.
Figure 4.56 - Line scan map of (a) M8TS-1250-2 and (b) T8SS-1450-60 showing distribution profiles of Zr$^{4+}$, Y$^{3+}$ and O$_2^-$ across the grain boundary.

Figure 4.57 – Line profile of M8TS-1250-2 showing elements distribution from Figure 4.56 (a).

Both figures show typical lines scan profile across the grain in M8TS-1250-2 and T8SS-1450-60 respectively. There is no display of segregation within the grain.
interior or at the grain boundary. The intensity remained within the range on the measured profile.

Figure 4.58 – Line scan profile of M8SS-1450-60 showing elements distribution from Figure 4.56 (a)

Figure 4.59 – HRTEM micrograph of grain boundary regions in M8TS-1250-2
Further analysis was carried out on the grain boundary regions, presented in Figures 4.59 and 4.60. Following the results shown earlier, no indication of an amorphous phase or segregation could be found in the cubic sample. Both figures display a clean grain boundary with a narrow width of less than 1 nm.

Figure 4.60 – HRTEM micrograph of grain boundary regions in T8SS-1450-60

4.5.4  AC impedance spectroscopy

4.5.4.1  Single crystal zirconia

Figure 4.61 illustrates a single crystal individual spectrum that consists of a semi-circle in the high frequency range, representing the bulk transport, and the start of a second semi-circle, representing the electrode impedance, which appears at low frequencies. Since the contacting electrodes were symmetrical, they are represented by a single semi-circle.
The first sub-circuit of the equivalent circuit consists of a resistance and capacitance in parallel representing the bulk transport properties. The second sub-circuit is composed of a resistance and a constant phase element, connected in parallel, shown in Figure 4.62.

The representative fit given in Figure 4.63 shows that the bulk resistance was lower by about one order of magnitude as compared to the electrode resistance. It was found that the power \( n \) of the constant phase element (the impedance of the constant phase element is given by \( Z = ((Aiw)^n)^{-1} \), where \( A \) and \( n \) are fit parameters) is close to 1, indicating that the electrode capacity is nearly ideal [234].
With increasing temperature the experimentally obtained spectra shifted towards the higher frequency range and the resistance of the sample decreased. Typical impedance spectra obtained at different temperatures are shown in Figure 4.63. The arc of a circle represents the characteristic of the bulk conductivity.

![Impedance spectra of single crystal zirconia at different temperatures](Image)

**Figure 4.63** – Impedance spectra of single crystal zirconia at different temperatures

The values of the bulk conductivity as a function of the temperature have been plotted in Figure 4.64.
These results are in agreement with reported literature by Vladikova, obtained for a single crystal zirconia [235].

The fact that the activation energy is dependent on the temperature range has been observed and is consistent with the assumption that two different oxygen diffusion mechanisms are present in the material. Oxygen vacancies are the majority defects in zirconia; they are created by charge compensation with yttrium and form complexes [236]. As suggested by oxygen tracer self-diffusion measurements, at temperatures higher than about 500°C, many vacancies and complexes are free and mobile, whilst at lower temperatures they are interacting strongly, forming domains in which the migration enthalpy of vacancies and their local concentration are higher [56].
Figure 4.65 – Arrhenius plot of single crystal as a function of temperature

4.5.4.2 Polycrystalline zirconia

Figure 4.66 – Polycrystalline zirconia spectrum at 300°C
In the low temperature range (250°C to 450°C) two semi-circles are observed in the impedance plot, see Figure 4.66. The high frequency arc is the bulk component and the low frequency arc corresponds to the grain boundary component. Because of the depression of the arcs in some cases, the use of a simple capacitor is not sufficient to model the electrical response of the materials, so a more complex equivalent circuit with frequency-dependent elements such as constant phase elements was used to fit results. The impedance spectra can be fitted or modelled with a series of three electrical circuits, having resistance and constant phase elements coupled in parallel, Figure 4.67.

![Figure 4.67 – Equivalent circuit of polycrystalline zirconia](image)

![Figure 4.68 – Impedance spectra of 3 mol.% YSZ with mean grain sizes of 100 nm and 500 nm at 250°C](image)
Increased resistance of both bulk and grain boundaries was observed for 3 mol.% YSZ with a mean grain size of 500 nm in Figure 4.68. The resistance of grain boundary dominates over bulk in both grain sizes.

