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SCANDIA AND CERIA STABILIZED ZIRCONIA BASED ELECTROLYTES AND ANODES FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS: MANUFACTURING AND PROPERTIES

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Materials Science and Engineering in the College of Engineering and Computer Sciences at the University of Central Florida Orlando, Florida

Spring Term
2013

Major Professor: Nina Orlovskaya
ABSTRACT

Scandia and ceria stabilized zirconia (10 mol% Sc$_2$O$_3$ – 1 mol% CeO$_2$ – ZrO$_2$, SCSZ) has superior ionic conductivity in the intermediate temperature range for the operation of solid oxide fuel cells, but it does not exhibit good phase stability in comparison with yttria stabilized zirconia (8 mol% Y$_2$O$_3$ – ZrO$_2$, YSZ). To maintain high ionic conductivity and improve the stability of the electrolyte, layered structures with YSZ outer layers and SCSZ inner layers were designed, along with the referential electrolytes containing pure SCSZ or YSZ. The electrolytes were manufactured by tape casting, laminating, and pressureless sintering techniques. After sintering, while the thickness of YSZ outer layers remained constant at ~30 μm, the thickness of inner layers of SCSZ for the 3-, 4- and 6-layer designs varied at ~30, ~60 and ~120 μm, respectively. Selected characterizations were employed to study the structure, morphology, impurity content and the density of the electrolytes. Furthermore, in situ X-ray diffraction, neutron diffraction and Raman scattering were carried out to study the phase transition and lattice distortion during long-term annealing at 350 °C and 275 °C for SCSZ and YSZ, respectively, where the dynamic damping occurred when Young’s modulus was measured.

In YSZ/SCSZ electrolytes, thermal residual stresses and strains were generated due to the mismatch of coefficients of thermal expansion from each layer of different compositions. They could be adjusted by varying the thickness ratios of each layer in different designs of laminates.
The theoretical residual stresses have been calculated for different thickness ratios. The effect of thermal residual stress on the biaxial flexural strength was studied in layered electrolytes. The biaxial flexure tests of electrolytes with various layered designs were performed using a ring-on-ring method at both room temperature and 800 °C. The maximum principal stress during fracture indicated an increase of flexural strength in the electrolytes with layered structure at both temperatures in comparison with the electrolytes without compositional gradient. Such an increase of strength is the result of the existence of residual compressive stresses in the outer YSZ layer. In addition, Weibull statistics of the strength values were built for the layered electrolytes tested at room temperature, and the effect of thermal residual stresses on Weibull distribution was established. The calculation of residual stress present at the outer layers was verified.

The high ionic conductivity was maintained with layered electrolyte designs in the intermediate temperature range. It was also established that the ionic conductivity of layered electrolytes exhibited 7% – 11% improvement at 800 °C due to the stress/strain effects, and the largest improvements in a certain electrolyte was found to nearly coincide with the largest residual compressive strain in the outer YSZ layer.

In addition to the study of layered electrolytes, mechanical properties of porous Ni/SCSZ cermet were studied. The anode materials were reduced by 65 wt% NiO – 35 wt% SCSZ (N65) and 50 wt% NiO – 50 wt% SCSZ (N50) porous ceramics in the forming gas. Young’s modulus as
well as strength and fracture toughness of non-reduced and reduced anodes has been measured, both at room and high temperatures. High temperature experiments were performed in the reducing environment of forming gas. It was shown that while at 700 °C and 800 °C the anode specimens exhibited purely brittle deformation, a brittle-to-ductile transition occurred at 800 – 900 °C, and the anode deformed plastically at 900 °C. Fractography of the anode specimens were studied to identify the fracture modes of the anodes tested at different temperatures.
To My Family
ACKNOWLEDGMENTS

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TABLE OF CONTENTS

LIST OF FIGURES ............................................................................................................. xiv

LIST OF TABLES ................................................................................................................ xxi

CHAPTER ONE: INTRODUCTION ..................................................................................... 1

1.1 Fuel Cells ..................................................................................................................... 1

1.2 Solid Oxide Fuel Cells ............................................................................................... 5

1.3 Motivation and Goal .................................................................................................... 10

1.4 Structure of the Dissertation ....................................................................................... 12

CHAPTER TWO: LITERATURE REVIEW ........................................................................ 13

2.1 Electrolytes for Solid Oxide Fuel Cells ...................................................................... 13

2.1.1 Materials Selection for Electrolytes .................................................................... 13

2.1.2 Y$_2$O$_3$-stabilized ZrO$_2$ ...................................................................................... 17

2.1.3 Sc$_2$O$_3$-stabilized ZrO$_2$ for Electrolytes .......................................................... 22

2.2 Anode for SOFC ......................................................................................................... 26

2.3 Residual Stress ........................................................................................................... 29

2.3.1 Design of Layered Structure for Residual Stress .............................................. 29

2.3.2 Effect of Stress and Strain on Ionic Conductivity ............................................. 31

CHAPTER THREE: DESIGN AND MANUFACTURING OF LAYERED ELECTROLYTES
FOR SOLID OXIDE FUEL CELLS .............................................................................. 41

3.1 Introduction ........................................................................................................ 41

3.2 Design of Layered Electrolytes .......................................................................... 42

3.3 Experimental ........................................................................................................ 44

3.3.1 Manufacturing of Layered Electrolytes ............................................................. 44

3.3.2 Characterization ................................................................................................ 46

3.3.2.1 Powder Characterization ............................................................................. 46

3.3.2.2 Characterization of Layered Electrolytes ................................................. 48

3.4 Result and Discussion ............................................................................................ 49

3.4.1 Powder Characterization .................................................................................. 49

3.4.1.1 Phase Structure and Impurity .................................................................. 49

3.4.1.2 Agglomerates and Granules ................................................................... 53

3.4.1.3 Crystallites ............................................................................................... 53

3.4.1.4 Sintering Shrinkage ................................................................................ 57

3.4.2 Manufacturing and Characterization of Layered Electrolytes ....................... 59

3.4.2.1 Design and Optimization of Manufacturing ............................................ 59

3.4.2.2 Dimension and Density of Electrolytes ................................................. 60

3.4.2.3 Pores and Impurities in the Layered Electrolytes ................................. 66
CHAPTER FOUR: RESIDUAL STRESS IN THE LAYERED ELECTROLYTES AND THEIR PROPERTIES

4.1 Introduction ............................................................................................................. 72

4.2 Experimental .......................................................................................................... 73

4.2.1 Young’s Modulus .............................................................................................. 73

4.2.2 Thermal Expansion .......................................................................................... 76

4.2.3 Biaxial Flexural Strength .................................................................................. 77

4.2.3.1 Measurement of Biaxial Strength ................................................................. 77

4.2.3.2 Calculation of Biaxial Strength .................................................................... 79

4.2.3.3 Weibull Statistics for Biaxial Strength ......................................................... 82

4.2.4 Ionic Conductivity ............................................................................................. 83

4.3 Results and Discussion ........................................................................................... 84

4.3.1 Density and Young’s Modulus ......................................................................... 84

4.3.2 Thermal Expansion and Residual Stress ......................................................... 88

4.3.3 Biaxial Flexural Strength .................................................................................. 96

4.3.3.1 Measurement ............................................................................................... 96

4.3.3.2 Calculation of Biaxial Strength ................................................................... 99
4.3.3.3 Strength Calculation by Residual Stress .................................................. 102

4.3.4 Adjustment of CTE and Verification of the Residual Stress ...................... 104

4.3.5 Ionic Conductivity ......................................................................................110

4.4 Conclusion .....................................................................................................117

CHAPTER FIVE: MECHANICAL PROPERTIES OF Ni / (Sc₂O₃)₀.₁(CeO₂)₀.₀₁(ZrO₂)₀.₈₉
CERMETS FOR SOFC ANODE .............................................................................. 120

5.1 Introduction ....................................................................................................120

5.2 Experimental .................................................................................................. 121

5.2.1 Sample Preparation ...................................................................................... 121

5.2.2 Characterizations of the Microstructure and Phase Structure .................. 123

5.2.3 Young’s Moduli ..........................................................................................124

5.2.4 Flexural Strength .......................................................................................124

5.2.5 Fracture Toughness ....................................................................................127

5.3 Result and Discussion .................................................................................... 132

5.3.1 Reduction and Pore Characterization .......................................................132

5.3.2 Characterization of the Phase Structures .................................................. 136

5.3.3 Young’s Moduli of Ni/SCSZ Cermets .......................................................141

5.3.4 Flexural Strength .......................................................................................143
5.3.5 Fracture Toughness ........................................................................................................... 148

5.4 Conclusion ............................................................................................................................. 153

CHAPTER SIX: REVISIT THE PHASE STRUCTURES OF THE TWO SOFC MATERIALS
...................................................................................................................................................... 155

6.1 Introduction ............................................................................................................................ 155

6.2 Experimental .......................................................................................................................... 156

6.2.1 X-ray Diffraction ............................................................................................................... 156

6.2.2 Neutron Diffraction .......................................................................................................... 157

6.2.3 Raman Spectroscopy ....................................................................................................... 158

6.3 Result and Discussion ......................................................................................................... 158

6.3.1 X-ray Diffraction ............................................................................................................... 158

6.3.2 Neutron Diffraction .......................................................................................................... 166

6.3.3 Raman Spectroscopy ....................................................................................................... 172

6.4 Conclusion ............................................................................................................................ 178

CHAPTER SEVEN: CONCLUSION AND FUTURE WORK ...................................................... 179

REFERENCE ............................................................................................................................... 183
LIST OF FIGURES

Figure 1: The sketch of the operation of fuel cells ................................................................. 3
Figure 2: Different configurations of single SOFC (A – anode; C – cathode, E – electrolyte) ...... 9
Figure 3: Arrhenius plots of different types of electrolyte materials. YSB [(Bi2O3)0.75(Y2O3)0.25]; LSGMC (La0.8Sr1.2Ga1-yMgyO3; x ≈ 0.8, y ≈ 0.8, z ≈ 0.085); CGO (Ce0.9Gd0.1O1.95); SSZ [(ZrO2)0.8(Sc2O3)0.2]; YDC (Ce0.8Y0.2O1.96); CDC (Ce0.9Ca0.1O1.8); YSZ [(ZrO2)0.92(Y2O3)0.08]; CaSZ (Zr0.85Ca0.15O1.85).............................................................................................................................. 14
Figure 4: Ionic conductivity versus the molar percent of dopant in YSZ (hollow dots) and SSZ (solid dots) ........................................................................................................................................... 15
Figure 5: Phase diagram for the zirconia rich portion of the zirconia-yttria system ............... 19
Figure 6: Structure of tetragonal ZrO2 drawn in the primitive tetragonal (subscripted with t) and pseudo-fluorite (subscripted with f) unit cell ...................................................................................................................... 20
Figure 7: Phase diagram for the zirconia rich side of zirconia-scandia binary system ............. 23
Figure 8: XRD patterns of 0.1Sc2O3 – 0.01CeO2 – 0.89ZrO2 at the temperature range between 300 °C and 500 °C ............................................................................................................................................ 24
Figure 9: (a) Logarithm of the long-range ionic conductivity (in S·cm⁻¹) of the trilayers STO/YSZ/STO vs. inverse temperature; (b) Conductance at 400 K of superlattices consisting of repeated layers of 1 nm YSZ / 10 nm STO, as a function of the number of interfaces (the number of
[YSZ/STO] repeats is half the number of interfaces) ......................................................... 32

Figure 10: Simplified dependence of the interface structure and the density of misfit dislocations from the lattice mismatch $f$ ................................................................. 34

Figure 11: Experiment setup for tensile test (a) and compressive test (b). Conductivity of 14 YSZ subjected to uniaxial tensile stress (c–d) and compressive stress (e–f) at 600 °C and 900 °C .... 36

Figure 12: Directional mean square displacement of oxygen ion in the direction of $[1 0 0]$, $[0 1 0]$ and $[0 0 1]$, subjected to uniaxial tensile stress (a–c) or compressive stress (d–f) in the $[1 0 0]$ direction at 1000 °C ................................................................. 38

Figure 13: Design of layered electrolytes ............................................................................. 43

Figure 14: Processing steps used to produce the layered electrolytes ......................... 45

Figure 15: X-ray diffraction patterns (A–D) of SCSZ and YSZ powders before and after sintering; and neutron diffraction patterns (E–F) of SCSZ and YSZ sintered powders ................. 51

Figure 16: SIMS of SCSZ with + secondary detection (A) and – secondary detection (B); SIMS of YSZ with + secondary detection (C) and – secondary detection ........................................... 52

Figure 17: Morphology of SCSZ (A–C) and YSZ (D–F) raw powders observed via SEM .... 54

Figure 18: Grains of SCSZ (A) and YSZ (B) raw powders observed via TEM, and high resolution TEM images of crystallites in SCSZ (C) and YSZ (D) ......................................................... 56

Figure 19: Shrinkages and their differentials of SCSZ and YSZ green body during sintering .... 58
Figure 20: Densities of layered electrolytes with different designs, in comparison with theoretical density (dash line) ................................................................. 63

Figure 21: Element distributions in (A) Y–1SC–Y, (B) Y–2SC–Y and (C) Y–4SC–Y ............ 65

Figure 22: (A) fracture surface of Y–2SC–Y samples in SEM; (B) pores near the interface of YSZ layer and SCSZ layer; (C) pores in outer YSZ layer; (D) pores in inner SCSZ layer; (E) fracture surface of 4–YSZ samples; and (F) fracture surface of 4–SCSZ samples ............................................. 67

Figure 23: Elements identified by SIMS in layered electrolyte, and the mapping of elements distribution on the fracture surface ................................................................. 69

Figure 24: The setup of Young’s modulus measurement by impulse excitation technique .......... 75

Figure 25: (A) The setup of ring-on-ring biaxial flexure test; (B) Sketch of ring-on-ring method. F – load; t – specimen thickness; a – radius of the supporting ring ........................................... 78

Figure 26: Maximum principal stress versus applied load for a ring-on-ring biaxial flexure test specimen ........................................................................................................... 81

Figure 27: Young’s modulus versus density of SCSZ and YSZ specimens .............................. 85

Figure 28: Young’s modulus versus temperature of SCSZ and YSZ ..................................... 87

Figure 29: Temperature dependences of the elongation (A) and the coefficients of thermal expansion (B) of YSZ and SCSZ .............................................................................. 89

Figure 30: Calculated residual stresses in layered electrolytes at room temperature (A) and at
Figure 31: (A) Two typical Load vs. Time biaxial flexure testing curves via ring-on-ring method; (B–C) specimen with low stress at the fracture; (D–E) specimen with high stress at the fracture

Figure 32: Loads at the biaxial flexure fracture of electrolytes tested at RT (A) and 800 °C (B)

Figure 33: Biaxial strength of electrolytes with selected design at room temperature (A) and at 800 °C (B)

Figure 34: Weibull statistics of the biaxial flexural strength at the fracture of 3–SCSZ (A), 3–YSZ (B), Y–2SC–Y (C) and Y–4SC–Y (D) tested at room temperature

Figure 35: Biaxial flexural strength of electrolytes as a function of thickness ratio at room temperature (A) and 800 °C (B). Solid line: calculation by residual stress; dots: experimental results; △: pure SCSZ; dot lines: reference line of pure YSZ and pure SCSZ without residual stress

Figure 36: The coefficients of thermal expansion of YSZ and SCSZ. (Dash line: previous results before adjusted; solid lines: adjusted data)

Figure 37: Adjustment of calculation: the residual stress at RT (A) and 800 °C (B); the biaxial strength at RT (C) and 800 °C (D). Dash line: previous results before adjusted; solid lines: adjusted data

Figure 38: Weibull statistics of biaxial strength at room temperature (A), and the plots with

Figure 39: Ionic conductivities of SCSZ, YSZ and layered Y–xSC–Y electrolyte samples........112

Figure 40: Sketch of the residual stress (A) and strain (B) in the layered electrolyte ..........114

Figure 41: (A) The improvement of the ionic conductivity in the layered electrolytes at different
temperature; dots along solid line – at heating; dots along dash line – at cooling; (B) Coefficients of
thermal expansion of SCSZ and YSZ as a function of temperature; (C) strain mismatch of SCSZ
and YSZ as a function of temperature ..........................................................116

Figure 42: The sketch (A) and photo (B) of the device of four-point bending test ............... 125

Figure 43: A simple reciprocating notching machine ..................................................128

Figure 44: Schematic diagram of fractured V-notched test piece and the positions at which notch
depths are measured. 1: Fractured surface; 2: V-notched surface.................................130

Figure 45: Weights of N65 and N50 in function of the time after reduction (m_0 is the initial mass
before reduction) ......................................................................................................133

Figure 46: Fracture surfaces of N65 sample before reduction (A) and after reduction (B)....... 134

Figure 47: Pore size distribution of N65 (A–B) and N50 (C–D) samples before and after reduction
........................................................................................................................................135

Figure 48: The X-ray diffraction spectra (A), (1 1 1) profiles (B) and (2 0 0) profiles (C) of pure
SCSZ powders, NiO–SCSZ ceramics and Ni/SCSZ cermets ............................................138
Figure 49: Raman spectra of the pure SCSZ (A), the NiO–SCSZ ceramic before reduction (B) and the Ni/SCSZ cermet after reduction (C) ................................................................. 140

Figure 50: Young’s modulus vs. density of N65 (A) and N50 (B) specimens ......................... 142

Figure 51: Weibull distributions of flexural strengths of N65 (A) N65m (B) and N50 (C) ....... 144

Figure 52: Load vs. Time curves of four-point bend testing (A) and Flexural strength vs. temperature plots (B) of N65 (RT) and N65m (high temperatures) ........................................ 147

Figure 53: Notches on the N65 specimens for room temperature testing (A–B) and N65m specimens for high temperature testing (C–D) ................................................................. 149

Figure 54: Load vs. Time curves of fracture toughness testing (A) and Fracture toughness vs. temperature plots (B) of N65 (RT) and N65m (high temperatures) ......................... 150

Figure 55: SEM micrographs of fracture surfaces of Ni/SCSZ cermets anode after testing at 800 °C (A) and 900 °C (B–D) in reducing atmosphere. The dimples (C and D) indicate the ductile fracture of the Ni grains ................................................................. 152

Figure 56: XRD patterns of YSZ and SCSZ at the beginning and the end of annealing (A); (4 0 0) profile of SCSZ (B) and YSZ (C) ........................................................................................................ 159

Figure 57: Selected peaks in the X-ray diffraction of SCSZ (A, C and E) and YSZ (B, D and F) during the annealing. (A–B): diffraction pattern. (C–F): intensity mapping with time. (Pseudo-cubic coordinates are used for index) .................................................................................. 160
Figure 58: Weight percentages (A), lattice parameters (B) and volumes of pseudo-cubic cell (C) of cubic and rhombohedral phases in SCSZ during annealing at 350 °C by X-ray diffraction...... 163

Figure 59: Neutron diffraction pattern of YSZ when annealing at 275 °C.......................... 168

Figure 60: The lattice parameters (A), volume of t unit cell (B), coordinates of oxygen ions (C) and occupancy of oxygen ions (D) of YSZ during annealing at 275 °C by neutron diffraction ...... 169

Figure 61: The lattice parameters (A), volume of t unit cell (B), coordinates of oxygen ions (C) and occupancy of oxygen ions (D) of YSZ during temperature ramping by neutron diffraction ..... 171

Figure 62: Raman spectra of SCSZ during the temperature ramping from 25 °C to 350 °C ..... 173

Figure 63: Raman spectra of SCSZ during annealing. (A) 0 – 26 h ; (B) 24 – 108 h ............... 174

Figure 64: Raman spectra of YSZ during the temperature ramping from 25 °C to 275 °C ...... 176

Figure 65: Raman spectra of YSZ during annealing. (A) 1.9 – 25.8 h ; (B) 26 – 216 h............. 177
LIST OF TABLES

Table 1: Technical characteristics of different kinds of fuel cells ................................................................. 2
Table 2: Composition of slurry ........................................................................................................................................ 45
Table 3: Lattice parameters of SCSZ and YSZ measured via X-ray and neutron diffraction ...... 50
Table 4: Average thicknesses of samples in 9 designs .................................................................................................. 61
Table 5: Average diameters of samples in 9 designs.................................................................................................... 61
Table 6: Material properties of YSZ and SCSZ ......................................................................................................... 92
Table 7: Thicknesses of layers in different designs .................................................................................................. 92
Table 8: Calculated residual stresses in layered electrolytes ...................................................................................... 94
Table 9: Weibull parameters of the electrolytes in biaxial flexure tests at room temperature .... 101
Table 10: Calculated residual stresses in layered electrolytes (Adjusted) ............................................................... 106
Table 11: Selected characterization of N65 and N50 anode samples before and after reduction 136
CHAPTER ONE: INTRODUCTION

1.1 Fuel Cells

In the year of 1839, William Grove reversed water electrolysis to generate electricity from hydrogen and oxygen, and discovered the basic operating principle of fuel cells [1]. A fuel cell is an electrochemical “device” that continuously converts chemical energy into electric energy (and some heat) for as long as the fuel and oxidant are supplied. Unlike a battery, recharging is not needed for a fuel cell with continuous fuel replenishment. The reactions inside the fuel cell are well controlled, and therefore it has a much higher efficiency of energy conversion (40% – 60%, and as high as 80% – 90% with co-generation) with lower waste emissions than traditional combustion energy (10% – 40%) [2,3].

A single fuel cell consists of an anode (negative side), a cathode (positive side) and an electrolyte. The anode and the cathode are the places where an oxidation of fuel and a reduction of oxygen occur when fuels and oxygen flow in, respectively. At the same time, the anode maintains a lower electric potential than the cathode, and therefore the electrons leaves the cell from the anode and comes back to the cathode after having a certain electrical work done through the external circuit. The electrolyte functions as a separation membrane between cathode and anode compartment, and it conducts ions but not electrons between the electrodes of the fuel cell.
<table>
<thead>
<tr>
<th>Types of fuel cell</th>
<th>Electrolyte</th>
<th>Operating $T$</th>
<th>Fuel</th>
<th>Oxidant</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline (AFC)</td>
<td>potassium hydroxide</td>
<td>50–200°C</td>
<td>pure hydrogen, or hydrazine</td>
<td>O$_2$/Air</td>
<td>50%–55%</td>
</tr>
<tr>
<td>Direct methanol (DMFC)</td>
<td>Polymer</td>
<td>60–200°C</td>
<td>liquid methanol</td>
<td>O$_2$/Air</td>
<td>40%–55%</td>
</tr>
<tr>
<td>Phosphoric acid (PAFC)</td>
<td>phosphoric acid</td>
<td>160–210°C</td>
<td>hydrogen from hydrocarbons and alcohol</td>
<td>O$_2$/Air</td>
<td>40%–50%</td>
</tr>
<tr>
<td>Sulfuric acid (SAFC)</td>
<td>sulfuric acid</td>
<td>80–90°C</td>
<td>alcohol or impure hydrogen</td>
<td>O$_2$/Air</td>
<td>40%–50%</td>
</tr>
<tr>
<td>Proton-exchange membrane (PEMFC)</td>
<td>polymer, proton exchange membrane</td>
<td>50–80°C</td>
<td>less pure hydrogen from hydrocarbons or methanol</td>
<td>O$_2$/Air</td>
<td>40%–50%</td>
</tr>
<tr>
<td>Molten carbonate (MCFC)</td>
<td>molten salt such as nitrate, sulphate, carbonates…</td>
<td>630–650°C</td>
<td>hydrogen, carbon monoxide, natural gas, propane, marine diesel</td>
<td>CO$_2$/O$_2$/Air</td>
<td>50%–60%</td>
</tr>
<tr>
<td>Solid oxide (SOFC)</td>
<td>ceramics</td>
<td>600–1000°C</td>
<td>natural gas or propane</td>
<td>O$_2$/Air</td>
<td>45%–60%</td>
</tr>
<tr>
<td>Protonic ceramic (PCFC)</td>
<td>thin membrane of barium cerium oxide</td>
<td>600–700°C</td>
<td>hydrocarbons</td>
<td>O$_2$/Air</td>
<td>45–60%</td>
</tr>
</tbody>
</table>

Figure 1: The sketch of the operation of fuel cells

Different kinds of fuel cells are mostly categorized by electrolyte [2,4]. The adapted fuels, operation temperature and mechanism of ion conduction are thus varied as well. Some typical kinds of fuel cells and their technical characteristics are listed in Table 1, and the operations of selected types are also demonstrated in Figure 1. It can be seen from the Table 1 that AFC, DMFC, PAFC, SAFC and PEMFC types of fuel cells have low operation temperatures but also low efficiency, while MCFC, SOFC and PCFC have higher operation temperatures and are thus able to utilize flexible fuels and more efficient with inherent generation (90% with heat recovery).

During the development for hundreds of years, the researchers gradually overcame the issues of the material and technique which directly determine the power, efficiency, reliability, duration and costs. More and more widely, the fuel cells are jumping into our daily lives. Due to the varied characteristics, those fuel cells adapt to different applications at present [5], such as portable fuel cells (PEMFC, DMFC, 5W – 20kW) that are designed to be moved, including auxiliary power units; stationary power fuel cells (PEMFC, MCFC, PAFC, SOFC, 0.5W – 400kW) that provide power to a fixed location; transport fuel cells (PEMFC, DMFC, 1kW – 100kW) that provide either primary propulsion or range-extending capability for vehicles.

The past five years were an important period with a rapid increase of fuel cell application in industry. It was reported that the overall fuel cell system shipments (excluding toys and education kits) had a 39% increase compared by 2010 and reach 24600, which firstly shipped an over 100 MW annual megawatts [5]. The increase was mostly led by the stationary power applications,
where PEMFC still dominated. However, PEMFC was gradually replaced by SOFC in some areas of stationary application because SOFC can offer higher energy conversion efficiency but produce less usable heat, and thus SOFC are better for continuous operation in electricity-led applications. SOFC shipments grew by more than 300% between 2010 and 2011, and the growth is predicted more rapid in the future [5].

This dissertation focuses on SOFC among kinds of fuel cells, and a brief introduction is given in next section.

### 1.2 Solid Oxide Fuel Cells

Among different types of fuel cells, solid oxide fuel cells (SOFCs) break the dominion of liquid electrolytes. This came to be when Wilhelm Nernst found a surprisingly high conductivity in the mixed oxides of zirconium, thorium, yttrium, and the rare earth elements at high temperatures in 1899 [6].

Taking advantage of the all-solid structure, SOFC has good stability and reliability without any loss of electrolyte or corrosion, and furthermore it has a long life expectancy (40000 – 80000 h) [7]. The SOFC are operated at high temperature range (600 – 1000 °C). It does not require expensive noble metal, such as Platinum, to function as the catalyst in the electrodes, and it has large fuel flexibility: H₂, CO, natural gas and other liquid fuels are acceptable without external reformation [8]. Meanwhile, some drawbacks are brought as well, such as the limitation of application due to
the high operation temperature of SOFC, the risks from the mismatch of the mechanical and thermal properties in each component, the severe requirement of high ionic conductivity and the manufacturing routine for the thin solid electrolyte.

The SOFC single cell basically consists of porous fuel and air electrodes (an anode and a cathode) and a dense an electrolyte. The anode or fuel electrode is the place where an oxidation of the fuel occurs. Taking H$_2$ as an example, the fuel flows in and reacts with O$_2^-$ which comes through the electrolyte from the cathode. The half reaction is:

$$H_2 + O_2^- \rightarrow H_2O + 2e^- \quad (1)$$

The free electrons released then go into the external circuit to convert the energy to electrical type. The anodes are thus required to have:

(a) high electronic conductivity (> 100 S·cm$^{-1}$); 
(b) non-negligible ionic conductivity (~0.1 S·cm$^{-1}$); 
(c) proper porosity, so that gas flows in easily and has a large three phase boundary (TPB) to react with O$_2^-$; 
(d) a cheap catalyst but high efficiency for H$_2$ oxidation; 
(e) chemical stability with regard to the electrolytes and interconnects in the reducing atmosphere; 
(f) good match of coefficient of thermal expansion (CTE) with other cell components; 
(g) good mechanical behaviors for support if it is in an anode-supported SOFCs.
A cermet composed of nickel and oxides with a high porosity is a promising material for an anode, due to its high activity for reformation and electrochemical oxidation of fuel, and ability to serve as a current collector. Among these oxides, yttria-stabilized zirconia (YSZ) is mostly chosen for its good ionic conductivity, chemical stability and reliability, thus Ni / (Y2O3)0.08(ZrO2)0.92 (Ni / YSZ) has been widely used in various applications.

The released electrons in the reaction (1) will come back to the cathode or air electrode through an external circuit, where the reduction of oxygen molecules O2 takes place:

\[
O_2 + 2e^- \rightarrow O^{2-} \tag{2}
\]

The requirements of cathode materials are similar to those of an anode, but a cathode should be stable in the oxidizing atmosphere. The catalyst mechanism of reaction (2) is not the same as that in the anode, and Ni is not a good catalyst that fits for a cathode. Instead, platinum is well-known as a good catalyst for splitting O2 molecule; however it too expensive to be accepted into the cathode of a SOFC. Rather, some perovskites such as La1-xSrxF3-z (M: Mn, Fe, Co, 0 \leq x \leq 1) are found to meet the requirements of a cathode.

An electrolyte standing between the cathode and the anode is used to separate them, with the exception of O2\(^{2-}\) ions which are permitted through. Therefore, the electrolyte requires high ionic conductivity (typically 0.1 S·cm\(^{-1}\)), negligibly low electronic conductivity, good gas tightness achieved by high density, along with good mechanical stability and robustness at the operating environment. The thermal expansion of the electrolyte should match the other cell components, so
that the delamination and crack are best avoided when the temperature varies.

In addition, the electrolyte is exposed to a rather complex set of materials and surroundings: cathode and anode materials, different impurities coming from fuel and air, along with reducing and oxidizing atmospheres existing on the opposite sites of the electrolyte. It is well known that Mn, Fe and/or Co ions are present in almost all SOFC cathodes, Ni ions are present in the anodes and their interaction/diffusion in the electrolyte could be detrimental for the electrolyte performance. Thus, the unwanted diffusion of cations coming from electrodes or impurities in fuels destabilizes and compromises the electrolyte performance. As a result, in addition to the high ionic conductivity, a stable and durable phase without fatal degradation in such complex operational environment is also required for an electrolyte.

There are many candidates of the materials for the solid electrolyte, such as ZrO$_2$-, CeO$_2$-, perovskite-based ceramics. Those materials are briefly reviewed in CHAPTER TWO.

There exist different types of single cell configurations [9], which are classified according to mechanically supporting layer, as shown in Figure 2. Typically, the supporting component has a thickness larger than 150 mm while the supported layers have a thickness of tens of microns [10]. The electrolyte-supported SOFC has a strong structural support due to dense and stable electrolyte, but thick electrolyte results in higher ohmic resistance and requirement of higher operation temperature. The anode- and cathode-supported SOFC can lower the thickness of electrolyte and thus the operation temperature, but they suffers from the failure risks due to the anode reoxidation.
and cathode reduction, respectively. Also, the thick electrode limits the mass transport. Beside the three self-supporting SOFC above, the interconnect-supported SOFCs and the porous substrate-supported SOFCs are external supporting. Both of them will be beneficial with the low operation temperature, but the former have to face the interconnect oxidation and the flowfield design limitation, and the latter have an increased complexity due to the new materials and the potential electrical shorts caused by the uneven substrate surface.


Figure 2: Different configurations of single SOFC (A – anode; C – cathode, E – electrolyte)
In order to increase the power of SOFC, the stacking designs are employed, such as the segmented-cell-in-series design, the tubular design, the monolithic design, and the planar design [11]. But the stacking design is beyond the scope of this dissertation and will not be further discussed.

1.3 Motivation and Goal

A stationary power application using a reliable electrolyte-supported solid oxide fuel cell is considered as the background. In order to lower the operation temperature of SOFC, the electrolytes with high ionic conductivity in intermediate or low temperature range will be designed and manufactured. In addition, the stability, reliability and good match with other SOFC component will be also characterized.

The thermal residual stress is rarely avoided in all-solid structures of fuel cells, and the stress effects are usually considered as a negative impact that will lead to a mechanical failure of SOFC. Instead of eliminating or minimizing the stress effects, however inversely, there is a possible attempt to design and control the stress, so that the stress effect is converted to be positive with its proper utilization to improve the SOFC performance.

Therefore, the ionic conductivity, structure stability, mechanical behavior and the stress effect in the SOFC will be concentrated on. In this dissertation, the research field is limited in the
electrolyte and anode, and the performance of the whole single cell is set as future work. Thereby, the goal of this dissertation is to design, manufacture and characterize the ZrO$_2$-based electrolyte and anode with improved performance for solid oxide fuel cells. Detailedly, it is expressed as follows.

1) In consideration of the good performance of 10 mol% Sc$_2$O$_3$ – 1 mol % CeO$_2$ stabilized ZrO$_2$ (SCSZ) and 8 mol% Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ), an approach of lamination is employed to design and manufacture the robust layered electrolytes.

2) The residual stress is calculated for the layered structure, and the improvement of the ionic conductivity and the mechanical strength is evaluated. The proper stress design is to be proved positive for the integral performance of the electrolyte.

3) The porous Ni/SCSZ anode cermets are tested in the nearly operational environment, and the mechanical behaviors as well as the microstructures are characterized.

4) During the manufacturing, sample preparation and testing of either the electrolyte or the anode, the relations between the material properties and structures are emphasized in the view of crystal structures. The *ex situ* and *in situ* experiments are carried out to study the structure, in order to reach a better understanding of the micro mechanisms of the performance as well as the stability and durability of the materials.
1.4 Structure of the Dissertation

In the previous section of this introductory chapter, the motivation and the goal of this dissertation are proposed. The work will be addressed in the following chapters starting with literature review in CHAPTER TWO, where the materials for the solid oxide fuel cells and the stress/strain effects on the material behaviors are reviewed. CHAPTER THREE presents the feasibility of manufacturing of the layered YSZ/SCSZ electrolytes along with the structural characterization. In CHAPTER FOUR, the residual stress is estimated in the layered YSZ/SCSZ electrolytes, and it interprets the improvement of the biaxial strength and ionic conductivity due to the layered design. CHAPTER FIVE discusses the application of the super ionic conductor SCSZ on the anode component, focusing on the structure stability and the mechanical behaviors at nearly operational environment. CHAPTER SIX comes back to the basic structural issue of materials used in the dissertation, where in situ experiments help to shoot the imperceptible lattice change during annealing at the temperature that the dynamic damping occurs at. CHAPTER SEVEN concludes the dissertation and proposes the future work.
2.1 Electrolytes for Solid Oxide Fuel Cells

2.1.1 Materials Selection for Electrolytes

In the view of the ionic conductivity which is the most important issue of solid electrolyte, many ceramics are considered as candidates for SOFC with intermediate operation temperature (600 – 800 °C), such as stabilized ZrO$_2$, doped CeO$_2$, LaGaO$_3$-based perovskite, stabilized Bi$_2$O$_3$ and so forth [12,13]. Those typical materials are presented in Figure 3 by Arrhenius plots in order to compare their ionic conductivities [10].

Among them, ZrO$_2$-based oxides have been widely used as electrolytes in SOFC due to the high ionic conductivity and good chemical stability under SOFC operation conditions. Especially, ZrO$_2$ is stable in both oxidizing and reducing atmosphere since zirconium ion has only Zr$^{4+}$ form without valence variation. Zirconia has a fluoride structure but the pure ZrO$_2$ experiences the polymorphic transitions among the cubic, tetragonal, monoclinic and rhombohedral phases when temperature changes. In order to stabilize the cubic phase, the ions with lower oxidation state, such as Sc$^{3+}$, Y$^{3+}$, Ca$^{2+}$ and so forth, is doped in the zirconia (Figure 3). The Sc$_2$O$_3$-stabilized ZrO$_2$ (SSZ) exhibits a much higher ionic conductivity due to the smallest mismatch of ionic radii between Zr$^{4+}$ and Sc$^{3+}$, which leads to a small energy for defect association and thus increases the mobility or
conductivity of oxygen ions [14–17]. The Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ) also has acceptable ionic conductivity, though much lower than SSZ, at high and intermediate temperature ranges for the applications using thin electrolyte. However, the CaO-stabilized ZrO$_2$ (CaSZ) with low ionic conductivity does not performed as a good oxygen ion conductor because of the large mismatch between Zr$^{4+}$ and Ca$^{2+}$ radii.


Figure 3: Arrhenius plots of different types of electrolyte materials. YSB [(Bi$_2$O$_3$)$_{0.75}$(Y$_2$O$_3$)$_{0.25}$]; LSGMC (La$_{x}$Sr$_{1-x}$Ga$_{y}$Mg$_{1-y-x}$Co$_{2}$O$_3$; $x \approx 0.8$, $y \approx 0.8$, $z \approx 0.085$); CGO (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$); SSZ [(ZrO$_2$)$_{0.8}$(Sc$_2$O$_3$)$_{0.2}$]; YDC (Ce$_{0.8}$Y$_{0.2}$O$_{1.96}$); CDC (Ce$_{0.9}$Ca$_{0.1}$O$_{1.8}$); YSZ [(ZrO$_2$)$_{0.92}$(Y$_2$O$_3$)$_{0.08}$]; CaSZ (Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$)
As shown in Figure 4, SSZ and YSZ reach the highest ionic conductivity with 10 mol% and 8 mol% dopant, respectively [14,18–21]. Those two stabilized zirconia are chosen as basic materials in this dissertation, and their properties in addition to ionic conductivity will be further reviewed in the following sections.


Figure 4: Ionic conductivity versus the molar percent of dopant in YSZ (hollow dots) and SSZ (solid dots)
Similar as ZrO$_2$, ceria (CeO$_2$) also has a fluorite structure, and the doped ceria has high ionic conductivity in the intermediate temperature range when the dopant with lower oxidation state introduces oxygen vacancies [22]. In consideration of small mismatch of ionic radii like the case of ZrO$_2$, Sm$^{3+}$ or Gd$^{3+}$ is the proper dopant for CeO$_2$ that brings superior ionic conductivity [23–25]. One of the gadolinium doped ceria Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ has been most extensively studied [26]. Unlike ZrO$_2$ however, the Ce ions has two valences +4 and +3. In the fluorite lattice, the Ce$^{4+}$ will be reduced into lower Ce$^{3+}$ when the electrolyte are exposed to low oxygen partial pressure or reducing environment ($p$(O$_2$) < 10$^{-19}$ atm) and high temperatures (> 600 °C) which it has to suffer from at the anode side [15,27]. Such reduction can probably lead to a mechanical failure due to the lattice volume change. Also, the substitution of Ce$^{3+}$ results in the emission of electron, and electronic leakage through the electrolyte will be significantly increased due to the formation of an n-type semiconductor [10].

The perovskite electrolytes such as Sr and Mg-doped LaGaO$_3$ (LSMG) exhibit much higher ionic conductivity than those of YSZ, SSZ and GDC [28]. The easily reducible ions are not contained, and LSMG is stable in low $p$(O$_2$) environment with low electronic conductivity. It is potentially offers sufficient performance for the electrolytes operated at low temperature as 400 °C [29]. However, The LSGM does not cost as cheap as ZrO$_2$- or CeO$_2$-based electrolytes, and it does not exhibit good durability when working with common cathode and anode materials. The interdiffusion between LSMG and cathode, which is also a perovskite, will eventually degrade the
performance of both, and the buffer ceria layer between them was reported not effective because a resistive phase would thus form [30–32]. At the other side, the reaction occurs between LSGM and Ni, which is usually contained in anode, and it turns out the resistive phase to barricade the mass transport [33].

Bi$_2$O$_3$-based ceramics also has high ionic conductivity, but most of this type of oxides is only stable in a narrow temperature ranges and suffering from the aging problems due to the easy transitions between phases [34,35]. The reduction at low oxygen partial pressures is also reported [13]. Those drawbacks bring great challenges before it is used as an electrolyte of solid oxide fuel cells.

Therefore, in consideration of both good ionic conductivity and stability of the material basically, the ZrO$_2$-based zirconia is selected for our electrolyte. The properties of YSZ and SSZ will be further review in next sections.

2.1.2 Y$_2$O$_3$-stabilized ZrO$_2$

As shown in Figure 4, the 8 mol% Y$_2$O$_3$ doping in ZrO$_2$ provides the highest ionic conductivity in Y$_2$O$_3$ – ZrO$_2$ system, and YSZ is stable in both oxidizing and reducing environments. YSZ also has sufficient mechanical behaviors to meet the requirement of electrolyte [36,37]. The 8 mol% Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ stands for this composition hereafter if without particular notes.) thus becomes one of the most popular materials for electrolytes and
has been used extensively in high temperature SOFCs [11,15,38–40].

Although the highest ionic conductivity is obtained at this composition, the cubic zirconia is not yet fully stabilized [41,42], as shown in the phase diagram in Figure 5. The cubic zirconia is not a stable phase at room temperature and the operation temperature for SOFC lower than 1000 °C. Rather, it is a metastable phase which has maintained the structure at high temperature. Instead of pure cubic phase (c), a small amount of lower symmetric phases such as monoclinic (m) and tetragonal phase (t) probably exist in the 8 mol% YSZ [42], but the phase transition is extremely slow because of the high energy barrier. If the metastable cubic phase is annealed at 1000 °C for as long as 1000 h, the cubic phase significantly transits to a stable tetragonal phase; and the t phase can return to c phase by annealing at 1600 °C for 10 h [14]. The tetragonal phase (P 4_2/n m c) is considered as a pseudo-fluorite structure with elongation along c-axis in comparison with cubic (F m 3 m). The coordinates of the two structures are shown in Figure 6 with comparison. There are two metastable tetragonal phases between cubic phase (c) and the stable tetragonal phase (t) in the equilibrium diagram, and they are noted as t’ and t” [42]. The t’ phase and t” phase have space symmetry P 4_2/n m c, the same as t phase; however the lattice parameter and the coordinates of the atoms are different. The t’ phase is stretched along c-axis as well, and the ratio c/\alpha is about 1.010 \sqrt{2} or lower; however in the stable t phase this ratio is much larger [43].

Figure 5: Phase diagram for the zirconia rich portion of the zirconia-yttria system
The t'' phase have equal lattice parameters \( a = b = c \) as those of cubic, but the cubic symmetry is lost due to the displacement of oxygen atoms displacing parallel or antiparallel with \( c \)-axis alternatively [42]. Therefore, the t'' phase cannot be distinguished from c phase by X-ray diffraction, but Raman spectroscopy is helpful to characterize the t'' phase [44]. The presence of tetragonal phase from cubic zirconia is attributed to the degradation of YSZ and results in the
decrease of ionic conductivity, due to the volume fraction, grain size and the distribution of the t
phase precipitation [45,46].