Both the bulk and grain boundary resistance was obtained from fitting the impedance spectra. Based on the equivalent circuit for an ionic conductor proposed by Bauerle [174], the resistance of bulk and grain boundary can be calculated through fitting the experimental date of the use of equivalent circuit, shown in Figure 4.67. The resistance data for each sample at different temperatures investigated was measured and the total resistance obtained according to:

\[
R_{\text{Total}} = R_{\text{Bulk}} + R_{\text{Grain boundary}}
\]

Resistance is converted to resistivity; conductivity is defined as:

\[
\sigma = \frac{1}{R} \frac{L}{A}
\]

Where; \( L \) = sample thickness / cm

\( A \) = sample area / cm\(^2\)

The conductivity data was plotted using an Arrhenius equation:

\[
\sigma = \sigma_0 \exp \left[ \frac{E_a}{kT} \right]
\]

Where; \( E_a \) = activation energy of electrical conduction (eV), \( k \) = Boltzmann’s constant (eV/K), \( T \) = absolute temperature (K), and \( \sigma_0 \) = pre-exponential factor, being a constant in a certain temperature range.
The electrical conductivities were extrapolated and the activation energies were calculated from the slope of Arrhenius plots.

The impedance measurements in this study were performed across the temperature range of 250°C to 450°C to distinguish the contribution of the bulk and grain boundary to the total conductivity of the samples with different grain sizes for 3 and 8 mol.% YSZ. From the analysis of the impedance spectra, both the bulk and the grain boundary contributions to the conductivity as a function of temperature in this study were found to be reproducible.

Figure 4.69 illustrates the effect of bulk and grain boundary on 3 mol.% YSZ of 100 nm mean grain size.

The conductivity of the fine microstructure, in Figure 4.69, with increased of grain boundary surface at lower temperatures, becomes significantly higher than that of the coarse grains. Note the different vertical axis scales in Figure 4.69 and 4.70.
Activation energy can be obtained from the slope of the Arrhenius plot, see Figures 4.71 – 4.73. A continuous change in activation energy was observed for samples with a mean grain size of 100 nm above 300°C, where the activation energy for ion motion reduces on heating, shown in Figure 4.72. This effect could be associated with the breaking up of defect clusters or also with a change from grain boundary to grain domination [155]. However, based on Badwal [167], this phenomenon should occur at about 550°C. It is well known that at high temperatures, the conductivity of the cubic phase is higher than the conductivity of a 3YSZ by a factor of 2 [155]. Increasing yttria concentration in the cubic phase increases defect association, which results in a reduction in the conductivity of the cubic phase [237].
Chapter 4 Results & Discussion

Figure 4.71 – Arrhenius plot of bulk and grain boundary in 3 mol.% YSZ of 100 nm mean grain size

Figure 4.72 – Expanded view of the Arrhenius plot from Figure 4.71
Figure 4.73 – Arrhenius plot of bulk and grain boundary in 3 mol.% YSZ of 500 nm mean grain size

Comparing Figure 4.71 and 4.73, reduced activation energy for the bulk and grain boundary was observed in the 100 nm mean grain size sample compared to the 500 nm mean grain size.

Divalent and trivalent dopants segregate to the grain boundary core due to charge and size effects. Dopant and yttrium cations are mobile at temperatures above 1200°C in YSZ; at lower temperature, the dopant concentration profiles are frozen and only oxygen ions and anionic defects equilibrate. Segregation produces a local negative charge in the core and stabilises cation vacancy and oxygen vacancy concentrations in the adjacent areas of the grains at levels different from the bulk equilibrium concentrations [238,239].
Figure 4.74 shows that there is very little difference in conductivity of samples with an average grain size of 100 to 400 nm. The 500 nm average grain size sample exhibited a slight decrease in conductivity, compared with the finer grain size samples, as reported earlier.

Just as Figure 4.72 revealed a change in activation energy above and below ~300°C for the finest 3 mol.% YSZ grain size, Figure 4.75 shows a similar reduced activation above 300°C for all the samples, independent of average grain size in the range of 100 to 500 nm. The approximate values were 0.60 and 0.86 eV above and below 300°C respectively.
Figure 4.75 – Total Arrhenius plot of 3 mol.% YSZ with varying grain size

Table 4.10 – Conductivity and activation energy of 3 mol.% YSZ with varying grain size

<table>
<thead>
<tr>
<th>Mean grain size / nm</th>
<th>Conductivity / S cm(^{-1}) at 350°C</th>
<th>Activation energy Bulk / eV</th>
<th>Activation energy Grain boundary / eV</th>
<th>Activation energy Total / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>$1.28 \times 10^{-5} \pm 6.42 \times 10^{-7}$</td>
<td>0.77 ± 0.04</td>
<td>0.93 ± 0.05</td>
<td>0.98 ± 0.05</td>
</tr>
<tr>
<td>200</td>
<td>$1.14 \times 10^{-5} \pm 5.72 \times 10^{-7}$</td>
<td>0.80 ± 0.04</td>
<td>0.95 ± 0.05</td>
<td>0.97 ± 0.05</td>
</tr>
<tr>
<td>300</td>
<td>$1.11 \times 10^{-5} \pm 5.56 \times 10^{-7}$</td>
<td>0.77 ± 0.04</td>
<td>0.98 ± 0.05</td>
<td>0.99 ± 0.05</td>
</tr>
<tr>
<td>400</td>
<td>$1.05 \times 10^{-5} \pm 5.25 \times 10^{-7}$</td>
<td>0.81 ± 0.04</td>
<td>0.97 ± 0.05</td>
<td>0.99 ± 0.05</td>
</tr>
<tr>
<td>500</td>
<td>$7.96 \times 10^{-6} \pm 3.98 \times 10^{-7}$</td>
<td>0.79 ± 0.04</td>
<td>1.01 ± 0.05</td>
<td>0.99 ± 0.05</td>
</tr>
</tbody>
</table>
Table 4.10 tabulates the effect of grain size on the conductivity as well as the thermal activation energy for ionic conduction at 350°C. There is no obvious trend in the activation energy gathered from this study. A comparison of the experimentally determined values of activation energy with literature values is shown in Table 4.11 below.

The grain boundary activation energy dominates over the bulk activation energy for both experimentally obtained values and literature values. The experimentally derived total activation energy values lie within the range stated by literature, however the measured grain boundary activation energy values are about 0.2 lower than those found in literature, and the bulk activation energy values are about 0.1 lower than those found in literature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Activation energy Bulk / eV</th>
<th>Activation energy Grain boundary / eV</th>
<th>Activation energy Total / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mol.% YSZ</td>
<td>0.73 [240]</td>
<td>1.24 [240]</td>
<td>0.97 [240]</td>
</tr>
<tr>
<td></td>
<td>0.97 [169]</td>
<td>1.21 [169]</td>
<td>1.12 [169]</td>
</tr>
<tr>
<td></td>
<td>0.98 [241]</td>
<td>1.12 [241]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.92 [241]</td>
<td>1.09 [241]</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.11 – Activation energy reported in literature for 3 mol.% YSZ

Even though no significant difference in activation energy was observed between samples of different grain size, the conductivity was observed to decrease with increasing grain size, shown in Figure 4.76.
Figure 4.76 – Effect of grain size on total conductivity of 3 mol.% YSZ at 350°C

Figure 4.77 – Effect of grain size on the bulk and grain boundary conductivity of 3 mol.% YSZ at 350°C
Bulk ionic conductivity dominates over grain boundary conductivity for nanostructured YSZ, as shown in Figure 4.77. There is no trend observed in bulk conductivity with grain size, however there is a decrease in grain boundary conductivity with increasing grain size.

![Conductivity graph](image)

**Figure 4.78 – Conductivity of bulk and grain boundary in 8 mol.% YSZ of 500 nm grain size**

The effect of bulk and grain boundary for 8 mol.% YSZ with mean grain size of 500 nm and 3000 nm are shown in Figure 4.78 and 4.79 respectively. The measurements carried out on grain size of 3000 nm were unable to detect the grain boundary contribution, due to the reduced surface area of grain boundaries per unit volume. However, it can be seen that the bulk conductivity of 3000 nm surpass the combined conductivity of 500 nm.
Chapter 4 Results & Discussion

Figure 4.79 – Conductivity of bulk in 8 mol.% YSZ of 3000 nm mean grain size

Figure 4.80 – Arrhenius plot of bulk and grain boundary in 8 mol.% YSZ of 500 nm mean grain size
Reduced activation energy was observed in 8 mol.% YSZ of grain size 500 nm below 400°C shown in Figure 4.81, similar to that observed in 100 nm 3 mol.% YSZ at 300°C. Higher activation energy occurred in coarser microstructures for 8 mol.% YSZ (3000 nm), however there was no trend found in 3 mol.% YSZ.
Microstructures with full density and suitable grain size are therefore essential prerequisites for a high performance ionic conductor. Grain size has a great effect on the ionic conductivity. Ramamoorthy [169] reported that the finer the grain size the more confined the passage of the conducting species within the grains, resulting in lower conductivity. This is clearly contradicted by the results presented earlier for 3 mol.% YSZ, whilst lower conductivity is observed in the 8 mol.% YSZ for finer grain sizes, shown in Figure 4.83. The phase change may also influence the ionic conductivity. However, as seen from the XRD, micro-Raman and HRTEM results, the nanocrystalline 3 mol.% YSZ sample consist of pure tetragonal phase with no trace of secondary phase. 8 mol.% YSZ, which consists of cubic phase is different from the nanocrystalline sample. Due to the less symmetry, monoclinic and tetragonal phases will be less conducting than cubic phase.
In Figure 4.83 the conductivity is seen to increase with grain size and temperature. The 3000 nm samples had a much higher conductivity of $3.3 \times 10^{-4}$ S cm$^{-1}$ at 400$^\circ$C than finer grain samples. Strickler [242] suggested that the decrease in conductivity can be attributed to the interaction or clustering of the vacancies, ordering of the vacancies and formation of secondary phase. Catlow [243] proposed the clusters provided deeper traps for the vacancies, resulting in a reduction in vacancy mobility.