Since the $Y^{3+}$ ions is doped in the zirconia and substitute the $Zr^{4+}$ ions, the oxygen vacancy
$V_{O}^{**}$ is introduced in order to maintain charge neutrality. The behavior of the oxygen vacancy has
directly relation to the ionic conductivity of the material. The vacancy ordering occurs at the
temperature above 800 °C [47], and it results in the anomalous behavior of ionic conductivity [48].
A short-range ordering of oxygen vacancies in YSZ causes a significantly drop of conductivity
after a long-term annealing at 810 °C [49]. At lower temperatures, the reorientation of $V_{O}^{**} - YZr'$
elastic/electric dipoles and the relaxation of oxygen vacancy are supposed, and the peaks are
measured in the mechanical loss spectrum [50]. Therefore, the oxygen vacancy in zirconia is
active with other defects. Besides the possible phase transition, even very slow, the behaviors of
the defects can also affect the properties of the material.

The YSZ can maintain its cubic structure, though metastable, in a wide temperature range and
exhibits good ionic conductivity 0.1 S·cm⁻¹ at 1000 °C, but it decreases drastically to 0.03 S·cm⁻¹ at
800 °C [51,52]. In the application of SOFC operated at intermediate (700 – 800 °C) or low (500 –
600 °C) temperature range, the ionic conductivity of YSZ is sufficient for anode-supported
SOFC because the electrolyte can be very thin (~10 μm) [53]. But such conductivity is not
sufficient for the electrolyte-supported SOFC, where the electrolyte thicknesses are on the order
of 100 – 300 μm. Therefore, another $ZrO_2$-based electrolyte material for electrolyte-supported
cells with higher ionic conductivity is required for the intermediate temperature solid oxide fuel cell (IT-SOFC) use.

2.1.3 Sc$_2$O$_3$-stabilized ZrO$_2$ for Electrolytes

The option of Sc$_2$O$_3$ doped ZrO$_2$ (SSZ) is an alternative to YSZ as the electrolyte material, and it drew a lot of attention in last decade due to its superior ionic conductivity in intermediate temperature range [15,54,55]. In addition to the promising high ionic conductivity, the mechanical performance of SSZ is similar with or better than that of YSZ with proper doping and processing [56–60]. The strength of an electrolyte is also of importance because it is necessary for a reliable long-life SOFC, especially for electrolyte-supported SOFC.

However, a vital weakness of SSZ is its problem of phase stability. As shown in Figure 7, the SSZ experiences a phase transition from cubic phase to β-rhombohedral phase at 300 – 500 °C [42,61], that is, the cubic phase loses stability in the phase transition, thus the electrical property will be weakened [62,63].

In order to prohibit the cubic to β-rhombohedral phase transition and retain the cubic fluorite structure, a lot of research on co-doping Sc$_2$O$_3$ with CeO$_2$, Bi$_2$O$_3$, Yb$_2$O$_3$, Mn$_2$O$_3$ or Al$_2$O$_3$ in ZrO$_2$ have been carried out [64–73]. Of those additives, it was shown that CeO$_2$- and Sc$_2$O$_3$-stabilized zirconia no longer exhibits an unfavorable phase transition, making this material an extremely promising option for the electrolyte of intermediate temperature solid oxide fuel cells [65,66,74].

Figure 7: Phase diagram for the zirconia rich side of zirconia-scandia binary system

Figure 8: XRD patterns of 0.1Sc$_2$O$_3$ – 0.01CeO$_2$ – 0.89ZrO$_2$ at the temperature range between 300 °C and 500 °C

One of the compositions 0.1Sc$_2$O$_3$ – 0.01CeO$_2$ – 0.89ZrO$_2$ (SCSZ) contains the cubic phase at room temperature and this has not been reported to transform during aging [65]. The Arrhenius plots of SCSZ reveal its superior ionic conductivity in the intermediate temperature range (700 – 800 °C), and the conductivity of SCSZ is much better than that of YSZ [75] in the intermediate
temperature range. However, despite promising high ionic conductivity, recent research found that the cubic phase in SCSZ at room temperature is a metastable phase [76,77], it still exhibits a reversible cubic-to-rhombohedral phase transition at 300 – 500 °C, as shown in Figure 8.

In addition to the unfavorable phase transition due to temperature changing, the electrolyte works with complicated surroundings and needs to encounter the unwanted diffusion of cations from electrodes and fuels. The cubic structure of SCSZ easily suffers from the destabilization by unwanted elements invading [78,79], and the ionic conductivity can also drop with Ni diffusion from common anode materials[80]. However, YSZ exhibits better performance than SCSZ. It is reported that the NiO from anode, for example, can dissolve in the cubic zirconia phase at high temperature, causing a decrease of lattice parameter and ionic conductivity in air. But in the reducing atmosphere, Ni is exsolved out of the YSZ because of the much lower solubility of metallic Ni in YSZ [81]. With NiO doped, the phase structure remains unaltered in 8 mol% YSZ [82]. In 3 mol% Y₂O₃ – ZrO₂ which has tetragonal structure, the NiO promotes the formation and growth of cubic phase grains [82]. The NiO doping helps with the stabilization of cubic phase and the grain growth in Y₂O₃ – ZrO₂ ceramics [83]. The effect of stabilization is beneficial to moderate the time-dependent degradation of ionic conductivity during the high temperature operation [84].

Despite cubic SCSZ having a much higher ionic conductivity at lower temperature, it is still not as stable as YSZ. Therefore, SCSZ electrolytes are more difficult to work solely. If it would be possible to create a core of the electrolyte with the higher conducting SCSZ composition, but
protect it from direct contact with the electrodes and fuel by placing thin layers of YSZ composition on the outer surfaces of SCSZ, this approach might be promising. Such an approach would allow for the advancement of the field of SOFCs, both increasing the mechanical properties and phase stabilities of three layered electrolytes, and at the same time at least partially retaining the high ionic conductivity at the lower operation temperatures of the SOFCs. Besides, as SCSZ and YSZ have slightly different coefficients of thermal expansion along with Young’s moduli [85], one can expect the appearance of proper thermal residual stresses in the layers without delamination or crack occurring.

2.2 Anode for SOFC

The anode is the place where the oxidation of fuel occurs in SOFC as described in Section 1.1 and 1.2. Porous Ni/YSZ cermet is one of the more popular anode materials because of its cheap and efficient catalyst Ni, good electrical conductivity and ionic conductivity in the high temperature range [86]. In the anode cermet, the oxide component plays an important role, as described in the following [87]:

(1) To adjust the thermal expansion mismatch between the ZrO$_2$-based electrolyte and the nickel based anode to avoid delamination of the anode layer from the electrolyte;

(2) To impart mechanical stability to the anode layer by forming a zirconia network inside the anode;
(3) To increase the anode performance by providing a larger number of three phase boundaries (TPBs), which are the active interfaces among the oxide, nickel and gas phase.

YSZ is usually chosen as the oxide in anode due to its good phase stability, but the Ni/SCSZ cermet with superior ionic conductivity has also attracted attentions on the synthesis, optimization of operating conditions, flexibility and performance for hydrogen and hydrocarbon fuels, interaction between metal Ni and stabilized ZrO$_2$, and so forth [88–94]. The following review of the properties and performances of Ni/SCSZ is based on the comparison to those of Ni/YSZ.

There are two types of phase transformations in the SCSZ component in the anode but not in the YSZ component [87]. The first type is that a part of the cubic phase SCSZ transforms into the rhombohedral phase by annealing in air at 1400 °C in the presence of NiO. This may be because the CeO$_2$, which can stabilize cubic SSZ from the c → β transition, probably has some interaction with NiO in the anode mixture. The second one is the c and β phases of SCSZ in the anode transform to tetragonal phase (t) when reduced at 900 °C for 2 h. This transformation is reversible since the t phase of SCSZ in the anode returns to c and β phases by re-oxidation in air at 800 °C. This second type of phase transformation can be detected by Raman but not by X-ray diffraction because it is induced by the slight displacement of oxygen ions along the c-axis while retaining the cubic symmetry of cations. Therefore, YSZ can maintain the cubic symmetry after the reduction process but a c → β transition occurs in the SCSZ, and this degradation will bring a decrease of about 1/2 – 1/3 in electrical conductivity [95].
Like their behaviors when playing roles in electrolytes of SOFCs, SCSZ in an anode does not have as good stability as YSZ in an anode; however, in comparison to the Ni/YSZ anode, Ni/SSZ or Ni/SCSZ shows better long-term performance when hydrocarbon fuels are used. It is widely known that carbon will form and deposit on a Ni/oxide electrode under high temperature if hydrocarbon fuels are used in the SOFC instead of pure hydrogen. The deposition of carbon leads to the detrimental destruction of the anode microstructure and cell performance during the internal reforming mode of operation. When methane was used as the fuel, carbon deposition on Ni/SSZ cermet anode was found to descend with elevating temperature but ascend on Ni/YSZ under the same operating conditions [96]. The results of TPR (Temperature-programmed-reduction), BET and SEM implied that Ni and oxide had a stronger interaction in Ni/SSZ than that in Ni/YSZ, and that Ni agglomeration was more serious in Ni/YSZ than in Ni/SSZ. In the long-term testing, the degradation rate of Ni/YSZ was faster than that of Ni/SCSZ, and the CH₄ conversion was stabilized for the long period in Ni/SCSZ cermet, while the activity of Ni/YSZ dropped abruptly after 600 min of operation [97]. The more stable operation was in accord with the smaller amount of deposited carbon in Ni/SCSZ. Besides the factors of materials, there are two ways to avoid carbon deposition or remove the carbon itself [92]:

1. Decrease operation temperature of SOFCs, which decreases the carbon deposition rate.

2. Increase fuel utilization rate to increase oxidants (H₂O and CO₂) which will be supplied to the carbon deposition part in the anode and remove the carbon.
2.3 Residual Stress

2.3.1 Design of Layered Structure for Residual Stress

In the symmetric three-layered system, the two materials forming layers suffer from a mismatch strain \( \varepsilon_m \) when the layered materials are cooled down from joining temperature \( T_0 \) to a particular temperature \( T \) [98]. This strain depends on the difference of the coefficients of thermal expansion (CTE) of two materials. That is

\[
\varepsilon_m = \int_{T_0}^{T} (\alpha_2 - \alpha_1) dT
\]

Where \( \alpha \) is CTE, suffix 1 stands for the outer layers and suffix 2 stands for inner layers. The suffixes have the same meaning through this entire report. Because of the strain, the thermal residual stress in outer layers \( \sigma_{r1} \) and inner layers \( \sigma_{r2} \) are

\[
\sigma_{r1} = -\frac{\varepsilon_m E'_1}{1 + \frac{t_1 E'_1}{t_2 E'_2}}
\]

and

\[
\sigma_{r2} = -\sigma_{r1} \frac{t_1}{t_2}
\]

where

\[
E'_j = \frac{E_j}{1 - \nu_j}
\]

\( t_1 \) and \( t_2 \) are the total thickness of outer layers and inner layers, respectively; \( E \) is the Young’s modulus and \( \nu \) is the Poisson’s ratio.
The residual stresses are controlled by the mismatch of CTEs and the thickness ratio. If the material of the outer layers has a lower CTE than that of the inner layer, the system will have a compressive stress present in the outer layer, which will hinder crack growth. The design of lamination structure has been employed in SiC-, B₄C- and Si₃N₄-based ceramics, and the strength and toughness have been enhanced by the effects of residual compressive stress designed [56,99–103]. If the layered system is used in the electrolytes for SOFC with a residual compressive stress designed at the outer layer, not only the robustness of the electrolyte but also the ionic conductivity of outer layers will be increased, as discussed in the following sections.

A special case which is worthwhile further discussing is the one with a thin outer layer, which is at the limit \( t_1/t_2 \to 0 \). Then the residual compressive stress \( (\alpha_1 < \alpha_2) \) in the outer layer will be

\[
\sigma_{r1} = -\frac{\varepsilon_m E_1}{1 - \nu_1} \quad (7)
\]

and the tensile stress in the inner layer will be

\[
\sigma_{r2} = 0 \quad (8)
\]

It is indicated that the ratio of \( t_1/t_2 \) can be controlled and adjusted, so that the compressive \( \sigma_{r1} \) will reach some required value range, and the outer layers will be reinforced; the tensile \( \sigma_{r2} \) can be as low as possible, and the fracture is not promoted in the inner layer. Furthermore, taking YSZ as outer layers and SCSZ as an inner layer, as an example, it creates a smaller ratio \( t_1/t_2 \), meaning less fraction of YSZ which has insufficient ionic conductivity in the intermediate temperature range and more fraction of SCSZ with superior ionic conductivity in those temperatures. Thus, the entire
system receives both reliable mechanical behavior and good ionic conductivity in the intermediate temperature range.

2.3.2 Effect of Stress and Strain on Ionic Conductivity

Recently, a number of papers reported the improvement of ionic conductivity of stabilized zirconia due to tensile stress in both experimentation and simulation. The stress was induced by lattice misfit in the interface or applied uniaxial/biaxial stress.

J. Santamaria [104] reported an increase of the ionic conductivity by a surprisingly eight orders of magnitude due to the interface effect (Figure 9a) [105]. In that research, an epitaxial heterostructures were fabricated that a thin layer of YSZ with thickness of 1 – 62 nm was formed between two strontium titanate (STO) layers, which were much thicker than the YSZ layer. In comparison with the ionic conductivity of a bulk YSZ and a thin film with thickness of about 700 nm, the YSZ layer between STO showed colossal increase of ionic conductivity though they have the same nominal composition. In order to determine the dependence of conductivity increasing on the interface, the alternative STO and YSZ layers were built up to construct a superlattice. As shown in Figure 9b, a linear dependence on the number of layers was determined, and the effect of YSZ/STO interfaces on the ionic conductivity was clarified. The X-ray indicated a coherent interface between YSZ and STO. As well, the result of the electron energy-loss spectroscopy indicated the STO termination layer was always a TiO$_2$ plane. YSZ layer grew
epitaxially, with a 45° rotation of the cell in order to accommodate half of the diagonal of the YSZ unit cell to the STO unit cell. Since the lattice parameter $a_{YSZ}/\sqrt{2} = 0.361$ nm and $a_{STO} = 0.390$ nm, a 7% in-plane tensile strain was present on the YSZ layer. Thus in this configuration, YSZ with an FCC fluorite structure kept the positions of all the atoms, excluding the oxygen atoms, which were displaced to $z = 1/4$ along the $c$-axis instead of at the $z = 0$ plane. Although the cation lattice remained coherent, the interfacial O plane was likely highly disordered and contributed to the high ionic conductivity.


Figure 9: (a) Logarithm of the long-range ionic conductivity (in S·cm$^{-1}$) of the trilayers STO/YSZ/STO vs. inverse temperature; (b) Conductance at 400 K of superlattices consisting of repeated layers of 1 nm YSZ / 10 nm STO, as a function of the number of interfaces (the number of [YSZ/STO] repeats is half the number of interfaces)
C. Korte [106,107] studied ionic conductivity for oxygen in superlattices of multilayer systems CSZ (ZrO$_2$+CaO)/Al$_2$O$_3$ and YSZ (ZrO$_2$ + 9.5 mol% Y$_2$O$_3$)/Y$_2$O$_3$. The multilayer systems were prepared on (0 0 0 1) Al$_2$O$_3$ substrates by pulsed laser deposition. They derived the ionic conductivity in a multilayer system:

$$\sigma_{tot} = \sigma_{vol} + 2\delta(\sigma_{int} - \sigma_{vol}) \frac{1}{d} + 2\delta'\sigma_{gb} \left( \sigma_{gb} - \sigma_{vol} \right)$$  \hspace{1cm} (9)

Where \(\sigma\) is conductivity, and the suffixes tot, vol, int and gb stand for total, volume, interface and grain boundary, respectively; \(d\): layer thickness of ionic conductor; \(\delta\): thickness of each conductor/insulator boundary; \(\delta'\): thickness of grain boundary; \(c_{gb}\): the average density of grain boundaries.

When the density of the phase boundary or the reciprocal thickness $1/d$ of the individual layers increased, the ionic conductivity in the YSZ/Y$_2$O$_3$ multilayer systems exhibited a linear increase in the direction parallel to the heterophase boundaries.

In a coherent interface and a semicoherent interface, the ionic conductivity increases with increasing mismatch $f$.

$$\ln \sigma_{A,int}^{coh} \sim f$$ \hspace{1cm} (10)

$$\sigma_{A,int}^{sem} \sim f$$ \hspace{1cm} (11)

As a result of increasing mismatch $f$ or coherency strain, the density of misfit dislocation increases, and it leads to the enhancement of interface diffusivity and thus an increasing ionic conductivity, as shown in Figure 10. Therefore, increasing both the reciprocal thickness of layers
and the misfit in the interface is an approach to high ionic conductivity parallel to the heterophase multilayer systems.

Besides the increase of ionic conductivity due to nano effect and interface effect caused by stress or strain from superlattice structures or multilayer systems, ionic conductivity of YSZ bulk is also affected by external applied tensile or compressive stresses.

Source: Korte C, Peters A, Janek J, Hesse D, Zakharov N, Ionic conductivity and activation energy for oxygen ion transport in superlattices—the semicoherent multilayer system YSZ (ZrO$_2$ + 9.5 mol% Y$_2$O$_3$)/Y$_2$O$_3$, Physical Chemistry Chemical Physics, 10(31), 4623–35, 2008

Figure 10: Simplified dependence of the interface structure and the density of misfit dislocations from the lattice mismatch $f$
The 14 mol\%-yttria-doped zirconia (14YSZ) single crystals were studied in tensile and compressive tests [108]; the experiment setup is shown in Figure 11(a) and (b). The in-plane crystal orientations were <1 0 0> and <1 1 0>, and the out-of-plane orientation was (1 1 0). The specimens for the tensile and compressive tests were cut out from the plate. The orientation of each specimen was either <1 0 0> or <1 1 0> in the longer axis, depending on the direction of cutting. In the tensile test, the applied load was parallel to the <1 0 0> or <1 1 0> crystal direction. In the compressive test, the applied load was perpendicular to the <1 0 0> or <1 1 0> crystal direction. The four-terminal method was used to measure the impedance parallel to the crystal direction along the longer axis, which were the elongated directions in both tests. The impedance test was performed by applying a constant stress in the loading process. Also, the impedance during the unloading and reloading processes of several cycles was measured as well.

At the temperature of either 600 °C or 900 °C, the conductivity monotonically was increasing as the tensile stress was loaded, as shown in Figure 11c–d. The conductivity always exhibited the increase in the loading and several reloading processes while it decreased during the unloading processes. Like an elastic behavior, the ionic conductivity showed a reversible change during the processes. The same trend was observed for the specimen with the <1 1 0> orientation. For both orientations, the improvement due to the tensile stress of 20 MPa was higher at the lower temperature, that is 18 % at 600 °C while 12 % at 900 °C for the <1 0 0> orientation. The improvement of the <1 0 0> orientation was generally higher at both temperatures.
Figure 11: Experiment setup for tensile test (a) and compressive test (b). Conductivity of 14 YSZ subjected to uniaxial tensile stress (c–d) and compressive stress (e–f) at 600 °C and 900 °C.

The conductivity increased with the compressive stress but saturates at the higher stress at both temperatures, as shown in Figure 11e–f. Like the case of tensile, the reversible process was similar to elastic deformation. The same trend was observed for the specimen with the <1 1 0> orientation. For both orientations, the improvement caused by the compressive stress of 19 MPa was generally higher at the lower temperature, e.g., 15 % at 600 °C and 8 % at 900 °C.

Therefore, the oxygen migration can be enhanced in the tensile direction whereas it can be decreased in the compressive direction, and the improvement is higher at the lower temperatures. Similar experiments were carried on in 8YSZ, and the same trends were obtained [109]. The maximum improvement was about 18% at 700 °C, while the simulation showed 40% at this temperature. The phenomenon of ionic conductivity decreasing under compressive stress was also observed in the zirconia–alumina composites [110].

Using molecular dynamics simulations in 8 mol % yttria doped zirconia, W. Araki et al [108,109,111] studied the oxygen ionic conductivity in different crystal directions when uniaxial stress was applied along [1 0 0]. Under a uniaxial tensile stress, the oxygen ions preferred migrating along the direction of the tensile stress but rarely in the other directions perpendicular with the tensile stress (Figure 12a–c). In the other case under a uniaxial compressive stress, the ionic conductivity decreased in this direction, but slightly increased in other directions perpendicular to it (Figure 12d–f). They used the mechanism of the recovery force between ions to explain this: the tensile stress would lead to a recovery force, and it drew the neighboring oxygen
ion toward vacancy, while the compressive stress would cause a repulsive force to hinder the migration of oxygen ions.


Figure 12: Directional mean square displacement of oxygen ion in the direction of [1 0 0], [0 1 0] and [0 0 1], subjected to uniaxial tensile stress (a–c) or compressive stress (d–f) in the [1 0 0] direction at 1000 °C
In regards to lattice deformation and ion displacement, the intensity of the second neighboring distance of $O^{2-}–O^{2-}$ under tensile stress was slightly decreased, and it contributed to the gradual decrease of the elastic modulus. At the beginning of the decrease, the oxygen displacement was the largest, and the diffusion coefficient was at the maximum, the strain under which was optimized for the maximum diffusion enhancement.