The grain boundary resistance is related to grain size, segregation of impurities, and the presence of other grain boundary phases [239]. Changes in grain size and impurity content have much less effect on the grain interior since impurities will usually segregate to the grain boundaries during sintering [171]. The major variable affecting the bulk conductivity in YSZ will be the yttria concentration and any secondary crystalline phase [153].
Figure 4.84 depicts a continuous decrease in activation energy with increasing temperature above 400°C for the 500 nm samples, however the reverse in seen in the 800 nm samples above 350°C.

![Graph showing Arrhenius plots for 500 nm, 800 nm, and 3000 nm samples]

\[ y = -12.859x + 10.87 \]

Figure 4.84 – Total Arrhenius plot of 8 mol.% YSZ with varying mean grain size

Table 4.12 shows the effect of grain size on conductivity and activation energy and amongst all, 3000 nm displayed the highest conductivity at 350°C whilst there is no trend shown on activation energy. A comparison of the experimentally determined values of activation energy with literature values is shown in Table 4.13 below.

The grain boundary activation energy is similar to that of the bulk activation energy for experimentally derived values. Note that grain boundary activation energy was not obtainable above 500 nm. The experimentally obtained total activation energy values are quite similar to those stated by literature, however the measured grain boundary activation energy values are about 0.2 lower than those found in literature, and the bulk activation energy values are similar to those found in literature.
### Table 4.12 – Conductivity and activation energy of 8 mol.% YSZ with varying grain size

<table>
<thead>
<tr>
<th>Mean grain size / nm</th>
<th>Conductivity / S cm⁻¹ at 350°C</th>
<th>Activation energy Bulk / eV</th>
<th>Activation energy Grain boundary / eV</th>
<th>Activation energy Total / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1.68×10⁻⁶ ± 8.38×10⁻⁷</td>
<td>1.01 ± 0.05</td>
<td>1.02 ± 0.05</td>
<td>1.15 ± 0.06</td>
</tr>
<tr>
<td>800</td>
<td>2.62×10⁻⁵ ± 1.31×10⁻⁶</td>
<td>0.95 ± 0.05</td>
<td>-</td>
<td>0.95 ± 0.05</td>
</tr>
<tr>
<td>3000</td>
<td>6.10×10⁻⁵ ± 3.03×10⁻⁶</td>
<td>1.11 ± 0.06</td>
<td>-</td>
<td>1.11 ± 0.06</td>
</tr>
</tbody>
</table>

Table 4.13 – Activation energy reported in literature for 8 mol.% YSZ

<table>
<thead>
<tr>
<th>Material</th>
<th>Activation energy Bulk / eV</th>
<th>Activation energy Grain boundary / eV</th>
<th>Activation energy Total / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 mol.% YSZ</td>
<td>0.90 [240]</td>
<td>1.15 [240]</td>
<td>0.96 [240]</td>
</tr>
<tr>
<td></td>
<td>1.11–1.17 [244]</td>
<td>1.11–1.25 [244]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.04–1.07 [245]</td>
<td>1.21–1.23 [245]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.00 [246]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.91–0.96 [167]</td>
</tr>
</tbody>
</table>

Li [193] reported that in general, the surface atoms of nanostructured ceramics should have a higher diffusion coefficient than that of bulk, and the grain boundaries should have lower resistance than that of bulk. However the observed values of
resistance in the grain boundaries were higher than that of bulk, suggested to be caused by the presence of impurities. An increase in the activation energy is well established with an increasing yttria concentration [169]. The proposed cause is due to the oxygen vacancies experiencing a binding energy to the dopant atoms caused by a combination of an electrostatic attraction and repulsive lattice relaxation energy [247]. This leads to certain anion sites being low energy positions for oxygen vacancies, and thus, extra energy is required to move the vacancies from these sites. Secondly, yttrium ions have a greater ionic radius compared to the zirconium ions, and thus, their presence in the lattice sterically hinders the motion of the oxygen ions (moving in the opposite direction to the oxygen vacancies) [247]. As the concentration of yttrium ions in the lattice increases, the probability that the oxygen ions will have to pass them also increases, increasing the activation energy.

Bulk activation energy increases at a 20 – 25 mol.% yttria content, indicating an increase in defect clustering. Grain boundary conductivity decreases and activation energy increases with yttria content [248,249]. An increase in the activation energy is well established with increasing yttria content. There are several proposed causes for this observation. Firstly, the oxygen vacancies experience a binding energy to the dopant atoms caused by a combination of an electrostatic attraction and a repulsive lattice relaxation energy [250]. This leads to certain anion sites being low energy position for oxygen vacancies, and thus, extra energy is required to move the vacancies from the sites. Secondly, yttrium ions have a greater ionic radius compared to the zirconium ions, and thus, their presence in the lattice sterically hinders the motion of the oxygen ions (moving in the opposite direction to the oxygen vacancies) [251]. As the concentration of yttria ions in the lattices increases, the probability that the oxygen ions will have to pass them also increases, increasing the activation energy.

Ion conduction will be dominated by the bulk conductance in the high temperature range and dominated by grain boundary conductance at lower temperatures. On the other hand, the oxygen vacancy trapping mechanism suggests that at high
temperatures the ion conduction is also controlled by bulk resistance, whilst in the low temperature range it is controlled by migration of free oxygen vacancies and also by thermal dissociation of defect-associates [252]. Therefore, in the high temperature range, the dominant factor governing ion transportation within zirconia-based electrolytes is bulk resistance for both single crystal and polycrystalline materials. In zirconia, the activation energy for ion transportation is independent of the grain boundary resistance at high temperature. However, at lower temperatures, the ion transportation is mainly controlled by the grain boundary resistance, thermal dissociation of defect-associates and bulk resistance. The non-linear Arrhenius behaviour reported by many researchers [56,152,159,174,253,254] for both single crystal and polycrystalline materials, demonstrates that the bulk resistance is not the dominant factor for ion conduction in zirconia based material at low temperatures. With single crystal YSZ free of grain boundaries, the dominant factor for ion transportation at low temperature is the thermal dissociation of defect-associates. With polycrystalline YSZ, the dominant factor depends on the relative values of the activation energy for ion transportation across grain boundaries and the activation energy for thermal dissociation of defect-associates. Therefore, when the activation energy for ion transportation across grain boundaries is larger than that for thermal dissociation of defect-associates the grain boundary resistance will be dominant, whereas grain boundary resistance will not dominate the ion conduction. This can be explained by a mechanism involving the trapping of oxygen vacancies due to the absence of grain boundaries [255].

4.5.5 DC 4-probe

DC 4-probe measurements were carried out on 3 mol.% and 8 mol.% YSZ with varying grain size and the results of the effect of grain size as a function of temperature on conductivity are shown below.

As seen in Figure 4.85, there is no significant difference in the samples at below about 500°C. Above 500°C, the 500 nm average grain size sample shows reduced conductivity compared with the finer grain size samples of below 400 nm.
There are insignificant differences in activation energy between the studied grain sizes, shown in Figure 4.86. On the other hand, there is a reduction in activation energy above 600°C, shown by the change of gradient. Both AC impedance analysis and DC 4-probe measurements displayed a reduction in activation energy at higher temperature. However this phenomenon was observed at different temperatures for the two different techniques.
Figure 4.86 – Arrhenius plot of 3 mol.% YSZ with varying mean grain size

Table 4.14 tabulates the conductivity at 950°C and activation energy of 3 mol.% YSZ at the studied grain size between 100 to 500 nm.

<table>
<thead>
<tr>
<th>Mean grain size / nm</th>
<th>Conductivity / S cm⁻¹ at 950°C</th>
<th>Activation energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.038 ± 1.91×10⁻³</td>
<td>0.88 ± 0.04</td>
</tr>
<tr>
<td>200</td>
<td>0.036 ± 1.82×10⁻³</td>
<td>0.83 ± 0.04</td>
</tr>
<tr>
<td>300</td>
<td>0.036 ± 1.80×10⁻³</td>
<td>0.92 ± 0.05</td>
</tr>
<tr>
<td>400</td>
<td>0.030 ± 1.48×10⁻³</td>
<td>0.87 ± 0.04</td>
</tr>
<tr>
<td>500</td>
<td>0.023 ± 1.13×10⁻³</td>
<td>0.85 ± 0.04</td>
</tr>
</tbody>
</table>

Table 4.14 – Conductivity and activation energy of 3 mol.% YSZ with varying grain size
The effect of grain size on conductivity at 950°C is shown in Figure 4.87. Fine microstructures of 100 nm were observed to display the highest conductivity compared with coarser grained samples. Even though no significant difference in activation energy was observed between samples of different grain size, the conductivity was observed to decrease with increasing grain size.

Figure 4.87 – Effect of grain size on total conductivity of 3 mol.% YSZ at 950°C

8 mol.% YSZ displays the opposite trend of 3 mol.% YSZ, it exhibits increased conductivity in large grained samples and a decrease in smaller ones. This effect is shown in Figure 4.88, whilst Figure 4.89 shows insignificant variation in the activation energy of 8 mol.% YSZ at different grain sizes.
Chapter 4 Results & Discussion

Figure 4.88 – Total conductivity of 8 mol.% YSZ with varying mean grain size

Figure 4.89 – Arrhenius plot of 8 mol.% YSZ with varying mean grain size
There are insignificant differences in activation energy between the studied grain sizes, shown in Figure 4.89. AC impedance analysis displayed a change in activation energy with increasing temperature, however, no trend was observed for DC 4-probe measurements.