Also, the biaxial strain effects on the oxygen vacancy mobility in YSZ were studied by A. Kushima et al [112] using density functional theory and nudged elastic band simulations. They explained the microscopic mechanism by correlating the oxygen migration barrier with the presence of the lattice strain, and there are two competing processes in parallel fundamentally. One is the migration spacing of the oxygen or the cation–cation distance midst the path for the oxygen migrating. The other one is the bonding strength between the oxygen and the nearest cation which prevents the oxygen from migrating. In consideration of the two processes, the migration barrier of oxygen vacancy can be decreased by enlarging the migration spacing and weakening the strength of oxygen–cation bond. It was found that the macroscopic oxygen diffusivity increased exponentially in YSZ until the biaxial tensile strain reached the critical value. This impact at lower temperatures was more significant. If the strain went beyond that critical value, the oxygen diffusivity in YSZ was worsened because the oxygen–cation bond was strengthened by the local relaxation. Thus, the critical strain can be considered as the optimal strain, or the fastest strain, where the oxygen diffusivity is best benefited by the biaxial tensile lattice strain.
Therefore, the appearance of residual stresses in ionic conductors can be very beneficial for the performance of the electrolytes. On one side, controlling the distribution of tensile and compressive stresses in the layered electrolytes may enhance the ionic conductivity. On the other side, the appearance of compressive stress in the thin outer layers will lead to improved mechanical stabilities and reliability [98–103]. Thus, the ideas of design and manufacturing of symmetric layered electrolytes using SCSZ and YSZ layers will well bring immediate benefits to SOFC performance at lower temperatures.
CHAPTER THREE: DESIGN AND MANUFACTURING OF LAYERED ELECTROLYTES FOR SOLID OXIDE FUEL CELLS

3.1 Introduction

Among various candidates for the electrolytes of SOFC as reviewed in CHAPTER TWO, the ZrO$_2$-based ceramics were chosen for our study in consideration of the good stability in the dual atmosphere as well as reliable durability under circling. The 10 mol% Sc$_2$O$_3$ – 1 mol% CeO$_2$ – ZrO$_2$ (SCSZ) ceramic has superior ionic conductivity, and it exhibits stabilized cubic phase both at room temperature and around 800 °C. However, the degradation during the operation occurs when the unwanted cations from the electrodes and fuels invade the electrolyte and destroy the stability of SCSZ unfortunately. The SCSZ electrolytes will barely play a solo with the superior ionic conductivity. An effective approach is to be accompanied by another similar but more stable material with protection against the impurities outside. The 8 mol% Y$_2$O$_3$ – ZrO$_2$ (YSZ) is selected.

The insight of building the robust electrolyte is employing a layered structure to laminate SCSZ with YSZ. The SCSZ is set as the inner layer(s), and the SCSZ core will bring high ionic conductivity to the electrolyte at the operation temperature 800 °C. The single YSZ layers are assembled as the outer layers for the SCSZ core, and thus the good mechanical behavior, phase
stability and reliability are brought by the YSZ skin. Because the SCSZ layers are completely encapsulated by YSZ layers, the degradation of SCSZ due to directly receiving the unwanted elements from the electrode or impurity from fuels is avoided. The protection by YSZ ensures the SCSZ maintains its phase structure and ionic conductivity during the operation of the SOFC, while the more stable and reliable outer YSZ layers are less affected by the impurity elements.

Since both SCSZ and YSZ are ZrO$_2$-based ceramics with fluoride-type structure, they can be compatible in the bulk of electrolyte. However, the slight difference in the thermal expansion between YSZ and SCSZ introduces residual stresses in every layer of the electrolytes after co-sintering. The compressive stress in outer layers will enhance the strength of the electrolytes, which is another motivation for employing layered structures. The effects of the residual stress and the relation to the layered design will be further discussed in CHAPTER FOUR.

In this chapter, the three-layered electrolytes with different ratios of thicknesses were produced. The characterization of phase structure and microstructure proved the feasibility of the manufacturing.

### 3.2 Design of Layered Electrolytes

Nine designs were carried out for the manufacturing of layered electrolytes with different volume fractions of YSZ outer layers and SCSZ inner layers by adjusting the number of layers of each composition used in the laminates. Thus, the inner core SCSZ structure consisted of one, two,
and four single layers. The outer skin YSZ structure was always assembled using one single YSZ layer; therefore the ratio of the thicknesses of the core and skin layers can be varied in a precise and well-controlled manner. Besides Y–xSC–Y layered composite electrolytes, the electrolytes with three, four, and six layers of single x–YSZ and x–SCSZ compositions were also assembled in order to compare the performance of composite and single phase electrolytes. The schematic designs of layered electrolytes are shown in Figure 13.

Figure 13: Design of layered electrolytes
3.3 Experimental

3.3.1 Manufacturing of Layered Electrolytes

Electrolytes were processed using the following steps shown in Figure 14. The slurry of SCSZ and YSZ powders were prepared in accordance with *Tape casting theory and practice* by Mistler and Twiname [113]. The composition of slurry for tape casting was listed in the Table 2. The powders were purchased from Daiichi Kigenso Kagaku Kogyo, Japan – 0.1 Sc₂O₃–0.01 CeO₂–0.89 ZrO₂ (SCSZ) powders and Tosoh, Japan – 0.8 Y₂O₃–0.92 ZrO₂ (YSZ). Taking the SCSZ slurry as an example, the SCSZ powders were mixed with Menhaden fish oil (dispersant), Xylenes (solvent) and Ethyl alcohol (solvent), and the mixture was ball-milled in a plastic container for 24 h at 58 rpm. Afterwords, polyvinyl butyral (binder), Butylbenzyl phthalate (plasticizer) and Poly alkylene glycol (plasticizer) were added into the mixture, it was ball-milled for another 24 h at 58 rpm. After the slurry was prepared, a desiccator with a vacuum pump was used to remove gas bubbles (degas) in the slurry using a pressure of 635 mmHg for 8 min. The viscosity of the slurry was measured by a viscometer (Brookfield Dv-II+ Pro, USA) with an RV4 spindle at 20 rpm. The degassed slurry was then tape casted in the Precision tape casting equipment (Pro Cast, USA), with 200 μm gap of the doctor blade set up for the tape casting. Then, the green tapes were ready for further processing after drying in air for at least 24 h. From the tapes, SCSZ discs were punched out for subsequent lamination. YSZ discs were prepared via the same procedure as described above.
Table 2: Composition of slurry

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Chemical function</th>
<th>Weight percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ/SCSZ</td>
<td>Powders</td>
<td>47.3%</td>
</tr>
<tr>
<td>Menhaden fish oil, blown Z-3</td>
<td>Dispersant</td>
<td>1.7%</td>
</tr>
<tr>
<td>Xylenes</td>
<td>Solvent</td>
<td>21.1%</td>
</tr>
<tr>
<td>Ethyl alcohol, anhydrous denatured</td>
<td>Solvent</td>
<td>21.1%</td>
</tr>
<tr>
<td>Polyvinyl butyral</td>
<td>Binder</td>
<td>4.4%</td>
</tr>
<tr>
<td>Butylbenzyl phthalate</td>
<td>Plasticizer I</td>
<td>2.2%</td>
</tr>
<tr>
<td>Poly alkylene glycol</td>
<td>Plasticizer II</td>
<td>2.2%</td>
</tr>
</tbody>
</table>

Figure 14: Processing steps used to produce the layered electrolytes
The SCSZ discs and YSZ discs were stacked in a certain order (Figure 13) with in-plane rotation by \((360^\circ / n)\) for every layer \((n\) is the number of layers), to achieve both the required design and homogeneous thickness of the electrolyte after sintering. The stacked layers were heated up to 120 °C and further laminated under a pressure of 25 MPa using a heated hydraulic press. In order to avoid curvature and buckling during the sintering, each laminated electrolyte disc was placed in between two \(\text{ZrO}_2\) coated \(\text{Al}_2\text{O}_3\) setter platens, each of which has a weight of about 10.6 g, to provide the flatness of the electrolyte after sintering. The discs with setter platens were set up in the high temperature furnace (MHI, USA), and the multilayer discs were pressureless co-sintered at 1550 °C for 5 h to produce the layered electrolytes, with temperature holds at 300 °C and 600 °C for 3 h each time in order to completely decompose and remove the present organics; the heating and cooling rates were 1 °C/min and 2 °C/min, respectively.

3.3.2 Characterization

3.3.2.1 Powder Characterization

In the sample preparation for microscopy, the raw powders of YSZ and SCSZ were dispersed in acetone by ultra-sonic vibration for 10 min, and the suspension was dropped on the conductive tape stuck on an aluminum stub. After coated by a thin layer of gold, the powders were observed by a scanning electron microscope (SEM, Ultra-55, Zeiss, USA). To prepare the specimens for the transmission electron microscope (TEM), the copper grids with carbon membranes were
immersed in the suspension and then dried. The powders were studied in the TEM (Tecnai F30, FEI, Netherlands). The phase structures of raw powders were determined by a theta-theta powder X-ray diffractometer with a copper target (Rigaku, Multiflex, Japan) under 40kV and 30 mA. The pure SCSZ and pure YSZ sintered electrolytes were also ground into powders, and then the X-ray diffraction patterns were collected using the same method.

Besides, the lab X-ray diffraction technique is insufficient to reveal the lattice distortion due to the displacement of light ions (e.g. O^{2-}). The compensatory oxygen vacancy and other defects due to doping Y^{3+}, Sc^{3+} and Ce^{4+} in ZrO_2 lattice are not characterized by XRD either. The neutron diffraction technique was further employed to study the crystal structure of YSZ and SCSZ ground powders using POWGEN neutron powder diffractometer at the Spallation Neutron Source in Oak Ridge National Laboratory, Oak Ridge, TN. The collected time-of-flight powder neutron diffraction data were refined using the GSAS software package and the EXPGUI interface.

In order to measure the shrinkage of the material during sintering, the SCSZ and YSZ raw powders were pressed into 4 mm × 4 mm × 7 mm bars using a uniaxial pressure of 20 MPa. Then the specimens were set up in a dilatometer (Thermoanalyse, BAHR, Germany), and the temperature was increased at a rate of 3 °C/min from RT to 1530 °C in air. The shrinkage and the differential of shrinkage were measured and calculated.
3.3.2.2 Characterization of Layered Electrolytes

SEM imaging (Ultra-55, Zeiss, USA) was used to study the fracture surface of the electrolytes, and energy dispersive X-ray spectroscopy (EDS) was used to measure the distribution of Y and Sc atoms in the layers along the thickness. The thickness of each layer in the electrolytes was calculated by the profile of the atom distributions. In order to detect and analyze the impurity elements and their distributions, Adept-1010 Dynamic SIMS System (Physical Electronics USA, ULVAC-PHI, Kanagawa, Japan) has been used to collect mass spectra for the samples. An O₂ primary beam of 8 kV and 5 nA was rastered over an area of 300 μm × 300 μm. Only positive secondary ions were collected for ion imaging. An auxiliary e-gun was used for charge neutralization.

The densities of the sintered electrolytes in nine designs were measured by the Archimedes method using deionized water. The density is calculated by

\[
\rho = \frac{m_0}{m_0 - m_1} \rho_L
\]

where \(m_0\) is the weight of the specimen; \(m_1\) is the apparent weight when the specimen is completely immersed in the liquid; \(\rho_L\) is the density of reference liquid used immerse the specimen. Deionized water was used as the reference liquid, and the densities at the particular temperature were looked up in the handbook.
3.4 Result and Discussion

3.4.1 Powder Characterization

3.4.1.1 Phase Structure and Impurity

The X-ray diffraction (XRD) patterns of SCSZ and YSZ raw powders along with the sintered electrolytes are shown in Figure 15A–D. It suggests the cubic phase in both SCSZ and YSZ raw powders. The SCSZ raw powders may contain a small amount of low symmetric phases or unknown impurities (Figure 15A, pointed by ▼). In the sintered electrolytes, the previous impurity peaks disappear in the electrolyte samples after the sinter processing, but the XRD profiles of SCSZ also suggested the existence of some low symmetric phase, which is still not identified (Figure 15B, pointed by ▽). In the XRD profiles of YSZ powders after sintering (Figure 15C–D), only the pure cubic phase is observed without impurity detected. It is clarified that the splitting peaks at high angles were due to the Kα2 radiation and nothing to the rhombohedral or tetragonal phase. The (4 0 0) profile near 2θ = 75° provided the counterexample: the rhombohedral lattice would not split (4 0 0) peak while the splitting (4 0 0) peaks in tetragonal phase would have a weaker one at the lower angle but a stronger one at the higher angle. It is thus concluded that the shoulders at the right are not caused by the presence of rhombohedral or tetragonal phase but due to the Kα2 radiation.

Similarly, neither a rhombohedral phase nor a tetragonal phase was detected by neutron diffraction (Figure 15E–F), otherwise peak splits at (2 0 0) or (1 1 1) would have occurred. The
results indicate a better phase stability in YSZ than in SCSZ, which is not unexpected. Accordingly, the layered electrolytes with YSZ outer layers and SCSZ inner layer were designed and manufactured in order to introduce stable outer layers.

The lattice parameters were calculated and listed in Table 3. In comparison with that of raw powders before sintering, the lattice parameter of the cubic phase decreased by 0.2% in SCSZ and 0.6% in YSZ after sintering. With the refinement of neutron diffraction, the concentrations of oxygen vacancy in YSZ and SCSZ were estimated to be 7.3% and 9.8%, respectively. The higher value in SCSZ coincides with the higher ionic conductivity.

The Secondary Ion Mass Spectrometry (SIMS) shows that unwanted impurities Na and Cl were found in the raw powder beyond the nominal composition (Figure 16), but no obvious Si, Mg or Al were found. The Cs spectrum appeared because the Cs primary beam was used.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameter / Å</th>
<th>Oxygen vacancy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-ray diffraction</td>
<td>Neutron diffraction</td>
</tr>
<tr>
<td>YSZ</td>
<td>raw powder</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>after sintering</td>
<td>5.12</td>
</tr>
<tr>
<td>SCSZ</td>
<td>raw powder</td>
<td>5.08</td>
</tr>
<tr>
<td></td>
<td>after sintering</td>
<td>5.07</td>
</tr>
</tbody>
</table>
Figure 15: X-ray diffraction patterns (A–D) of SCSZ and YSZ powders before and after sintering; and neutron diffraction patterns (E–F) of SCSZ and YSZ sintered powders.
Figure 16: SIMS of SCSZ with + secondary detection (A) and – secondary detection (B); SIMS of YSZ with + secondary detection (C) and – secondary detection
3.4.1.2 Agglomerates and Granules

The micrographs of SCSZ and YSZ raw powders by the scanning electron microscope (SEM) are shown in Figure 17.

The SCSZ grains with uniform grain size of 135 ± 25 nm (Figure 17C) are assembled into larger agglomerates with size of 10–15 μm (Figure 17A–B), with some of them being spherically shaped granules (Figure 17B).

Similar agglomeration is observed in YSZ. In comparison with the SCSZ grains, the YSZ grains were slightly smaller, the average diameter of which was about 70 ± 16 nm (Figure 17F). YSZ particles self-assembled into the agglomerates of irregular shape and no spherical granules have been found (Figure 17D–E).

3.4.1.3 Crystallites

The micrographs of the SCSZ and YSZ powders via TEM are shown in Figure 18. The particle size of measured in the TEM images are coincident with the results by SEM. The observed average grain size of the YSZ powders (89 ± 26 nm) is smaller than the size of the SCSZ powders (110 ± 12 nm). The lattice images of SCSZ and YSZ are shown in Figure 18C–D. Most of the particles of SCSZ show only one periodicity of the lattice fringes with a typical structure presented in Figure 18C. The spacing of (1 1 1) plane is $d_{111} = 0.292$ nm, as determined by measuring the distances and angles between the spots in the Fast Fourier transform (FFT) pattern (Figure 18C insert).
Figure 17: Morphology of SCSZ (A–C) and YSZ (D–F) raw powders observed via SEM
Assuming a cubic structure, the lattice parameter calculated for this $d$-spacing is 0.506 nm, which closely matches the XRD result in Table 3. However, by indexing the other, more faint diffraction spots in the FFT, it is determined that $d_{111} = 0.283$ nm. Such a difference could simply arise from measurement error in determining the precise location of the diffraction spot, but might also suggest the presence of the slight rhombohedral distortion in SCSZ fluorite structure occurring on the nanoscale level, but not detectable on the microscale. Confirming this hypothesis will require a more in-depth investigation which is beyond the scope of this dissertation, but from another angle in CHAPTER SIX, the structures of the SCSZ and YSZ lattices will be studied by neutron diffraction.

In the YSZ raw powders, smaller nanoparticles with different orientations were found within the individual grains. A high resolution TEM image of two neighboring nanoparticles is shown in Figure 18D. By studying the FFT pattern, the crystallite (A) in the right-bottom was indexed, as shown in Figure 18D. The spacing of the (1 1 1)A plane is $d_{(1 1 1)A} = 0.304$ nm, which is larger than the (1 1 1) spacing in SCSZ, due to the fact that the Y$^{3+}$ ion has a larger radius than Sc$^{3+}$ ion. Another matrix crystallite, indicated as B in the Figure 18D, shows lattice fringes, which is determined to be a (2 2 0)B plane with the spacing $d_{(2 2 0)B} = 0.187$ nm. Again assuming a cubic structure, the lattice parameter calculated from either $d$-spacing is 0.527 nm, which is slightly higher than the value measured by XRD reported in Table 3. Interestingly, the (1 1 1)A and (2 2 0)B planes are parallel, and the overlap in the two nanoparticles.
Figure 18: Grains of SCSZ (A) and YSZ (B) raw powders observed via TEM, and high resolution TEM images of crystallites in SCSZ (C) and YSZ (D)
It is concluded that SCSZ powder contained single crystal grains while the YSZ grains were made up of a more complex structure of smaller nanoparticles.

3.4.1.4 Sintering Shrinkage

In order to determine the sintering behavior of SCSZ and YSZ powder, the longitudinal shrinkages of SCSZ (DKKK, Japan) and YSZ (TZ-8Y, Tosoh, Japan) pressed bars were measured (Figure 19). It was determined that the SCSZ sample had a maximum shrinkage rate detected at 1194 °C while the YSZ sample showed its highest shrinkage rate at 1375 °C. At 1500 °C, the SCSZ sample was almost sintered with shrinkage of 31% in comparison with the initial length of the bar at room temperature. The YSZ samples had not reached the highest density at 1500 °C, and it shrunk by 27%. Therefore, in comparison with SCSZ, YSZ needs a longer time and higher temperature to completely densify with the same ramp rate. Regarding the trends of the shrinkage profiles, it can be deducted that if the SCSZ and YSZ samples are dwelled at a temperature such as 1550 °C for a certain period where both samples have passed the temperatures with their the maximum shrinkage rate, the SCSZ and YSZ powders will be co-sintered, and the temperature higher than that with the fastest shrinkage will provide proper free energy for driving the grain growth. The profile of YSZ also suggests that the shrinkages of YSZ sample will probably get to about 30% and closed to that of the SCSZ sample, and it indicates the little mismatch of the shrinkage after the co-sinter of both samples.
Figure 19: Shrinkages and their differentials of SCSZ and YSZ green body during sintering
3.4.2 Manufacturing and Characterization of Layered Electrolytes

3.4.2.1 Design and Optimization of Manufacturing

After ball-milling and degassing with a vacuum pump, the SCSZ slurry showed a viscosity in the range of 3400 – 3700 mPa s, while YSZ slurry viscosity was measured to be in the range of 500 – 1700 mPa s with an RV4 spindle at 20 rpm. Although the different viscosity values for SCSZ and YSZ slurries were a result of different particle sizes and specific surface areas of SCSZ and YSZ powders, the values lie within the proper range for the tape casting of slurries as it was suggested [113]. Therefore, it was decided that the viscosity of both slurries is in an acceptable range for high quality tape casting.

The processing parameters, such as degassing time and the amount of additives, have a significant effect on quality of slurries and, as a result, on the quality of the green tapes. If the amount of binder for the slurry preparation was decreased from 4.4% to 2.4%, the viscosity of SCSZ slurry would drop from 500 – 1700 mPa·s to 100 – 200 mPa·s. Such a decrease in the viscosity of slurry leads to the formation of cracks in the tapes during tape casting. Also, if the time of degassing increased from 8 min to 15 min, the viscosity of the SCSZ slurry would increase to larger than 6000 mPa·s values because of the intensive evaporation of the solvent. Therefore, it was important to follow the procedure described in *Tape casting theory and practice* by Mistler and Twiname [113], and any modification on the composition or processing of the slurry should be carefully made in order to obtain good quality tapes for ease of handling and with uniform
thickness.

In last section it was determined that the shrinkages of SCSZ and YSZ bars made from dry pressed powder were 31% and 27% after the sintering. However, it was determined that the lateral shrinkage of the tapes differed from the axial shrinkage of SCSZ and YSZ powders, possibly due to the presence of large amounts of organics in the tapes, and also because the axial and lateral shrinkages of the materials are typically different and depend both on the properties of the powder and on the technique used for packing.

By a series of trial and error experiments, it was determined that a punch with the inner diameter of 47 mm was used to produce electrolyte discs from the two compositions with a 36 mm targeted diameter of the electrolytes after pressureless sintering at 1550 °C for 5 h. In this case, the lateral shrinkage of the SCSZ tape was equal to 23.6% after sintering, and the lateral shrinkage of the YSZ was 23.8%. As an alternative dimension with smaller diameter, if the targeted diameter of the sintered electrolyte was about 21.5 mm in diameter, then a 28 mm inner diameter punch was used to produce electrolyte discs from the tape for further lamination.