<table>
<thead>
<tr>
<th>Mean grain size / nm</th>
<th>Conductivity / S cm⁻¹ at 950°C</th>
<th>Activation energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.06 ± 3.10×10⁻³</td>
<td>0.87 ± 0.04</td>
</tr>
<tr>
<td>800</td>
<td>0.09 ± 4.7×10⁻³</td>
<td>0.91 ± 0.05</td>
</tr>
<tr>
<td>3000</td>
<td>0.10 ± 5.05×10⁻³</td>
<td>0.86 ± 0.04</td>
</tr>
</tbody>
</table>

Table 4.15 – Conductivity and activation energy of 8 mol.% YSZ with varying grain size

<table>
<thead>
<tr>
<th>Yttria / mol.%</th>
<th>500°C</th>
<th>600°C</th>
<th>800°C</th>
<th>850°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>7.4×10⁻⁵ [169]</td>
<td></td>
<td>0.022 [167]</td>
<td>0.075 [23]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.059 [256]</td>
</tr>
<tr>
<td>8</td>
<td>1.59×10⁻³ [257]</td>
<td>0.022 [258]</td>
<td>0.037 [258]</td>
<td>0.089 [23]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0185 [257]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.050 [259]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.020 [260]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.013 [261]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.16 – Conductivity reported in literature for 3 and 8 mol.% YSZ
The results displayed in Table 4.15 are the conductivities at 950°C and the calculated activation energies for 8 mol.% YSZ. Table 4.16 presents the reported literature for the conductivity of both 3 and 8 mol.% YSZ at different temperatures. The experimentally obtained conductivity values for 3 mol.% YSZ at 950°C, shown in Table 4.14, sit between the literature stated values for 850°C and 1000°C. However the experimental values are more closely matched to the literature values at 850°C, this indicates a large increase in conductivity between 950°C and 1000°C. The experimentally acquired conductivity values for 8 mol.% YSZ at 950°C, shown in Table 4.15, lie between the literature stated values for 800°C and 1000°C. However, the conductivity values are seen to increase with increasing grain size for 8 mol.% YSZ, whereas the opposite is seen for 3 mol.% YSZ.

![Figure 4.90 – Effect of yttria concentration of mean grain size 500 nm on total conductivity](image)

The conductivity values for 500 nm 8 mol.% YSZ at 950°C are more than double the values for 3 mol.% YSZ, shown in Figure 4.90, which is to be expected due to the increased number of oxygen vacancies. The values are consistent with literature values of 0.03 and 0.08 S cm\(^{-1}\) at 1000°C.
Figure 4.91 shows the combined results of the effect of grain size on conductivity for 3 mol.% and 8 mol.% YSZ. The conductivity is shown to increase with grain size for 8 mol.% YSZ, whereas the opposite is seen for 3 mol.% YSZ. At 950°C, the conductivity values of the 500 nm 8 mol.% YSZ samples are more than a factor of two greater than the 500 nm 3 mol.% YSZ values. At larger grain sizes, above 800 nm, this difference becomes much more significant.

Error bars are used to show the error associated with the data values when more than one measurement was made.
The effect of ageing carried out at 950°C under atmospheric condition is shown in Figure 4.92. The conductivity of both the 100 nm and 500 nm mean grain size samples decreases with time. There is a greater decrease seen in the 100 nm grain size samples, however, even after 1000 hours the conductivity values remain about 0.01 S cm\(^{-1}\) greater than the values for the 500 nm samples. This decrease could be due to polarisation, a time dependent phenomenon [262].

The values of conductivity obtained from this study at 950°C were comparable to the values reported by Badwal [167]. For 3 mol.% YSZ, the experimentally derived values of grain boundary activation energy obtained from impedance analysis for conductance is around 0.95 eV, except for the 500 nm average grain size sample, where it was 0.79 eV. Activation energy from the DC 4-probe measurements demonstrates a lower activation for both 3 mol.% and 8 mol.% YSZ. However, the literature has reported that the activation energy of conduction measured from the
4-probe DC method and the grain boundary activation energy for conductance derived from the impedance analysis are almost the same [42,169]. Because grain boundary is the highest resistance path, the activation energy determined by 4-probe method is expected to be close to the value of activation energy for grain boundary conduction. Up till now, there was no systematic study available to correlate the value of activation energy for conductance with the grain size ranging from submicrometre to nanometre. The decrease in activation energy when grain size reduces to the nano range is most likely due to the presence of the high volume of grain boundary in the nanostructure. As a result, the concentration of segregated ions (dopants as well as impurities) at the grain boundary region would be less in nanostructured samples than its submicrometre or micrometre grained counterparts. This may cause less resistance to oxygen ion mobility from grain to grain in nanostructured samples.
Chapter 5
Conclusions

The particle size study using a transmission electron microscope (TEM) revealed the primary particle size differences between Tosoh powders and MEL nanosuspensions. The MEL nanosuspension exhibited primary particles in the size range of 10 to 15 nm, whereas the Tosoh powders were around 100 to 200 nm.