3.4.2.2 Dimension and Density of Electrolytes

The laminated discs were sintered to produce the electrolytes. The dimensions of the electrolytes of the nine types of designs were measured by a caliper and a micrometer. The Table 4 and Table 5 list the average dimension from about 30 pieces of electrolytes with each design.
Table 4: Average thicknesses of samples in 9 designs

<table>
<thead>
<tr>
<th>Design</th>
<th>3-layered</th>
<th>4-layered</th>
<th>6-layered</th>
<th>Average thickness per layer / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>x–YSZ</td>
<td>116.2 ± 14.5</td>
<td>123.9 ± 13.7</td>
<td>215.0 ± 38.1</td>
<td>35.01</td>
</tr>
<tr>
<td>x–SCSZ</td>
<td>101.5 ± 8.3</td>
<td>146.1 ± 17.6</td>
<td>201.0 ± 35.5</td>
<td>34.51</td>
</tr>
<tr>
<td>Y–xSC–Y</td>
<td>90.6 ± 9.5</td>
<td>129.2 ± 46.5</td>
<td>179.1 ± 14.0</td>
<td>30.69</td>
</tr>
</tbody>
</table>

Table 5: Average diameters of samples in 9 designs

<table>
<thead>
<tr>
<th>Design</th>
<th>3-layered</th>
<th>4-layered</th>
<th>6-layered</th>
<th>Average diameter / mm</th>
<th>Average shrinkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>x–YSZ</td>
<td>35.86 ± 0.19</td>
<td>35.82 ± 0.15</td>
<td>35.83 ± 0.16</td>
<td>35.84</td>
<td>23.8%</td>
</tr>
<tr>
<td>x–SCSZ</td>
<td>36.00 ± 0.09</td>
<td>35.83 ± 0.12</td>
<td>35.98 ± 0.09</td>
<td>35.94</td>
<td>23.6%</td>
</tr>
<tr>
<td>Y–xSC–Y</td>
<td>36.65 ± 0.18</td>
<td>36.89 ± 0.18</td>
<td>36.87 ± 0.12</td>
<td>36.80</td>
<td>21.7%</td>
</tr>
</tbody>
</table>
Using the measured thicknesses of the layered electrolyte discs, it was determined that the nominal average thickness of one tape casted layer was in the range of 30 – 35 μm after sintering. The deviation of the thickness mostly attributes to the uneven tape in the tape casting procedure – the discs from the heading and ending sections of a certain tape have varied thickness.

It was also determined that shrinkage of the layered composite electrolytes was different and did not follow the rule of mixture from those sintered using a single SCSZ or YSZ composition. As shown in Table 5, the lateral shrinkages were 23.6% and 23.8% for SCSZ and YSZ, respectively, but the layered Y–xSC–Y electrolyte only densified 21.7%, which is obviously smaller than the shrinkage of those samples with single composition of either YSZ or SCSZ, although they were produced with the same processing. While the exact reason for such behavior is not known, one possible reason is the interface effect between inner SCSZ layer and the outer YSZ layers, where inter-diffusions of Y, Sc, and Ce atoms across the interface as well as the presence of mismatches of shrinkage and thermal expansion between the layers were present. The densification was then probably retarded at the layered electrolytes.

The densities of electrolytes for all nine designs were measured, and the data are presented in Figure 20. The theoretical density for each design were also calculated using the rule-of-mixture for the volume fractions of different phases, the phases’ nominal compositions, and the lattice parameters calculated from the diffraction data in Table 3. The measured densities are almost always lower than those calculated theoretical values, except for the on Y–1SC–Y layered design.
This can attribute to the difficulties in obtaining the accurate measurements as the masses of the samples is quite low (~500 mg) and to the uncertainties in the exact volume fraction of the SCSZ and YSZ phases in composite electrolytes. The density measurement results suggest that a small amount of pores are still present in the electrolytes after sintering.

Figure 20: Densities of layered electrolytes with different designs, in comparison with theoretical density (dash line)
The SEM micrographs of fracture surfaces along the out-of-plane direction of three-, four- and six-layered Y–xSC–Y electrolytes are shown in Figure 21. The electrolytes have rather homogeneous and continuous fracture surfaces without delamination along the interfaces between layers. In the view of EDS analysis (in line scanning mode) along the electrolyte thickness, the outer YSZ layers and inner SCSZ layer are indicated by the distribution of Y and Sc ions, as shown in Figure 21. The thickness of the layers can also be estimated. As designed, the thickness ratios in Y–1SC–Y, Y–2SC–Y, and Y–4SC–Y layered electrolytes are expected to be 1:1:1, 1:2:1 and 1:4:1, and the elemental line profiles reflect the anticipated ratios in all three designs. Some small deviations from the designed ratios are expected because of the nonuniformity in thickness of tapes along the width of the tape after tape casting as well as the variation of the thicknesses of tapes in different tape batches. For these reasons, the thicknesses of the sintered electrolytes presented in Figure 21 deviate from the values listed in Table 4, which were measured using the micrometer and given as average numbers for statistical purpose.

It is also important to notice the interdiffusion of Y$^{3+}$ and Sc$^{3+}$ ions at the interfaces after sintering, as detected by EDS analysis. The dash lines in Figure 2.9 represent the thickness of the interfaces between layers with different composition. The thickness of interfaces varied between 5 and 10 μm, and appears to increase with the thickness of the SCSZ layer. However, it should be noted that the spot size of the EDS probe used in the measurement was about 3 – 5 μm, and the edge effects from the large probe could contribute to the gradient of the concentration profile.
Figure 21: Element distributions in (A) Y–1SC–Y, (B) Y–2SC–Y and (C) Y–4SC–Y
3.4.2.3 *Pores and Impurities in the Layered Electrolytes*

As it was indicated from the density measurements, a certain amount of porosity is expected to be found in the sintered electrolytes. The SEM micrographs of Y–2SC–Y electrolyte are shown in Figure 22, where the presence of porosity in YSZ and SCSZ layers can be clearly seen. Many large pores were observed in YSZ outer layers, while fewer and smaller pores were detected in the inner SCSZ layer. The lower magnification images (Figure 22A–B) show the difference in the porosity between YSZ and SCSZ layers in layered electrolytes. The difference in pore density allows the interfaces between layers to be clearly distinguished. The images with higher magnification (Figure 22C–D) reveals that SCSZ layer has lower porosity and pores are located both along the grain boundaries and inside grains. The YSZ layers contained which were preferably located along the grain boundaries. Such difference in shrinkage and pore formation in YSZ and SCSZ layers could be explained by the development of thermal residual stresses during constrained sintering of layered electrolytes. For comparison, the porosity and location of the pores were analyzed in the pure YSZ and SCSZ electrolytes, which were manufactured using the same approach as the layered Y–xSC–Y electrolytes, but they do not contain a compositional gradient. In the pure YSZ and SCSZ electrolytes, the porosity is much lower, the pore size is smaller, and most of the pores are located inside the grains, where very little intergranular porosity can be found (Figure 22E–F). Thus, the constrained sintering of the layered Y–xSC–Y electrolytes are probably one of the reasons for the exclusive formation of the intergranular porosity in the layered electrolytes.
Figure 22: (A) fracture surface of Y–2SC–Y samples in SEM; (B) pores near the interface of YSZ layer and SCSZ layer; (C) pores in outer YSZ layer; (D) pores in inner SCSZ layer; (E) fracture surface of 4–YSZ samples; and (F) fracture surface of 4–SCSZ samples.
Because of preferential pore locations along the grain boundaries, the grain size of the YSZ and SCSZ ceramics can be estimated. From the estimation, one can tentatively suggest that YSZ ceramics have smaller grain size than SCSZ ceramics.

The unfavorable impurities, such as silica, alumina, and titania, which segregate along the grain boundaries and prohibit/hinder the densification, are also important to investigate. In order to indentify the impurities present in the layered electrolytes, SIMS was used to analyze the elements present and build in the maps of their distribution along the electrolyte thickness (Figure 23). The three layers of the electrolyte can be clearly distinguished from the distribution of Y, Sc and Ce ions maps. Zr ions are present in all layers and the total thickness of the electrolyte can be determined using Zr ion map. As anticipated, Y is found in the outer layers, and Sc and Ce are found in the inner layer of the electrolyte. Similar to the EDS line mapping, presented in Figure 21, the interdiffusion and blurred element distribution along the interface between YSZ and SCSZ layers were detected by SIMS, which can also be a result of relatively broad (about 5 μm) O₂ beam. In addition, Al and Mg ions were also found. Their increased concentration, indicated by a higher brightness on Mg and Al ion maps in Figure 23, was found in the outer regions of the electrolytes. Thus, the source of these two impurities might have originated from the sample exposure to the processing environment during the manufacturing. SIMS results also indicate some spots with high Si content, which can originate from the raw materials or the manufacturing environment.
Figure 23: Elements identified by SIMS in layered electrolyte, and the mapping of elements distribution on the fracture surface
The presence of impurities and the constrained sintering of layered electrolyte might hinder the densification of YSZ outer layers leaving the intergranular porosity in after sintering. The pores in Figure 22C are probably a result of these impurities precipitating at the grain boundary or their diffusion along the grain boundary by preference. This hypothesis has not been verified yet because of insufficient resolution of mapping by SIMS, making the grain and grain boundary indistinguishable. A better procedure should be found to sinter the electrolytes, since both mechanical and electrical performances of the single cells will be affected if pores are present.

3.5 Conclusion

The three-, four- and six-layered YSZ/SCSZ electrolytes with outer YSZ layers and inner SCSZ layers were designed and produced, in order to use the advantages of both YSZ (phase and chemical stability) and SCSZ (superior ionic conductivity) ceramics in the layered electrolytes. The electrolytes were manufactured via slurry preparation, tape casting, laminating and presureless co-sintering. The sintering behavior was studied using high temperature dilatometry, density measurements, and microscopy. The thickness per layer was about 30 – 35 μm. The linear scanning via EDS verified the layered structure after sintering and suggested inter-diffusion regions about 5 μm in width. The SEM images showed well-joint interfaces between layers without delamination, but there were larger pores sitting at the grain boundary in the outer YSZ layers. The SIMS detected some unwanted impurities such as Al and Mg in the electrolytes, which
might be related to the pores at the grain boundary. The processing needs to be further modified to eliminate the pores in the dense electrolyte which would affect the electrical and mechanical properties. The X-ray diffraction and neutron diffraction showed almost pure cubic phase in the YSZ and SCSZ electrolytes. Some rather low impurity peaks were shown in the pattern of the raw powders before sintering but disappeared in the patterns of the electrolytes after sintering. The YSZ electrolyte maintained the pure cubic phase while a small amount of low symmetric phase in the sintered SCSZ was detected.

In addition, YSZ and SCSZ raw powders were also studied. The granules and aggregations were observed by SEM, and the crystallites were imaged by TEM. Although, the results of X-ray diffraction and neutron diffraction suggested cubic phase of both powders at room temperature, the images from TEM indicated more complicated structures at the nanoscale level.
4.1 Introduction

To harness the favorable properties of both YSZ and SCSZ ceramics, a layered electrolyte design was adopted, as described in CHAPTER THREE. The idea explored was to place thin YSZ layers on the outer surfaces of the SCSZ electrolyte, which would improve phase and structural stability and robustness of the electrolytes, and the layered electrolytes would maintain high ionic conductivity due to the SCSZ layers.

At the same time, the layered structure brought thermal residual stresses in the layers during cooling of the electrolyte from the sintering temperature because of the mismatch in the thermal expansions of the two materials. Thermal compressive residual stress can develop in materials with lower coefficient of thermal expansion, while thermal tensile residual stress can appear in materials with higher coefficient of thermal expansion. The values of the compressive and tensile residual stresses can be adjusted by controlling the thickness ratio of layers with compressive and tensile residual stresses [98]. The designing of the high compressive residual stress in the outer layers of a laminate will enhance the strength and fracture toughness of laminates [101,103], and it was also shown in numerous reports that the appearance of certain stress/strain states in the
electrolyte improves the ionic conductivity of the material [108,109].

In this chapter, the mechanical properties such as Young’s moduli and thermal expansions of the two material SCSZ and YSZ were measured in order to calculate the residual stress in the layered design. The biaxial flexural strengths and ionic conductivities of layered electrolytes were tested. The performance of the electrolytes will demonstrate the improvements brought by the thermal residual stress, and by a reverse thinking, the residual stress states in the electrolytes are thus verified.

4.2 Experimental

4.2.1 Young’s Modulus

In order to prepare the SCSZ and YSZ specimens for Young’s modulus measurement, the following process were performed. The SCSZ powders (ScCeSZ-TC, NexTech Materials, USA) and YSZ powders (TZ-8Y, Tosoh, Japan) were cold pressed into bars under 25 MPa. Those bars, covered with the same raw powders in the crucible, were sintered at 1550 °C for 5 h and then machined into specimens with the dimension of 4 mm × 3 mm × 45 mm. The density of SCSZ and YSZ specimens were measured by Archimedes’ principle, as described in Section 3.3.2.2.

The specimens were dried in an oven with a constant temperature of 60 °C for 24 h. Young’s moduli of SCSZ and YSZ were measured by the impulse excitation technique [114], and the setup
The specimen was supported by two rollers at the nodal points (positions of minimum amplitude) of the fundamental (first order) vibration, which were at a distance of 22.4% of the total length from each end. A small harmer was used to hit the center of the top surface slightly, and the microphone below the specimen received the vibration with the specific resonant frequency. This frequency was measured by the impulse excitation apparatus (Grindo Sonic, J. W. Lemmens, Belgium). Following the standard, the dynamic elastic modulus was calculated from the flexural mode equation:

\[ E = 0.946 \left( \frac{mf_f^2}{b} \right) \left( \frac{l}{h} \right)^3 A_f \]  

(13)

where \( E \) is the Young’s modulus, expressed in Newton per square meter (N·m\(^2\)) or Pascal (Pa); \( f_f \) is the resonance frequency for fundamental mode flexural vibration, expressed in Hertz (Hz); \( b \) is the width of test piece, expressed in meters (m); \( h \) is the thickness of test piece, expressed in meter (m); \( m \) is the mass of test piece, expressed in kilogram (kg); \( A_f \) is the shape factor given by:

\[ A_f = 1 + 6.585 \left( \frac{h}{l} \right)^2 \]  

(14)

The same principle was employed for the measurement at high temperatures, and the setup of the instruments was modified. The impulse exciting part of the device was set in an oven. The specimen, which had also been dried in the oven at 60 °C for 24 h to remove any possible moisture in the specimens, was hung by two thin platinum wires at the nodal points [114] in the oven.
Figure 24: The setup of Young’s modulus measurement by impulse excitation technique
A ceramic pipe was fixed over the center of the specimen, and it extended outside the top of the oven. A steel ball could drop through the pipe onto the top center of the specimen to activate the impulse. There was another ceramic pipe located at the bottom center of the specimen, and it extended outside the bottom of the oven. The vibration of the impulse excitation was conducted by the pipe to the receiving part outside, which was a Grindo-Sonic Mk5 Industrial frequency analyzer (Lemmens, Belgium). During the measurement, the oven temperature increased from room temperature to 950 °C with a ramp rate of 5 °C/min. The temperature was hold at every 50 °C for minutes until it stayed constant, and then the steel ball was dropped through the upper pipe. The frequency analyzer collected the vibration and calculated the Young’s modulus. Five measurements were carried out for each temperature point.

4.2.2 Thermal Expansion

To study the thermal expansion of YSZ and SCSZ, the 6 mm in diameter and 12 mm in length YSZ and SCSZ cylindrical specimens were prepared. The powders were unaxial pressed at 20 MPa and then sintered at 1550 °C for 5 h to densify. The specimens were setup in a pushrod dilatometer (DIL 402C, NETZSCH, Germany) and heated up from room temperature to 1000 °C with a heating/cooling rate of 5 °C/min in air. The coefficient of thermal expansion (CTE) is a second order tensor like strain. In the one dimension expansion testing, CTE of the isotropic material was obtained by the differential of the elongation measured by the dilatometer.
\[
\alpha = \frac{1}{L} \frac{dL}{dT} \approx \frac{d(\Delta L/L_0)}{dT}
\]

where \(\alpha\) is the coefficient of thermal expansion; \(L\) is the length of specimen; \(L_0\) is the initial length of the specimen and \(\Delta L = L - L_0\); \(T\) is the temperature.

To calculate the derivative, the recorded dependence of \(\Delta L/L_0\) on \(T\) was approximated by a second order polynomial \(\Delta L/L_0 = aT^2 + bT + c\). By taking the first derivative of the polynomial function, the linear dependencies of CTE as a function of temperature were obtained.

4.2.3 Biaxial Flexural Strength

4.2.3.1 Measurement of Biaxial Strength

The ring-on-ring testing approach [115] is widely used to determine the biaxial flexural strength of thin ceramic substrates at room temperature. The ceramic specimens are considered to be brittle and perfectly elastic. In comparison with other test methods such as the ring-point test, one of the advantages of the ring-on-ring test method is the large testing surface and volume. Also, the ring-on-ring test is closer to the situation of a working electrolyte-supported SOFC, and it is a proper characterization of the strength of designed electrolytes.

The specimens of the layered electrolytes with a total of 9 designs (Figure 13), which had been manufactured as described in CHAPTER THREE, were tested via the ring-on-ring method in order for the biaxial strength. Before testing, the electrolyte specimens were dried in the oven with constant temperature 60 °C for 24 h in order to remove the moisture on the surface of the specimen.
Figure 25: (A) The setup of ring-on-ring biaxial flexure test; (B) Sketch of ring-on-ring method. $F$ – load; $t$ – specimen thickness; $a$ – radius of the supporting ring
For room temperature measurements in the uniaxial testing machine (Z005, Zwick/Roell, Ulm, Germany), the support ring with diameter of 30 mm and the concentric loading ring with diameter of 12 mm were used for loading at a 1.5 mm/min constant crosshead velocity until fracture occurred (Figure 25). The loading curve as well as the critical load at the fracture was recorded for the strength calculation. A total of about 30 pieces of specimens with each electrolyte design were tested at room temperature.

For the high temperature tests at 800 ºC, electrolyte specimens of selected layered designs were tested, including 6–SCSZ, 6–YSZ, Y–4SC–Y and Y–2SC–Y (as shown in Figure 13) with a diameter of approximately 31 mm. The diameters of the support ring and load ring were 25 mm and 12.5 mm, respectively, and the same 1.5 mm/min loading rate was used as the experiments performed at room temperature. The testing parts of the machine, including the rings and the specimen, were enclosed in a furnace for heating. The temperature was gradually increased from room temperature to 800 ºC at a heating rate of 2 ºC/min, and then one hour dwelling at 800 ºC was allowed to achieve a homogeneous temperature distribution inside the furnace before the loading started. After testing, the entire device cooled down in the furnace.

4.2.3.2 Calculation of Biaxial Strength

The fracture occurred at the specimen tested by the ring-on-ring method at a certain load. The crack started on the tensile side of the electrolyte, where the failure stress reached. If the deflection
of the specimen before failure is very small, the relation of the stress and load at the fracture is simply linear in according to the ASTM standard [115], as follows:

\[
\sigma_f = \frac{3F}{2\pi t^2} \left[ (1-\nu) \frac{D_S^2 - D_L^2}{2D^2} + (1+\nu) \ln \left( \frac{D_S}{D_L} \right) \right]
\] (16)

where \( \sigma_f \) is the failure stress; \( F \) is the load at the fracture; \( t \) is the thickness of the specimen; \( \nu \) is the Poisson’s ratio; \( D, D_S \) and \( D_L \) are diameters of the specimen, support ring and load ring, respectively.

To satisfy the linear relationship between load and stress in Equation (16), the following criterions of the specimen and the ring-on-ring setup have to be fulfilled [115]

\[
\frac{D_S}{10} \geq t \geq \sqrt{\frac{2\sigma_f D_S^2}{3E}}
\] (17)

\[
D - D_S \geq 2t
\] (18)

\[
\frac{t}{\delta} > 2
\] (19)

Where \( E \) is the Young’s modulus of the specimen, and \( \delta \) is the maximum deflection of the specimen occurring in the center.

Based on the Equation (17)–(19), the linear assumption asks for large thickness and high stiffness of specimen as well as a low critical stress at fracture and a relatively small support ring size. If the deflection of the specimen tested using the ring-on-ring experimental setup is large (\( \delta > t / 2 \) [115]), then a non-linear dependence between stress and load is observed (Figure 26) [116] and Equation (16) is not valid any more. In the case of thin specimen with large deflection, finite
element modeling (FEM) is required to calculate the maximum tensile stress in the specimen at the given load.


Figure 26: Maximum principal stress versus applied load for a ring-on-ring biaxial flexure test specimen

As in our experiments, the conditions in Eq (17)–(19) were not fulfilled, and hence the calculation of stress during ring-on-ring biaxial strength measurements were performed using
finite element analysis in COMSOL Multiphysics® 4.3a version with the Structural Mechanics module. To simplify the problem, a two-dimension (2D) axisymmetric model of the electrolyte was developed. The loading and support rings have a line contact with the specimen and were approximated as distributed point loads in 2D. The number of elements used was approximately 23000. The geometric non-linear behavior was accounted for in COMSOL Structural Mechanics Module [117,118]. When the geometric nonlinearity is activated, Green-Lagrangian finite strain tensor (instead of infinitesimal strain) is used and the model is solved using a total Lagrangian formulation. The load-to-stress conversion using FEM was performed by Amjad Aman in our research group in University of Central Florida.

4.2.3.3 Weibull Statistics for Biaxial Strength

Standard Weibull statistics [119–122] was used to analyze the maximum principal stress at the fracture of layered the electrolytes by the likelihood method. About 30 pieces of specimens of each group were tested at room temperature. The probability of material failure is assumed to obey Weibull statistics, in which the volume of the specimen has been normalized,

\[
P_f(\sigma) = 1 - \exp \left[ - \left( \frac{\sigma}{\sigma_0} \right)^m \right]
\]

(20)

where \( P_f(\sigma) \) is the probability of failure; \( \sigma \) is the flexural stress at the fracture; \( m \) is the Weibull modulus; and \( \sigma_0 \) is the characteristic stress. The parameter \( \sigma_0 \) and \( m \) will reveal the strength and
reliability of the specimens, and thus they are to be figured out by the experiment and analysis.