In the process of suspension concentration, TAC shifts the isoelectric point towards the acidic region, giving a high value of zeta potential at pH greater than 9. 3 wt.% tri-ammonium citrate (TAC) is an ideal amount for MEL 3 mol.% YSZ (M3) as it provides a good level of dispersion without an excessive amount of organics present in the suspension. The viscosity of the concentrated suspensions is of great importance for spray freeze drying, which is dependent on the solid content, pH, dispersants used, zeta potential and the size of the particles. It was found that about 20 mPa s is an ideal viscosity to perform the granulation process.

For the forming of 3 mol.% YSZ green bodies, by both the wet and dry routes, a solid content of 55 to 57 wt.% yields an ideal viscosity, producing the best granules for dry forming and the best slip casts. Due to the higher viscosity of 5 and 8 mol.% YSZ suspensions, useful suspensions that can be slip cast and granulated are limited to lower solid contents, 45 and 33 wt.% respectively. A green density of greater than 55% theoretical density is required to produce fully dense sintered samples with a homogeneous nanostructure. For die pressing, the flowability and crushability of granules are key to achieve a flaw free, homogenous green compact with a high green density.

The use of Freon as a foaming agent has proven successful. FEGSEM images revealed the flaws produced by the Freon, which considerably improves the
crushability of granules. Uncrushed granules in the green compact are regions of higher density leading to excessive grain growth. Spray freeze drying has been used to improve the flowability of granules over spray dried powders.

The use of two-step sintering provided more control over grain size compared with conventional single-step sintering. The best 3 mol.% YSZ samples were achieved using a two-step sintering profile of 1150°C (0.1 minute) – 1050°C (600 minutes), producing a mean grain size of 100 nm. The best 5 mol.% YSZ samples were achieved using a two-step sintering profile of 1200°C (0.1 minute) – 1100°C (600 minutes), producing a mean grain size of 100 nm. The best 8 mol.% YSZ samples were achieved using a single-step sintering profile of 1400°C (60 minutes) yielding a mean grain size of 100 nm. However, attempts to produce fully dense samples of nano 5 mol.% YSZ were unsuccessful as it was found that the green sample lacked of homogeneity, this could be due to the presence of agglomerates, which were not eliminated before sintering. No further analysis was carried out on samples of 5 mol.% YSZ.

Closed porosity occurred at about 95% of theoretical density; all the samples used in the further studies achieved a minimum theoretical density of 98.5%. The sintering results indicated that a two-step sintering profile gives better control over grain size and density, compared to conventional single-step sintering. Increasing yttria concentration resulted in a higher temperature required to achieve full densification of the sample. The optimum two-step sintering cycle to achieve above 99% theoretical density 3 mol.% YSZ samples with fine microstructures was found to be different for samples with higher yttria concentration. Grain size inevitably increased as a result. In the comparison of sintering temperatures for nano and submicron samples, much lower temperatures were required for sintering of nano zirconia. Over-sintering can result in decrease in sintered density and abnormal grain growth, if surface diffusion dominates, grains grow too rapidly, and pores coalesce. In general, the sintering temperatures for nano zirconia are approximately 300°C lower than for submicron zirconia.
X-ray diffraction phase analysis of YSZ sintered samples revealed that, M3 and T3 exhibit a tetragonal phase whilst M8 and T8 possess a fully stabilised cubic phase with no indication of a secondary phase. Ageing performed at 950°C for 1000 hours on M3 samples with mean grain size of 100 nm did not undergo phase transformation, which indicates the stability of nanostructured zirconia. However there was an increase in grain size by about 20 nm based on the FEGSEM analysis. The results obtained were supported by analysis from micro-Raman studies.

HRTEM analysis revealed no segregation or secondary phase present in nanostructured 3 mol.% YSZ. However, the submicron sample, sintered at higher temperature, 1600°C gave indication of the presence of Y³⁺ ion segregation in both STEM-EDS element mapping and line scan. This was explained by the phase transformation that occurred during sintering, which was not found to be valid in the HRTEM micrographs grain boundary interface, over a width of approximately 5 nm. 8 mol.% YSZ at different grain sizes displayed consistent results in terms of element distribution and phase stability. No indications of segregation, amorphous phase or impurities were determined through the analysis.