Considering an $N$-piece ($N \sim 30$) batch of tested specimens of a certain design, all measured $N$ biaxial strength values are ranked in an increasing order numbered from 1 to $N$. Then, a specimen with a failure stress $\sigma$ is ranked at the $n$th place in the whole batch, and the relation is established that $n = n(\sigma)$. Using the rank of the stress ($n(\sigma)$), the probability of failure at that stress ($P_f(\sigma)$) is estimated by

$$P_f(\sigma) = \frac{n(\sigma) - 0.5}{N}$$ (21)

Therefore, the Weibull distributions can be plotted by the $P_f \sim \sigma$ pair values of each specimen, and Weibull parameters are determined.

4.2.4 Ionic Conductivity

Our collaborators J. Neutzler and X. Huang in University of South Carolina tested the ionic conductivity using the layered electrolyte discs with diameter of about 21.5 mm. The measurement was performed using Electrochemical Impedance Spectroscopy (EIS) on a Zahner IM6 electrochemical workstation. Before testing, the silver paste (Heraeus) electrodes of 8.5 mm in diameter were aligned, masked, and applied to both sides of the electrolytes. The silver meshes were applied to the electrodes with paste and 4-wire conductors (one working/counter electrode wire and one voltage sensing wire for each side). The sample was mounted in a tube furnace
programmed with the following thermal profile: temperature rise/decline rate of 5 °C/min with 35 min dwell in approximately 50 °C increments from 500 °C to 800 °C in air. The sample was allowed to soak for 30 min before taking AC impedance measurements, which were carried out from 100 Hz – 1 MHz with excitation amplitude of 10 mV.

4.3 Results and Discussion

4.3.1 Density and Young’s Modulus

The density of YSZ and SCSZ specimens were measured by Archimedes’ principle. The SCSZ and YSZ ceramics were sintered to almost full density (ρ = 5.679 ± 0.003 g/cm³ for SCSZ and ρ = 5.883 ± 0.019 g/cm³ for YSZ). The YSZ specimens have a slightly larger average density than the SCSZ specimens. As a theoretical density of SCSZ and YSZ was calculated to be equal to 5.724 g/cm³ and 5.914 g/cm³, the 0.79% and 0.54% porosity was calculated to exist in each material, respectively. A nominal 8 mol% Y₂O₃ – ZrO₂ and 10 mol% Sc₂O₃ – 1 mol% CeO₂ – ZrO₂ compositions were used for the calculation of the theoretical density without taking into account the possible impurities present in the powder, and the lattice parameter was obtained from data of the X-ray diffraction in Section 3.4.1.1.

The average Young’s moduli measured via the impulse excitation technique are 207.1 ± 2.3 GPa and 202.4 ± 2.8 GPa for SCSZ and YSZ, respectively. They are in line with reported Young’s
modulus values for these materials [37,85] Because the specimens were well densified ceramics without large defects that would affect the vibration frequency of specimen, the Young’s moduli do not show obvious dependence on density, as shown in Figure 27.

![Graph showing Young's modulus versus density of SCSZ and YSZ specimens](image)

Figure 27: Young’s modulus versus density of SCSZ and YSZ specimens

The Young’s moduli in the temperature range between RT and 950 °C were measured for SCSZ and YSZ, in order for the residual stress calculation in the later section in this chapter. Figure 28 shows their temperature dependences. In the $E~T$ curves of both SCSZ and YSZ, the
Young’s moduli for both materials remain almost constant in RT – 150 °C temperature range with non-significant softening of the lattice due to an input of thermal energy. However, in the range of 200 – 400 °C the measured values of the Young’s modulus become too low to be considered reliable with the measurement technique used in the current studies. At 400 °C the Young’s moduli were measured to be 112 ± 29 GPa and 146 ± 2 GPa for SCSZ and YSZ, respectively, which is explained by a significant softening of the lattice. The further decrease of Young’s modulus was measured in 400 – 500 °C temperature range, where a decrease was much stronger in SCSZ ceramics, where the lowest measured value $E = 88 ± 17$ GPa is reported at 500 °C for SCSZ, but the lowest measured $E = 128 ± 1$ GPa is reported at 600 °C for YSZ. Upon further increase of temperature, the Young’s moduli of both ceramics keep increasing with $E = 162 ± 2$ GPa at 950 °C for SCSZ ceramics, and $E = 151 ± 2$ GPa at 950 °C for YSZ ceramics.

In the ranges of 100 – 400 °C for SCSZ and 200 – 350 °C for YSZ, the impulse could not activate the resonance vibration in the specimen, and the apparatus thus could not detect the vibration frequency. In YSZ, this abnormal frequency damp might be related to the reorientation of $V_0^{**}$–$Y_{Zr}^+$ pairs which are the elastic and electric dipoles, and to the relaxation of oxygen vacancies within a cluster of two or more yttrium ions [37,50]. They caused the energy loss when the impulse was input. In SCSZ however, there is a cubic-to-rhombohedral-to-cubic phase transition occurring in such temperature range 200–600 °C, and the drastic drop of $E$ is attributed to the phase transition which change the local coordinates of the atoms in the SCSZ lattice. When
the temperature went higher than 600 °C, the vibration mode recovered, and it showed a slight increasing in 600 – 950 °C. It is reported that the $E$~$T$ curves of SCSZ (DKKK, Japan) and SCSZ (Praxair, USA) show a similar trend and vibration damping [85].

![Figure 28: Young’s modulus versus temperature of SCSZ and YSZ](image)

Young’s moduli of SCSZ and YSZ were closed to each other, but SCSZ has a little higher value than YSZ in the temperature ranges $T < 100$ °C or $T > 600$ °C. In the temperature range 400 – 600 °C, where the reversible phase transition occurs in SCSZ, the phase-stable YSZ showed higher modulus. Those measurements and results are sufficient for the subsequent calculation for residual
stresses at room temperature and 800 °C. However, at the damping temperature range, the complexity was shown with indefinite values of Young’s modulus. Besides the possible explanations as above given by reference [37,50], our further work has been carried out focusing on the structural relationship of the dynamic damping, and the results will be discussed in CHAPTER SIX.

4.3.2 Thermal Expansion and Residual Stress

The temperature dependence of thermal expansion of YSZ and SCSZ during both heating and cooling in the temperature range of 20 – 1000 °C are plotted in Figure 29A. As both ceramics have similar fluorite structure, the difference in thermal expansion of both materials is almost imperceptible. However, when the coefficient of thermal expansion (CTE) is calculated using the differential of the data presented in Figure 29A, the distinct difference can be detected (Figure 29B). The second order polynomial approximation \( \Delta L/L_0 = aT^2 + bT + c \) was applied to fit the elongation data in Figure 29A, the CTE \( \alpha \) as a linear function of temperature were obtained as expressed by the form of \( \alpha_j = A_jT + B_j \), where \( j = 1, 2 \) and stands for YSZ and SCSZ, respectively. The linear relations will be used in further residual stress calculation. It is shown that the CTE of SCSZ is lower than CTE of YSZ in the temperature range between room temperature and about 600 °C, but becomes higher in the temperature range between about 600 °C and 1000 °C in comparison with YSZ.
Figure 29: Temperature dependences of the elongation (A) and the coefficients of thermal expansion (B) of YSZ and SCSZ
The sintering temperature 1550 °C for the electrolytes is not covered in the thermal expansion measurement; however, it is 1550 °C that was determined as the “joining” temperature $T_{\text{join}}$ when residual stresses started to appear in layered Y–xSC–Y electrolytes upon cooling after sintering. As the CTEs of the materials were not determined using experimental data from 1000 °C to 1550 °C sintering temperature, the extrapolated CTE data were calculated, presented as dashed lines in Figure 29B.

For the design of the layered electrolytes, the concept of high thermal compressive residual stress and low thermal tensile stress was adopted [98]. The thermal residual stresses were calculated using the following approach [123]. In each layer, the total strain after sintering is the sum of an elastic component and a thermal component. In the case of a perfectly rigid bonding, the residual stresses in the layers of a two-component material with symmetrical structure are [124]:

$$\sigma_{r1} = \frac{E'_1 E'_2 f_2 (\alpha_2 - \alpha_1) \Delta T}{E'_1 f_1 + E'_2 f_2}$$

(22)

and

$$\sigma_{r2} = \frac{E'_1 E'_2 f_1 (\alpha_1 - \alpha_2) \Delta T}{E'_1 f_1 + E'_2 f_2}$$

(23)

where $E'_j = E_j / (1 - \nu_j)$, $f_j = t_j / t$; $E_j$ and $\nu_j$ are the elastic modulus and Poisson’s ratio of $j$-th component; $t_j$ is the thickness of layers of $j$-th component, respectively; $\alpha_1$ and $\alpha_2$ are the thermal expansion coefficients of the first and second components, respectively; $\Delta T = T - T_{\text{join}}$ is the difference between the current temperature $T$ and the joining temperature $T_{\text{join}}$, and $t$ is the total
thickness of the specimen. If \( \alpha_1 \) and \( \alpha_2 \) are the linear functions of temperature then

\[
(\alpha_1 - \alpha_2)\Delta T = \int_{T_{\text{join}}}^{T} (\alpha_1(T) - \alpha_2(T))dT = \left[ \left( A_1 \frac{T + T_{\text{join}}}{2} + B_1 \right) - \left( A_2 \frac{T + T_{\text{join}}}{2} + B_2 \right) \right] \Delta T
\]  

(24)

where \( \alpha_1(T) = A_1T + B_1 \) and \( \alpha_2(T) = A_2T + B_2 \). Therefore

\[
(\alpha_1 - \alpha_2)\Delta T = [\alpha_1(<T>) - \alpha_2(<T>)]\Delta T
\]  

(25)

where \( <T> = (T + T_{\text{join}}) / 2 \) is the average temperature in temperature range from \( T \) to \( T_{\text{join}} \).

It is important to calculate the values of the residual stresses in laminates both at room temperature and at 800 °C, since the biaxial strength measurements were performed at both temperatures. Both of \( \Delta T \) and \( <T> \) were determined: \( \Delta T = -1530 \) °C and \( <T> = 785 \) °C for room temperature experiments, and \( \Delta T = -750 \) °C and \( <T> = 1175 \) °C for testing at 800 °C. Using these parameters as well as the materials’ properties (Table 6) and the electrolytes’ dimensions (Table 7) the values of residual stresses calculated using Equation (22) and (23) are presented in Table 8. The calculated thermal tensile and compressive residual stresses in SCSZ and YSZ layers in the Y–xSC–Y electrolytes as a function of thickness ratio between layers is shown in Figure 30.

In the inner SCSZ layer, the residual tensile stress has the highest value when \( t_2 / t_1 \rightarrow 0 \), and the stress is decreasing as the thickness ratio \( t_2 / t_1 \) is increasing. In contrast, the residual compressive stress in the outer YSZ layer is calculated as 0 when \( t_2 / t_1 \rightarrow 0 \), and then it increases as \( t_2 / t_1 \) increases. Since the compressive stress is favorite in the outer YSZ layer and the tensile stress is unwanted, the electrolytes with high \( t_2 / t_1 \) value is preferred, that is, with a thick inner SCSZ layer and thin outer YSZ skins. For example, in the electrolyte with largest \( t_2 / t_1 \) value equaling to 4, the
compressive and tensile stresses at room temperature are calculated as −85 MPa (the negative stands for the compressive) and 42.5 MPa, respectively. As the average <T> is higher and CTEs difference between layers is also larger at 800 °C testing temperature, the values of residual stresses in SCSZ and YSZ layers differ more significantly at 800 °C. Still taking \( t_2/t_1 = 4 \) layered electrolyte as the example, the tensile residual stress of 46.5 MPa in SCSZ layer and compressive residual stress of −93 MPa in YSZ layer were calculated at 800 °C.

Table 6: Material properties of YSZ and SCSZ

<table>
<thead>
<tr>
<th>Properties</th>
<th>YSZ</th>
<th>SCSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus at room temperature (GPa)</td>
<td>202</td>
<td>207</td>
</tr>
<tr>
<td>Elastic modulus at 800 °C (GPa)</td>
<td>137</td>
<td>158</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>Temperature parameter ( A_j ), ((10^{-6} \text{°C}^{-2}))</td>
<td>(3.01 \times 10^{-9})</td>
<td>(4.58 \times 10^{-9})</td>
</tr>
<tr>
<td>Temperature parameter ( B_j ), ((10^{-6} \text{°C}^{-1}))</td>
<td>(9.05 \times 10^{-6})</td>
<td>(8.2 \times 10^{-6})</td>
</tr>
</tbody>
</table>

Table 7: Thicknesses of layers in different designs

<table>
<thead>
<tr>
<th>Design</th>
<th>Thickness of YSZ layer ( t_1 ) (μm)</th>
<th>Thickness of SCSZ layer ( t_2 ) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y–2SC–Y</td>
<td>30.69</td>
<td>61.38</td>
</tr>
<tr>
<td>Y–4SC–Y</td>
<td>30.69</td>
<td>122.76</td>
</tr>
</tbody>
</table>
Figure 30: Calculated residual stresses in layered electrolytes at room temperature (A) and at 800 °C (B)
Table 8: Calculated residual stresses in layered electrolytes

<table>
<thead>
<tr>
<th>Design</th>
<th>Room Temperature</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive residual stress in YSZ layer (MPa)</td>
<td>–64</td>
<td>–85</td>
</tr>
<tr>
<td>Tensile residual stress in SCSZ layer (MPa)</td>
<td>64</td>
<td>42.5</td>
</tr>
</tbody>
</table>

In the inner SCSZ layer, the residual tensile stress has the highest value when $t_2 / t_1 \to 0$, and the stress is decreasing as the thickness ratio $t_2 / t_1$ is increasing. In contrast, the residual compressive stress in the outer YSZ layer is calculated as 0 when $t_2 / t_1 \to 0$, and then it increases as $t_2 / t_1$ increases. Since the compressive stress is favorite in the outer YSZ layer and the tensile stress is unwanted, the electrolytes with high $t_2 / t_1$ value is preferred, that is, with a thick inner SCSZ layer and thin outer YSZ skins. For example, in the electrolyte with largest $t_2 / t_1$ value equaling to 4, the compressive and tensile stresses at room temperature are calculated as –85 MPa (the negative standing for the compressive) and 42.5 MPa, respectively. As the average $< T >$ is higher and CTEs difference between layers is also larger at 800 °C testing temperature, the values of residual stresses in SCSZ and YSZ layers differ more significantly at 800 °C. Still take $t_2 / t_1 = 4$ layered electrolyte as the example, the tensile residual stress of 46.5 MPa in SCSZ layer and compressive residual stress of –93 MPa in YSZ layer were calculated at 800 °C.
Before the end of this section, a question may be raised that why not produce an infinitely thin outer YSZ layers and a thicker inner SCSZ layer since the large $t_2 / t_1$ value is the favor. Firstly, if the Equation (22) and (23) encounter the limit $t_2 / t_1 \to \infty$, the residual compressive stress and tensile stress turn out to be

$$\sigma_{r1} \to E_1'(\alpha_2 - \alpha_1)\Delta T$$

(26)

and

$$\sigma_{r2} \to 0$$

(27)

Since both of the residual stresses functions are constringent and approach to constant at the limit $t_2 / t_1 \to \infty$, it indicates that the further efforts on increasing the value $t_2 / t_1$ will bring less and less improvement of the stress states. Secondly, the much thinner outer layer will challenge the manufacturing technique, as the good uniformity and high density of the thin layer are required. It is unfairly to spend high costs on processing but produce a little improvement on the property. Also, much thicker inner layer is not acceptable because the Ohmic loss will increase subsequently. Thirdly, the outer layer has to be stable, reliable and durable besides the thin enough thickness. The element inter-diffusion and electrolyte degradation can be alleviated technically but not avoided completely. The thinner layer may cause less stability, reliability and durability of the electrolytes. Therefore, the infinite large $t_2 / t_1$ value is the best theoretically, but a good layered design with a proper thickness ratio, $t_2 / t_1 = 4$ in our case, is realistically the appropriate choice in consideration of the holistic performance of the electrolyte.
4.3.3  Biaxial Flexural Strength

4.3.3.1  Measurement

The strength of layered electrolytes was measured using ring-on-ring biaxial loading. As a result of the variation of qualities or defects on the tensile surface, the electrolyte specimens failed with different applied loads at the brittle fracture point, and the specimen broke into a numbers of pieces, varied from 2 to more than 10 pieces. Two typical examples of the load versus time plots collected during loading are presented in Figure 31A, and the photographs of the broken electrolyte specimens after testing are shown in Figure 31B–E. Usually some specimens which have fracture occurring at higher fracture stress ruptured fiercely with a loud cracking sound and broke into many small pieces to release the energy, while some specimens that broke into 2 – 3 large pieces showed lower stress with less noise.

The critical loads at the fracture of the electrolyte specimens with total 9 designs tested at RT are presented in Figure 32A. About 30 pieces of specimens of every design were tested, and each bar in Figure 32 corresponds to the critical load of each specimen. The values of loads are rather widely dispersed because of various defects on the surface and varied thicknesses of all specimens. The results of tests at 800 °C are presented in Figure 32.
Figure 31: (A) Two typical Load vs. Time biaxial flexure testing curves via ring-on-ring method; (B–C) specimen with low stress at the fracture; (D–E) specimen with high stress at the fracture
Figure 32: Loads at the biaxial flexure fracture of electrolytes tested at RT (A) and 800 °C (B)
4.3.3.2 Calculation of Biaxial Strength

In order to eliminate the size effects due to the varied thicknesses, the load needs to convert to the principal stress of each specimen at the fracture. The linear approach can be applied for the calculation of biaxial strength only if Equation (17)–(19) are satisfied; otherwise, the load–stress dependence is non-linear. To verify our case, $\sigma_t = 100$ MPa is assumed, and then using parameters $E = 210$ GPa, $D_s = 30$ mm and Equation (17), it is calculated that the thickness $t$ should be in the range $530 \mu m < t < 3000 \mu m$ if the linear relation is applicable to our case. However, thicknesses of the electrolytes produced were too thin ($90 – 210 \mu m$) and much lower than that, and the linear relation is then no longer valid due to the large deflection. Finite element modeling (FEM) and analysis are thus necessary to build the non-linear load–stress relation.

Using FEM by COMSOL and the load data in Figure 32, the values of critical stress (biaxial strength) were calculated for some selected designs: SCSZ, YSZ ($t_2 / t_1 = 0$), Y–2SC–Y ($t_2 / t_1 = 2$) and Y–4SC–Y ($t_2 / t_1 = 4$) tested both at RT and at 800 °C. The appearance of tensile stresses or biaxial strengths of the specimens, eventually leading to failure, is schematically shown in Figure 33. The plots of Weibull statistics of SCSZ, YSZ, Y–2SC–Y and Y–4SC–Y tested at RT are shown in Figure 34. For a simpler presentation, the Equation (20) is linearized and transferred in the form as below:

$$\ln \left[ \ln \left( \frac{1}{1 - P_f} \right) \right] = m \ln \sigma - m \ln \sigma_0$$  (28)
Figure 33: Biaxial strength of electrolytes with selected design at room temperature (A) and at 800 °C (B)
Table 9: Weibull parameters of the electrolytes in biaxial flexure tests at room temperature

<table>
<thead>
<tr>
<th>Design</th>
<th>Characteristic stress $\sigma_0$ (MPa)</th>
<th>Weibull modulus $m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3–SCSZ</td>
<td>217.3</td>
<td>4.31</td>
</tr>
<tr>
<td>3–YSZ</td>
<td>201.9</td>
<td>3.32</td>
</tr>
<tr>
<td>Y–2SC–Y</td>
<td>222.3</td>
<td>4.16</td>
</tr>
<tr>
<td>Y–4SC–Y</td>
<td>227.2</td>
<td>4.63</td>
</tr>
</tbody>
</table>

Figure 34: Weibull statistics of the biaxial flexural strength at the fracture of 3–SCSZ (A), 3–YSZ (B), Y–2SC–Y (C) and Y–4SC–Y (D) tested at room temperature
After figuring out the slope and intercept of the line in Figure 34, the Weibull parameters are determined and listed in Table 9.

As compressive residual stresses appeared in the outer YSZ layers of Y–xSC–Y electrolytes, they helped to inhibit the growth of the crack and thus contributed to the strength increase of the layered structures in comparison with pure YSZ and SCSZ. As shown in Figure 33, both at room temperature and especially at 800 °C, the biaxial strength of the layered Y–xSC–Y electrolytes is higher than those of pure YSZ and SCSZ electrolytes. The characteristic stresses ($\sigma_0$) at the fracture calculated via Weibull plots also reveal the improvement of strength by using the layered design. The larger thickness ratio $t_2 / t_1$ value brings a higher strength. The Weibull modulus ($m$) of each design is rather closed to each other, and it indicates the same fracture mechanism and similar defects on the tensile surface in the specimens with different designs.

4.3.3.3 Strength Calculation by Residual Stress

The biaxial strength of layered electrolytes Y–2SC–Y and Y–4SC–Y can be calculated as the value that strength of outer layer without residual stress minus corresponding calculated residual stress in this layer, or $\sigma_l = \sigma - \sigma_{1l}$. It can be seen that the compressive residual stress (negative value of $\sigma_{1l}$) will increase the effective strength ($\sigma_l$) of the laminate while the tensile stress (positive value of $\sigma_{1l}$) will cause a decrease of $\sigma_l$. 
Figure 35: Biaxial flexural strength of electrolytes as a function of thickness ratio at room temperature (A) and 800 °C (B). Solid line: calculation by residual stress; dots: experimental results; Δ : pure SCSZ; dot lines: reference line of pure YSZ and pure SCSZ without residual stress.
In our case, the strength of outer layer without residual stress can be taken from the average biaxial strength of pure YSZ from the previous section. The residual stress in the outer layer ($\sigma_{r1}$) is a function of the thickness ratio $t_2 / t_1$. Then the dependence of biaxial strength on the ratio of layer thickness can be calculated and estimated, as presented in Figure 35 (solid lines). For comparison, the measured strengths of pure YSZ and SCSZ electrolytes along with the strength of layered Y–xSC–Y electrolytes are also plotted.

The strength function of thickness ratio calculated by the residual stress well predicts the increasing trend of biaxial strength measured experimentally. However, the estimated strength values do not convincingly coincide with the values from experimental data (dots). The mismatch is probably caused by the error in any measurement. In next section, the results of the residual stress and biaxial strength calculation will be modified, and then their calculations will receive verification mutually.

4.3.4 Adjustment of CTE and Verification of the Residual Stress

As mentioned in last section, when the increase of the biaxial strength was modeled using the value of residual stresses calculated from the measured thermal expansion (solid lines in Figure 35), a significant deviation with experimentally measured strength values was obtained. Such deviation can be explained if one recognizes that uncertainties in determination of the CTEs values of YSZ and SCSZ ceramics could exist, since a second order polynomial approximation was
applied in the calculation of thermal expansion. Also, the thermal expansion was measured only up
to 1000 °C and CTEs were extrapolated until 1550 °C from the measured results assuming the
linear behavior. The deviation can be probably amplified from the extrapolated data, thus leading
to the error in estimation of both CTEs and thermal residual stresses. The opposite approach was
then adopted which would allow bringing the measured strength of layered electrolytes with the
proposed model of the biaxial strength.

Figure 36: The coefficients of thermal expansion of YSZ and SCSZ. (Dash line: previous results
before adjusted; solid lines: adjusted data)
In order to receive a good correlation with measured strength and the proposed model, the CTEs of YSZ and SCSZ ceramics were adjusted. In the adjustment, the linear dependence and the intercept of each line were maintained, but a small modification was performed on the slope of both lines, such that the difference between them was slightly decreased in the high temperature range. By a trial and error process, the biaxial strengths calculated for different designs better coincide with the experiment data measured at RT. As the results of the adjustment, the intercepts $B_j$ was maintained while the slope $A_1$ was increased from $3.01 \times 10^{-9}$ °C$^{-2}$ to $3.19 \times 10^{-9}$ °C$^{-2}$, and $A_2$ was decrease from $4.58 \times 10^{-9}$ °C$^{-2}$ to $4.39 \times 10^{-9}$ °C$^{-2}$. The new adjusted curves of CTE versus temperature are presented as solid lines in Figure 36, in comparison with the previous calculation (dash lines). The residual stresses and biaxial strength were recalculated using the adjusted CTE data and listed in Table 10.

<table>
<thead>
<tr>
<th>Design</th>
<th>Room Temperature</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive residual stress in YSZ layer (MPa)</td>
<td>-21</td>
<td>-28</td>
</tr>
<tr>
<td>Tensile residual stress in SCSZ layer (MPa)</td>
<td>21</td>
<td>14</td>
</tr>
<tr>
<td>Calculated biaxial strength (MPa)</td>
<td>203</td>
<td>210</td>
</tr>
</tbody>
</table>

Table 10: Calculated residual stresses in layered electrolytes (Adjusted)
The calculated tensile and compressive stresses based on the adjusted CTE values are presented in Figure 37A and B as solid lines. As shown in Figure 37, the values of both tensile and compressive residual stresses have lower values in comparison with the original calculation because adjusted CTEs have smaller difference at high temperature. Using the updated values, a better correlation between measured and calculated biaxial strength data is obtained (solid lines in Figure 37C and D). While the strength values are higher at room temperature in comparison with the values obtained at 800 °C, the effect of thermal residual stresses on the biaxial strength of laminates is more pronounced at high temperature.

Note that the adjusting of CTEs was carried out using only room temperature strength data, but the biaxial strength of layered electrolytes calculated for high temperature using these adjusted CTEs is also in good agreement with experimentally measured strength values (Figure 37D). Therefore, the modification of the CTE is feasible, and the existence of such residual stress in the laminates is valid.

The Weibull distribution of biaxial strength also provides verification for the residual stress. In the case of the layered ceramic composites, where the presence of the residual stress will affect the Weibull distribution of strength [123], the stress $\sigma$ can be represented as the sum of the applied stress $\sigma_a$ and the residual stress $\sigma_r$, or $\sigma = \sigma_a + \sigma_r$. In the non-layered monolith ceramic material the residual stress is considered to be zero, and Weibull distribution is presented by Equation (20). In the layered ceramic composites, however, the compressive residual stress is taken into account.
Figure 37: Adjustment of calculation: the residual stress at RT (A) and 800 °C (B); the biaxial strength at RT (C) and 800 °C (D). Dash line: previous results before adjusted; solid lines: adjusted data.
Figure 38: Weibull statistics of biaxial strength at room temperature (A), and the plots with removal of the effect of residual stress (B). (■: YSZ; ○: Y–2SC–Y; ×: Y–4SC–Y)
Therefore, the Weibull distribution is modified to account for the addition of the residual stress and failure probability is presented by

\[
P_f(\sigma) = 1 - \exp \left(-\left(\frac{\sigma_a + \sigma_r}{\sigma_0}\right)^m\right)
\]

(29)

If we assume that \( \sigma_a = \sigma_f \) in the case of pure YSZ and Y–xSC–Y layered electrolyte ceramics, where \( \sigma_f \) is a measured strength of electrolytes, then \( \sigma_a = 0 \) for pure YSZ electrolytes and \( \sigma_a = \sigma_{r1} \) for Y–xSC–Y layered electrolytes, where \( \sigma_{r1} \) corresponds to the compressive residual stress in the outer YSZ layer, calculated using Equation (22). Three different biaxial strength distributions are presented in Figure 38A, when a failure probability \( P_f \) is plotted against \( \sigma = \sigma_f \) without consideration of the effect of residual stress. However, when a failure probability \( P_f \) is plotted against \( \sigma = \sigma_f + \sigma_{r1} \) by taking into account the compressive residual stresses in the outer YSZ layer, the biaxial strength distribution of all the designs almost coincide with each other as shown in Figure 38B, which provides an additional verification for the calculation of the thermal residual stresses in Y–xSC–Y layered electrolytes.

4.3.5 Ionic Conductivity

 Ionic conductivities of the electrolytes with different designs are presented in Figure 39A and B in the form of Arrhenius plots within the temperature range between 500 – 800 °C (773 – 1073 K). In Figure 39A shows the plots of three-, four- and six-layered pure SCSZ and YSZ, and it does
not reveal significant ionic conductivity dependence on the number of layers except the deviation in the range of error. The uniformity indicates that seldom defects were introduced due to the interface between layers. The SCSZ samples have much higher ionic conductivity than the YSZ samples in the whole temperature range between 500 – 800 °C. The results of the measurement have good agreement with the values in the reference [10,125].

The ionic conductivities of layered Y–xSC–Y lie in between, depending on different layered designs, as shown in Figure 39B. At 800 °C which is usually the operation temperature of IT-SOFC, ionic conductivities of SCSZ, Y–4SC–Y, Y–2SC–Y, Y–1SC–Y and YSZ were measured as 0.1162, 0.0886, 0.0689, 0.0601 and 0.0424 S/cm, respectively. In comparison with pure YSZ, the layered electrolytes performed improved ionic conductivity in IT range. Though not as good as pure SCSZ, the Y–4SC–Y electrolyte exhibited sufficient conductivity for electrolyte-supported SOFC use.

With a certain layered design, the total ionic conductivity of the whole electrolyte can be calculated by the series-type mixing rule:

\[
\frac{2t_1 + t_2}{IC} = \frac{2t_1}{IC_1} + \frac{t_2}{IC_2}
\]

or

\[
IC = \frac{1 + 2t_1/t_2}{\left(\frac{2t_1}{t_2}\right)\frac{1}{IC_1} + \frac{1}{IC_2}}
\]
Figure 39: Ionic conductivities of SCSZ, YSZ and layered $Y$–$\alpha$SC–$Y$ electrolyte samples
In the equations above, \(2t_1\) is the total thickness of YSZ layers, \(t_2\) is the total thickness of SCSZ layers, \(IC_1\) and \(IC_2\) are the ionic conductivities in YSZ and SCSZ, respectively, and \(IC\) is the total ionic conductivity of the layered electrolyte.

The values of ionic conductivities by experiments are compared with the results of calculation, as shown in Figure 39C. Although the mixing rule of series is approximately obeyed, a slightly larger value was measured in each layered electrolyte than calculated. For example at 800 °C, Y–1SC–Y, Y–2SC–Y and Y–4SC–Y exhibit the improvement by 9%, 7% and 11%, respectively. The deviation reveals the positive effects on ionic conductivity due to the layered design. There are some possible reasons for the improvements, such as the thermal residual stress/strain and the interfacial effect due to the inter-diffusion of the dopants. The influence of the residual stress/strain is to be discussed as follows.

As the discussion in Section 4.3.2, a compressive residual stress was present in the outer YSZ layer while a tensile residual stress was present in the inner SCSZ layer during the electrolyte cooling down to the room temperature. The residual stress state and residual strain state in each layer are schematically drawn in Figure 40. The in-plane residual stress induced the out-of-plane residual strain, which is parallel with oxygen ion transporting direction. As reviewed in Section 2.3, the ionic conductivity can be affected by strain effects. The tensile strain will result in an increase of the ionic conductivity in the parallel direction, while the compressive strain brings a decrease of ionic conductivity in the antiparallel direction. Since the residual stress and strain configurations in
Figure 40 are similar with the situation in Figure 11(b), it is reasonable to suppose that each layer of the electrolyte has the ionic conductivity changed due to the thermal residual stress/strain, that is, the ion conducting in the out-of-plane direction is enhanced in the outer YSZ layer, which is experiencing the in-plane residual compressive stress/strain, but it is retarded in the inner SCSZ layer, which is suffering from the in-plane residual tensile stress/strain.

In comparison with the calculation results which do not take into account the stress/strain effect, there are a positive deviation $\Delta IC_1$ in the YSZ and a negative one $\Delta IC_2$ in the SCSZ due to the residual stresses/strains. Since $\Delta IC_1$ and $\Delta IC_2$ are small, the increase of the total ionic
conductivity $\Delta IC$ is estimated by the differential of Equation (30), where the thicknesses $t_1$ and $t_2$ are supposed as constants since a certain layered design is in consideration. The following expression is obtained with the first-order approximation:

$$\frac{\Delta IC}{IC} = \frac{1}{1 + \frac{t_2 IC_1}{2t_1 IC_2}} \cdot \Delta IC_1 + \frac{1}{1 + \frac{2t_1 IC_2}{t_2 IC_1}} \cdot \Delta IC_2$$

(32)

In the electrolyte designs, the thickness ratio $2t_1 / t_2$ is in the range of 0.5 – 2, and the ratio of ionic conductivities $IC_2 / IC_1$ is in the range of 2.5 – 3.5. Obviously, the coefficient of $\Delta IC_1$ term is much larger than that of $\Delta IC_2$ term, and thus the $\Delta IC_1$ term is the dominant one to affect the increase of total ionic conductivity. In another word, the improvement of the total $IC$ mostly depends on the increase of the $IC_1$ in the outer YSZ layer. The simple deduction therefore predicts that the largest residual in-plane compressive strain or out-of-plane tensile strain in the YSZ layer (Figure 40B), which acts as a bottleneck, will bring the largest improvement of $IC$ for a certain layered design in varied temperatures.

Figure 41A shows the temperature dependence of $(IC_e - IC_c) / IC_c$ in each layered design, which represents the improvement of ionic conductivity in comparison with the value from the calculation by the mixing rule, where $IC_e$ is the ionic conductivity measured from experiment, and $IC_c$ is the value from calculation. Figure 41A indicates that the ionic conductivities at 500 – 800 °C are all improved in comparison with the calculation. Though with different layered designs, the improvement of each design reaches the highest percentage at about 650 – 700 °C coincidentally.
Figure 41: (A) The improvement of the ionic conductivity in the layered electrolytes at different temperature; dots along solid line – at heating; dots along dash line – at cooling; (B) Coefficients of thermal expansion of SCSZ and YSZ as a function of temperature; (C) strain mismatch of SCSZ and YSZ as a function of temperature
This is close to such temperature where the largest residual in-plane compressive strain or out-of-plane tensile strain in the outer YSZ layer, where little variation of Poisson’s ratio in this temperature range is assumed. If revisiting Figure 36 or Figure 41B, the CTE versus T curves of SCSZ and YSZ intersect at about 708 °C, which are resolved using the adjusted data as described in Section 4.3.4. By mathematics, the intersect point implies the largest mismatch of thermal expansion or the highest value of residual in-plane compressive strain in outer YSZ layers. Using Equation (3) or Equation (24), the strain mismatch as a function of temperature were calculated, as shown in Figure 41C. It can be seem that the strain mismatch curve in Figure 41C has a similar trend of the ionic conductivity curves in Figure 41A. As a result of the residual stress/strain effects, it can be concludes that the highest strain mismatch or out-of-plane tensile strain in YSZ brings the largest improvement of $IC_1$ and therefore the highest percentage of $\Delta IC / IC$ in Equation (32).

The largest improvement of ionic conductivity and the highest strain mismatch in the layered electrolyte both point to such temperature range. It demonstrates evidence of residual strain effects on the improvement of ionic conductivity in the layered electrolytes. Also, the adjustment of CTE performed in Section 4.3.4 is thereby proved to be valid again.

4.4 Conclusion

Young’s moduli of YSZ and SCSZ were measured by impulse excitation technique in the temperature range of RT – 900 °C. Both YSZ and SCSZ specimens showed damping at 200 –
400 °C, and no resonance frequency was activated. The coefficients of thermal expansion of YSZ and SCSZ were also measured from RT – 1000 °C and extrapolated till the joining temperature 1550 °C.

The effect of thermal residual stresses on mechanical performance of layered Y–xSC–Y electrolytes is clarified. The layered Y–xSC–Y electrolytes were designed by an approach that compressive residual stress was present in the outer YSZ layers and tensile residual stress was present in the inner SCSZ layer. It is shown that the presence of the compressive stress in the outer layer contributed to the increase of the biaxial strength of the composite both for the room temperature experiments and for the testing performed at 800 °C. To eliminate the discrepancies between measured and calculated biaxial strength values, the extrapolated CTEs of the YSZ and SCSZ ceramics were slightly adjusted. This allowed the estimation of residual stresses more realistically since the values of measured and calculated strength showed an excellent coincidence. Additionally, the Weibull statistics also helped to verify the residual stresses and their influence on the mechanical behavior of layered Y–xSC–Y electrolytes for intermediate temperature solid oxide fuel cells.

The ionic conductivities of the electrolytes with different layered designs were measured at the temperature range between 500 °C and 800 °C. Pure x–SCSZ showed superior ionic conductivity, and it was much higher than that of pure x–YSZ. Bare dependence of ionic conductivity upon the number of layers was observed in the single composition designs. Among the layered Y–xSC–Y
composite designs, Y–4SC–Y maintained high ionic conductivity in the intermediate temperature range. The ionic conductivities basically obeyed the series-type mixing rule; however, 4% – 17% improvements were present in comparison with the calculation without consideration of the stress/strain effects. The temperature with highest improvements was found to nearly coincide with that with the largest residual compressive in-plane strain in the outer YSZ layer. The compressive stress/strain in YSZ due to the layered structure was considered as one of the important reason for the improvement of ionic conductivity.
CHAPTER FIVE: MECHANICAL PROPERTIES OF Ni / (Sc₂O₃)₀.₁(CeO₂)₀.₀₁(ZrO₂)₀.₈₉ CERMETS FOR SOFC ANODE

5.1 Introduction

Good mechanical behavior of an anode is required for a durable and reliable SOFC. Besides matching other components of SOFCs in thermal expansion, some specific design, such as anode supported SOFC, asks for a higher requirement of mechanical performance. The Ni/YSZ cerments are one of the more popular anode materials, and some research on its mechanical properties showed its strong dependence on processing of synthesis and reduction, grain size, porosity, etc. [126–129]. As SCSZ electrolytes become a more feasible option in single cells, the Ni/YSZ cerments may also need to be modified to replace YSZ with a SCSZ matrix in consideration of the higher ionic conductivity at 800 °C in SCSZ (0.11 S/cm) than in YSZ (0.044 S/cm). In addition, the Ni/scandia stabilized zirconia (SSZ) cerments demonstrate a better long-term catalytic activity in direct liquid hydrocarbon fueled SOFC system.

Although quite a lot of research on the structural characterization of Ni/SCSZ anodes along with the catalytic performance during SOFC operation was published, there are few reports on its mechanical properties at the operation environment by our knowledge. In this chapter, the porous Ni/SCSZ cerments were prepared, and the phase structures along with microstructures were
characterized. The mechanical properties of the porous cermets such as Young’s modulus, strength and fracture toughness have been measured both at room and high temperatures. The high temperature testing was performed in reducing atmosphere at 700 – 900 °C, which was close to the realistic operation conditions of the anode in SOFCs.

Two types of Ni/SCSZ cermets were studied with varied compositions. Before reduction, they are 65 wt% NiO – 35 wt% SCSZ and 50 wt% NiO – 50 wt% SCSZ. After complete reduction, the porous cermets from the former one are named as N65, and the porous cermets from the latter one are named as N50.

5.2 Experimental

5.2.1 Sample Preparation

The Ni/SCSZ cermets were produced by reducing a sintered oxide mixture, which were synthesized by solid phase routine. The 65 wt% NiO – 35 wt% SCSZ oxide mixture was prepared using the commercial powders NiO (Novamet, NJ) and 0.1 Sc₂O₃ – 0.01 CeO₂ – 0.89 ZrO₂ (Daiichi Kigenso Kagaku Kogyo, Japan). The mixture was ball-milled for 48 h in a plastic bottle using acetone and zirconia balls as the grinding media. The slurry after milling was immediately dried at 100 °C and sieved in order to break the formed agglomerates and thus to produce homogeneous fine oxide powders. After those powders were ready for processing, a uniaxial
pressing in a 10 mm × 75 mm steel die was used to shape the anode powders. A stress of 20 MPa was applied during the uniaxial pressing. The formed bars after uniaxial pressing were further hydrostatically pressed at 300 MPa using a cold isostatic press. The shaped bars were carefully moved into a tray, and the bars were covered with the powders with the same composition in order to minimize the evaporation from the samples during sintering. The pressureless sintering in the ambient atmosphere was performed at 1050 °C for 4 h using a 10 °C/min heating/cooling rate.

The sintered 65 wt% NiO – 35 wt% SCSZ anode bars were reduced in a tube furnace (STF 16/610, Carbolite, UK) with 95%N₂ – 5%H₂ forming gas flowing at 800 °C for 24 h. The samples after reduction are named as N65. After being cooled down to room temperature and given exposure to air, the mass of the samples were immediately measured with a high precision balance (Mettler AT201, Nänikon, Switzerland) as a function of time to evaluate the mass gain and re-oxidation kinetics.

Some of the sintered 65 wt% NiO – 35 wt% SCSZ bars were machined into 3 mm × 4 mm × 50 mm dimensions at Prematech Inc., USA. Then the machined samples were reduced with the same processing as above, and they were named as N65m. The Ni/SCSZ porous anodes with an alternative composition, for which the starting oxides were 50 wt% NiO – 50 wt% SCSZ, were prepared by the same method and named as N50.
5.2.2 Characterizations of the Microstructure and Phase Structure

The porosity and the pore size distribution in N65 and N50 samples both before and after reduction were measured using Hg–porosimetry (Pascal 140 and 440, POROTEC, Italy) and He–pycnometry (AccuPyc 1330, Micromeritics, USA). After N65 and N50 samples were ground into powders, the specific surface areas were determined with the N₂ adsorption isotherm by BET measurements (Beckman-Coulter SA3100, Beckman-Coulter, USA).

The crystal structures of N65 anode samples both before and after reduction were studied by X-ray diffraction (XRD). The anode samples were ground into powders using a set of agate mortar and pestle, and the powder diffractions were performed in a θ–θ powder X-ray diffractometer with a copper target (Rigaku, Multiflex, Japan) using 40 kV and 30 mA. The continuous XRD spectra of the anode samples were collected in 2θ = 10° – 90° range with 0.05° step size and 1 s collection time. In addition, more detailed profiles of (1 1 1) (2θ = 30° – 31.5°) and (2 0 0) (2θ = 35° – 36.5°) peaks were scanned with 0.01° step size and 5 s accumulation time. For comparison, the pure SCSZ powders were annealed at 1300 °C for 4 h at a 5 °C/min heating/cooling rate, and the crystal structure of the pure sintered SCSZ powders was analyzed by XRD as well.

A Renishaw InVia Raman microscope was used to study the vibrational spectra of ground N65 anode powders before and after reduction, as well as the pure SCSZ powders annealed at 1300 °C for 4 h for comparison. The Raman microscope system comprised a laser (532 nm line of solid Si) to excite the sample, a single spectrograph fitted with holographic notch filters, and an optical
microscope (a Leica microscope with a motorized XYZ stage) rigidly mounted and optically coupled to the spectrograph. Before collecting spectra of SCSZ, the spectrometer was calibrated with a standard silicon wafer using a Si band position at 520.3 cm$^{-1}$. The average collection time for a single spectrum was 300 s.