AC impedance analysis on 3 mol.% YSZ showed the total ionic conductivity to increase with increasing temperature. The bulk conductivity was proven to be three times higher than the grain boundary conductivity at 350°C. Reduced activation energy occurred for the nanostructured bulk material above 300°C compared with the submicron sample. There was a slight decrease in conductivity with increasing grain size. There was no noticeable change in activation energy with grain size. AC impedance analysis on 8 mol.% YSZ showed the resistance to decrease with increasing temperature. The bulk conductivity was proven to be higher than the grain boundary conductivity for the measured sample of 500 nm grain size. In the 800 nm and 3000 nm 8 mol.% YSZ samples, the measurements consist of only bulk contribution due to the excessive grain size. Reduced activation energy occurred for the submicron bulk material above 400°C compared with the micron sample. On the
Chapter 5 Conclusions

contrary to 3 mol.% YSZ, there was an increase in conductivity with increasing grain size. There was no observed change in activation energy with grain size.

DC 4-probe analysis on 3 mol.% YSZ showed that there was a slight decrease in conductivity with increasing grain size. Also, there was no noticeable change in activation energy with varying grain size, however reduced activation energy was observed for all grain size samples above 600°C. DC 4-probe analysis on 8 mol.% YSZ showed that there was no noticeable change in activation energy with varying grain size. Likewise for impedance analysis, the increase in grain size increases conductivity. Nanostructured 3 mol.% YSZ appears to have similar, possibly slightly higher, ionic conductivity than the submicron ceramic.

In the ageing of nano and submicron 3 mol.% YSZ samples, the ionic conductivity decreased more in the nanostructured sample, however the resulting conductivity was still higher than that of the submicron sample.

It can be concluded that whilst it is possible to produce fully dense, homogeneous, nanostructured 3 mol.% YSZ samples, the same processing route does not necessary work for 5 mol.% YSZ and 8 mol.% YSZ, a good understanding of the surface chemistry is needed. The presence of impurities, segregation of ions or amorphous phases is detrimental to the conductivity of the samples. Ionic conductivity and mechanical strength are the main properties required for fuel cell application for nano zirconia provides advantages of cost reduction and choice of materials used as connectors in the fuel cell.
Chapter 6

Future work

The issues associated with the use of organics in producing dispersed high solid content nanosuspensions are that they have a lower density, about 1 $\text{g cm}^{-3}$ as compared to 6 $\text{g cm}^{-3}$ for zirconia. Hence they lead to lower green densities in the die pressed compacts, making it more difficult to retain a fine grain size during sintering. Organics also reduce the crushability of the spray freeze dried granules, further reducing the homogeneity and green density achievable after compaction. It may be possible to improve the quality of green compacts by reducing the amount of organics present. Freon currently used to aid the crushability of granules is a harmful CFC, which needs to be eliminated from the spray freeze drying process. The crushability and flowability of the granules produced in this study need to be quantified, enabling optimisation of granules. The spray freeze dry process need to be modified or improved to achieve a higher yield of granules in the useful size range, currently 125 to 250 $\mu\text{m}$.

In the processing of 5 mol.% and 8 mol.% YSZ nanosuspensions, the high initial viscosity hinders the possibility to further concentrate the suspensions to above 50% solid content, without a large amount of dispersant, more than 5%.

The full potential of hybrid sintering must be taken advantage of to produce fully dense nanostructured samples with a lower sintering time, reducing operational costs. Optimised sintering cycles for zirconia samples of different yttria concentrations would enable better control over grain size and density.

Ionic conductivity measurements carried out on 3 mol.% YSZ showed a slight change over a narrow range of grain sizes, whilst more significant changes were observed for 8 mol.% YSZ with a wider range of grain sizes. This suggests a grain size dependence shift in properties. Higher conductivity values were achieved for 8
Chapter 6 Recommendations for future work

mol.% YSZ, whilst literature suggests that 3 mol.% YSZ possesses better mechanical properties. A balance between the studied yttria concentration and grain size could incorporate the combined properties and 5 mol.%, which was not fully studied needs to be further analysed for application in fuel cells. This could result in a potential cost reduction in reducing the amount of yttria required.

Mechanical testing such as fracture toughness and strength measurements needs to be analysed carefully to find the optimum yttria concentration, avoiding over stabilisation in nanostructured samples. This will enable a thinner electrolyte, with adequate mechanical strength to withstand the conditions required for fuel cell operation. This could be carried out over the studied range of yttria concentrations and grain sizes to obtain a better understanding of the dependence of the properties on these variables. This will require mass preparation and testing of samples to obtain a sufficient number of samples to carry out a standard deviation analysis.

Hydrothermal aging of different yttria concentration samples needs to be studied at fuel cell operating temperatures. At present hydrothermal aging is performed at about 250°C for less than 100 nm 3 mol.% YSZ.

Future work needs to be aimed at producing an aqueous YSZ ink for screen printing an electrolyte layer. Rheology is the most important factor in producing a good ink capable of being printed.
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composition and electrical properties of YSZ films deposited by ultrasonic spray