5.2.3 Young’s Moduli

Young’s moduli of N65, N50 and N65m specimens were tested by the impulse excitation technique at room temperature. The device, method and principle have been addressed in Section 4.2.1.

5.2.4 Flexural Strength

The flexural strengths of N65, N50 and N65m specimens were determined by the four-point bending method in a uniaxial testing machine (Z005, Zwick/Roell, Ulm, Germany). A 50/25 load geometry [130] was used for the as-sintered N65 and N50 specimens without machining, and a 40/20 mm load geometry was used for 3 mm × 4 mm × 50 mm machined N65m specimens.

The sketch and the real photo of the setup of a four-point bending test are shown in Figure 42. The part of the specimen between two loading points is in a state of pure bending, where the maxima of compressive stress and tensile stress are in the upper and lower surfaces, respectively.
Figure 42: The sketch (A) and photo (B) of the device of four-point bending test
On the tensile surface, the cracks were generated, prorogated and finally led to the fracture of the specimen. It is known that the relation of normal stress and moment is as below

\[ \sigma = \frac{Mc}{I} \]

(33)

where \( \sigma \) is the maximum stress on the surface; \( M \) is the bending moment; \( c \) is a half of the height of the specimen; and \( I \) is the moment of inertia of the cross-sectional area. In consideration of the anode specimens that have a rectangular cross-section, the bending moment and the moment of inertia are expressed with the load and dimensions of the specimen as below.

\[ M = \frac{1}{2}Fa \]

(34)

\[ c = \frac{1}{2}h \]

(35)

\[ I = \frac{1}{12}bh^3 \]

(36)

where \( F \) is the load on the specimen; \( a \) is the distance between the support point and the load point on the same side (as shown in Figure 42); \( b \) and \( h \) are the width and height of the specimen, respectively.

Then the maximum stress on the specimen under bending is calculated by the formula:

\[ \sigma = \frac{3Fa}{bh^2} \]

(37)

About 30 pieces of specimens of each group were tested at room temperature with a loading rate of 0.5 mm/min. Standard Weibull analysis [119–122] of strength data was carried out by the likelihood method. Section 4.2.3.3 has shown the step to build the Weibull distribution and determine the Weibull parameters in Equation (20). Comparing the Weibull distributions of N65,
N50 and N65s, the effects of machining and varied composition on the strength of porous anode cermets will be revealed.

High temperature four-point bending tests were carried out at 700 °C, 800 °C and 900 °C using twelve machined N65m specimens, four for each testing temperature. The N65m specimens were set up in the uniaxial testing machine inside a furnace in a 5% H₂ – 95% N₂ gas flow and heated to 700 °C, 800 °C and 900 °C with the ramp rate 5 °C/min. A 30 min dwell time was used to allow for a homogeneous temperature distribution over the specimen during the bending experiments.

5.2.5 Fracture Toughness

The fracture toughnesses of the anode porous specimens were measured by the single-edge V-notch beam (SEVNB) technique in accordance with CEN/TS 14425-5 standard [131–132].

The V-notch with about 2 mm depth was placed in N65 and N50 specimens. The pre-cutting was firstly carried out using a SiC blade to cut a slot with 0.5 mm width and 1.5 mm depth. The pre-notched specimens were cleaned in acetone using ultrasonic vibration for 2 min in order to remove oil, paste and other dirt. This washing procedure was carried out throughout the whole notching processing. After pre-cutting, the specimens were mounted on a simple reciprocating notching machine (Figure 43), where a micrometer was used to monitor the depth of the notch.
Figure 43: A simple reciprocating notching machine
By using a razor blade and medium grit size (10 μm) diamond paste, a finer notch was then placed at the bottom of the former pre-cut slot. When the total depth of the notch reached 1.8 – 1.9 mm, both the specimen and the simple reciprocating notching machine were cleaned again, the razor blade was replaced by a new one, and the 1 μm fine diamond paste was used for the final stages of notching until the total depth of the notch went to about 2 mm with a sharp tip, where the radius of curvature should be less than 5 μm.

The N65m specimens, which had 3 mm × 4 mm × 45 mm standard dimensions after machining, were notched using a razor blade with 10 μm diamond paste to place a 0.7 mm deep notch on the simple reciprocating notching machine without a pre-cutting, followed by further cutting with 1 μm diamond paste to reach the required depth of 0.8 – 1.2 μm. The tip should have a radius of curvature should be less than 5 μm. After being notched and cleaned, the specimens were dried in an oven at 60 ºC for 3 hours, and then tested via the four-point bending technique. The setup is shown in Figure 42.

The N65m specimens were tested at 800 ºC and 900 ºC in a reducing environment. The testing and heating parameters are the same as those described in Section 5.2.4. The fracture surfaces of the anode specimens after testing at different temperatures were studied by SEM (Ultra-55, Zeiss, USA and S4800, Hitachi, USA).

The values of fracture toughness \( K_{IC} \) of the anodes cermets are determined by Griffith’s solids theory (opening mode). The depth was measured from the fracture surface, as shown in Figure 44.
Figure 44: Schematic diagram of fractured V-notched test piece and the positions at which notch depths are measured. 1: Fractured surface; 2: V-notched surface
The average V-notch depth $a$ is calculated by

$$a = \frac{a_1 + a_2 + a_3}{3} \quad (38)$$

and the acceptable notch requires

$$\frac{a_{\text{max}} - a_{\text{min}}}{a} \leq 0.1 \quad (39)$$

where $a_{\text{max}}$ is the maximum among $a_1$, $a_2$, $a_3$; $a_{\text{min}}$ is the minimum among $a_1$, $a_2$, $a_3$. And, relative V-notch depth $\alpha$ is defined as

$$\alpha = \frac{a}{W} \quad (40)$$

Then the fracture toughness from the single-edge V-notch beam (SEVNB) method is calculated by

$$K_{c,\text{SEVNB}} = Y\sigma\sqrt{a} = \frac{F_{\text{max}}}{B\sqrt{W}} \times \frac{S_1 - S_2}{W} \times \frac{3\sqrt{\alpha}}{2(1-\alpha)^{3/2}} \times Y \quad (41)$$

where $\sigma$ is the stress at the fracture; $F_{\text{max}}$ is the load at the fracture; $B$ is the width of the specimen; $W$ is the depth of the specimen; $S_1$, $S_2$ are the spans ($S_1 > S_2$) of support points and loading points, respectively; $Y$ is the stress intensity shape factor determined by

$$Y = 1.9887 - 1.326\alpha - \frac{\alpha(1-\alpha)(3.49 - 0.68\alpha + 1.35\alpha^2)}{(1+\alpha)^2} \quad (42)$$
5.3 Result and Discussion

5.3.1 Reduction and Pore Characterization

The porous NiO-SCSZ ceramic samples had a light green color after sintering, and they became gray after reduction in 5% H\textsubscript{2} – 95% N\textsubscript{2} forming gas at 800 °C for 24 h due to the reduction of NiO to Ni. The weight loss during the samples’ reductions confirmed the complete reduction of NiO into metallic Ni in accordance with the chemical reaction

\[
\text{NiO (s) + H}_{2}\text{(g) == Ni (s) + H}_{2}\text{O (g)}
\]  

After exposure to air, the masses of N65 and N50 samples were then weighed. It was found that the reduced samples did not maintain a constant weight, but rather the weight increased slowly, indicating the slight re-oxidation of nickel particles upon exposure to air even at room temperature. The curves of the normalized mass vs. time are shown in Figure 45, where \(m_0\) is the initial mass before reduction. The weights tended to stabilize and remain constant after 100 h exposure time.

The SEM images of the fracture surfaces of N65 samples before and after reduction are shown in Figure 46. The grain size obviously changed during the reduction. The average grain size was measured to be about 400 – 450 nm before reduction but was decreased to 250 – 300 nm after reduction.

Some characterizations of pores in N65 and N50 samples before and after reduction are shown in Table 11. After reduction, the true densities by helium pycnometry, the porosities and the pore sizes of N65 and N50 samples increased. The pore size distributions are shown in Figure 47. After
reduction, the median pore diameter ($d_{50}$) moved slightly to the right, indicating larger average pore size. These trends correspond with the images of SEM. The BET specific area surface slightly increased after reduction in N65 but decreased in N50.

Figure 45: Weights of N65 and N50 in function of the time after reduction ($m_0$ is the initial mass before reduction)
Figure 46: Fracture surfaces of N65 sample before reduction (A) and after reduction (B)
Figure 47: Pore size distribution of N65 (A–B) and N50 (C–D) samples before and after reduction.
Table 11: Selected characterization of N65 and N50 anode samples before and after reduction

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density Helium pycnometer (g/cm³)</th>
<th>BET surface area (m²/g)</th>
<th>Porosity</th>
<th>Median pore diameter d₅₀ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N65</td>
<td>before reduction after reduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.38 ± 0.02</td>
<td>1.168</td>
<td>25.66%</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>7.46 ± 0.02</td>
<td>1.680</td>
<td>48.53%</td>
<td>0.28</td>
</tr>
<tr>
<td>N50</td>
<td>before reduction after reduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.35 ± 0.01</td>
<td>1.593</td>
<td>22.73%</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>6.59 ± 0.01</td>
<td>1.236</td>
<td>42.16%</td>
<td>0.20</td>
</tr>
</tbody>
</table>

5.3.2 Characterization of the Phase Structures

The X-ray diffraction patterns of the powders of ground N65 samples before and after reduction as well as the pattern of pure SCSZ are shown in Figure 48. Before 24 h reduction, the peaks of NiO and SCSZ were detected, and after reduction, only the peaks of Ni and SCSZ were found, while the NiO peaks were no longer present. Those patterns have confirm the full reduction of NiO after 24 h reduction in 5% H₂ – 95% N₂ forming gas at 800 °C. In comparison with the XRD pattern of the pure SCSZ powders, the profiles of SCSZ diffraction were maintained during the reducing process. Only the pure cubic SCSZ phase was found in anode samples both before and after reduction, and neither peak splitting nor additional peaks from secondary phase were observed.
The detailed profiles of (1 1 1) and (2 0 0) peaks, which are characteristic peaks to distinguish the cubic phase from rhombohedral and tetragonal phases, are shown in Figure 48. By analyzing those peaks of anode material before and after reduction and then comparing them with the sample of pure SCSZ used as the electrolyte in the SOFC, the indication was found that the presence of Ni helped to stabilize cubic SCSZ. In the pure SCSZ, there is a slight asymmetry present from the lower $2\theta$, which is an indication of the presence of a small quantity of the rhombohedral phase [76]. Thus, both cubic and rhombohedral phases are present. However, when either NiO or Ni phases are present, perfectly symmetric (1 1 1) and (2 0 0) peaks are observed, indicating that only the cubic SCSZ phase exists.

The peaks (1 1 1) and (2 0 0) in the NiO–SCSZ ceramic and the Ni/SCSZ cermet are shifted toward the lower $2\theta$ angle in comparison with (1 1 1) and (2 0 0) peak position in pure SCSZ. Such a shift is an indication of an increase in cubic SCSZ lattice parameters because of the diffusion of the Ni cation into the zirconia lattice and the formation of the solid solution of Ni. However, it was reported that the lattice parameters of cubic YSZ ceramic decrease when NiO is present during sintering. The decrease of YSZ lattice parameters was associated with the generation of oxygen vacancies by the occurrence of the defect reaction $\text{NiO} \xrightarrow{Z_{\text{Ni}}} \text{Ni}_2^\text{zr} + \text{V}_0^\text{o} + \text{O}_\text{zr}^\text{v}$. The oxygen vacancies formed stabilize the cubic structure in YSZ lattice and promote lattice shrinkage [82,133].
Figure 48: The X-ray diffraction spectra (A), (1 1 1) profiles (B) and (2 0 0) profiles (C) of pure SCSZ powders, NiO–SCSZ ceramics and Ni/SCSZ cermets.
Raman spectra also indicate the shift of the cubic $F_{2g}$ 623 cm$^{-1}$ Raman band in the cermet anode in comparison with pure SCSZ (Figure 49). The pure SCSZ spectrum was detailed in Reference [77], where it was found that, in addition to the 623 cm$^{-1}$ band, the spectrum consisted of 239, 315, 378, 480 cm$^{-1}$ bands. It was also established that 315 and 378 cm$^{-1}$ bands could be detected using 532 nm visible light, but could not be seen using another 785 nm near infrared laser. Thus it was concluded that 315 cm$^{-1}$ and 378 cm$^{-1}$ Raman bands did not belong to fluorite lattice vibrations, seemingly due to the presence of impurities.

It was also suggested that the appearance of the 480 cm$^{-1}$ band in the pure cubic ZrO$_2$ structure might indicate the presence of the tetragonal phase with a lower symmetry, which is difficult to distinguish from cubic structure by X-ray diffraction [66,136]. Raman spectra of anode samples both before and after reduction showed the significant shift of the $F_{2g}$ SCSZ peak to the lower wave numbers in comparison with the peak of pure SCSZ powders, which indicates the possible formation of a solid solution of NiO or Ni in SCSZ. The $F_{2g}$ SCSZ peak shifts to 599 cm$^{-1}$ in the case of the NiO–SCSZ anode sample before reduction and to 582 cm$^{-1}$ for the anode cermet after reduction. The two Raman bands, which appear at such lower wave numbers 76 cm$^{-1}$ and 93 cm$^{-1}$, are not the characteristic bands for cubic SCSZ, but probably indicate the local lowering of the cubic symmetry and the appearance of the tetragonal phase [44,137].
Figure 49: Raman spectra of the pure SCSZ (A), the NiO–SCSZ ceramic before reduction (B) and the Ni/SCSZ cermet after reduction (C)
5.3.3 Young’s Moduli of Ni/SCSZ Cermets

The Young’s modulus ($E$) of porous anode cermets was measured for the N65 and N50 specimens before and after reduction. In addition, the elastic modulus was also measured on N65m specimens, which had been machined to the dimensions of $3 \text{ mm} \times 4 \text{ mm} \times 50 \text{ mm}$ and then reduced. The results show that Young’s modulus of the anode varies with the density of the specimen and the processing history (Figure 50).

The average value of Young’s modulus of N65 is $67.5 \pm 4.2 \text{ GPa}$, and the increase in the porosity causes the Young’s modulus values to decrease. The average Young’s modulus value of the as-sintered anode specimens after reduction decreases to $25.4 \pm 2.5 \text{ GPa}$. Such drop is unlikely attributed to the compositional change of the sample during reduction, since Young’s moduli of dense Ni and NiO are quite closed to each other, equal to 214 GPa and 220 GPa, respectively [138,139]. Rather, the decrease of Young’s modulus is a reflection of the total porosity increasing in the specimens. It is also possible that during the reduction, micro-cracking occurred along the grain boundaries between zirconia and newly formed Ni grain, and the crack also contributes to the linear decrease of Young’s modulus. The Young’s modulus of N50 specimen has slight higher values than those of N65, and the $E$ of N50 also shows a similar decrease after the reduction (Figure 50). The defects, which were introduced into the surface of N65m specimens during machining, contributed to a 2 GPa decease in Young’s modulus in comparison with N65 specimens (Figure 50).
Figure 50: Young’s modulus vs. density of N65 (A) and N50 (B) specimens

(A) Before reduction
\[ E = 67.5 \pm 4.2 \text{ GPa} \]

After reduction
\[ E = 25.4 \pm 2.5 \text{ GPa} \]

After reduction and machining
\[ E = 23.3 \pm 3.1 \text{ GPa} \]

(B) Before reduction
\[ E = 74.4 \pm 11.4 \text{ GPa} \]

After reduction
\[ E = 38.9 \pm 6.9 \text{ GPa} \]
The specimens in the same states (before or after reduction) can have varied densities due to different porosities in each individual specimen. Since pores do not contribute to the stiffness of the specimen, Young’s modulus will show a linear dependence on density: higher density or lower porosity with higher $E$. Among the Young’s moduli of both N65 and N50 specimens with sintered and reduced states, good linear dependence on density was measured (Figure 50), as expected. The dependence is maintained in the N65m specimen although the values of Young’s moduli decrease with the induced defects during machining.

5.3.4 Flexural Strength

The reduced N65, N50 and N65m specimens were tested in four-point bending at room temperature in ambient environment. Since the load at the fracture of each specimen was measured, the flexural strengths were calculated by Equation (37). It is assumed that the occurrence of the material’s fracture via four-point bending obeys the Weibull distribution expressed by Equation (20). The relation of stress and the probability of fracture under such stress can be transferred to a linear form as

$$\ln \left[ \ln \left( \frac{1}{1 - P_f} \right) \right] = m \ln \sigma - m \ln \sigma_0$$

(44)

where, $\sigma$ is a certain stress, $P_f$ is the probability of failure at the stress $\sigma$, $\sigma_0$ is the characteristic stress and $m$ is the Weibull modulus.
Figure 51: Weibull distributions of flexural strengths of N65 (A) N65m (B) and N50 (C)
Based on Equation (44), curves of the Weibull distributions of N65, N50 and N65m at room temperature were created (Figure 51), and thus the Weibull parameters $\sigma_0$ and $m$ were calculated. Comparing the characteristic stress $\sigma_0$ in Figure 51, similarly with the situation of Young’s modulus, larger fraction of SCSZ in N50 specimens brings a higher $\sigma_0$ than that of N65 specimens, which suggests a higher strength in the N50 anode than in the N65 anode. If considering N65 and N65m specimens with the same SCSZ fraction, both characteristic strength and the Weibull modulus of the machined N65m specimens ($\sigma_0 = 35.09$ MPa and $m = 5.96$) are slightly lower than those of N65 specimens ($\sigma_0 = 33.03$ MPa and $m = 5.16$). It is because the N65m specimens had more defects on their surface due to machining despite of the same composition as N65 specimens. The Weibull moduli $m$ of N65, N50 and N65m are all in the range of 4.5 – 6.0, which are fairly low values. It is thus indicated dispersive pores’ sizes in those porous cermets, especially on the surfaces of the specimens.

In addition to the room temperature testing, the reduced N65m specimens were tested in four-point bending at high temperatures in a reducing environment to measure the flexural strength of the anode material. Typical load versus time plots for bending of Ni/SCSZ specimens at different temperatures are presented in Figure 52A. The linear dependence of load versus time is observed from specimens tested at RT, 700 °C and 800 °C, and indicates an elastic linear deformation of the cermet anode. The elastic behavior of cermet anode is mostly explained by the elastic deformation of the SCSZ matrix phase. But at 900 °C, there is non-linear load versus time
behavior, where plastic deformation in Ni particles significantly delays the time to failure of the cermet anode. Such non-linear deformation is rather desirable as it contributes to improved durability of the anode materials.

After measuring the load upon fracture of the materials, the fracture strength of the anode was calculated using the elastic equation in the calculation (Figure 52B). The strengths of the materials are rather low, being equal to 32.6 ± 6.1 MPa (reduced as-sintered N65 specimens) and 30.5 ± 8.3 MPa (reduced and machined N65m specimens) at room temperature. The flexural strength further decreases by 30% – 40% when the temperature increases to 700 ºC or 800 ºC. At 900 ºC, the calculated value of flexural strength is slightly higher than those measured at 700 ºC or 800 ºC, but the values are not absolutely correct as they were calculated using an elastic beam equation, which is valid only for brittle fracture with small deflection but not for such plastic deformation with large deflection. If one needs to calculate the fracture strength values without the assumption of elastic beam, the plastic deformation should be taken into account with a carefully measurement of the strains during bending. The observed plasticity can be explained by the fact that larger Ni grains in Ni/SCSZ cerments exhibit a brittle-to-ductile transition between 800 ºC or 900 ºC, and therefore the Ni phase deforms plastically, contributing to the overall deformation of the anode cerments.
Figure 52: Load vs. Time curves of four-point bend testing (A) and Flexural strength vs. temperature plots (B) of N65 (RT) and N65m (high temperatures)
5.3.5 Fracture Toughness

In order to measure the fracture toughness ($K_{lc}$), a V-notch was cut into the anode specimen. Following the method in Section 5.2.4, the approximately 2 mm notches in N65 and N50 specimens and approximately 1 mm notches in N65m specimens were prepared. The depth of the notch was about 1/3 of the specimen thickness, and the radius of the tip of the notch was about 5μm, which both correspond well for the requirements for fracture toughness testing [131,132].

Figure 53 shows the shapes of the notches under an optical microscope. After being tested by the four-point bend method, the fracture surfaces and the notches were observed with an optical microscope, and the depths of notches were measured as demonstrated in Figure 44. It turned out that Equation (39) was satisfied for all notches, and the loads measured were thus proved to be trustable for toughness calculation.

Two N50 specimens and four N65 specimens were tested at room temperature. The fracture toughness was measured that $K_{lc} = 0.711 \text{ MPa} \cdot \text{m}^{1/2}$ for N50 and $K_{lc} = 0.715 \text{ MPa} \cdot \text{m}^{1/2}$ for N65. These values are rather low because they were measured for the porous anode cermets. Similar to the testing of flexural strength, the load versus time plots exhibited a linear dependence (Figure 52). They do not show an obvious difference in $K_{lc}$ due to the composition changing in the anode cermets. The increasing amount of Ni does not change SCSZ’s dominant role in mechanical support at room temperature.
Figure 53: Notches on the N65 specimens for room temperature testing (A–B) and N65m specimens for high temperature testing (C–D)

The $K_{lc}$ testing at 800 °C and 900 °C were performed in reducing atmosphere using two N65m anode specimens per temperature. The testing curves and the values of $K_{lc}$ are showed in Figure 54. The fracture toughness of N65m anode cermets was decreased to 0.58 MPa·m$^{1/2}$ at 800 °C and further dropped to 0.49 MPa·m$^{1/2}$ at 900 °C in comparison with the value at room temperature.
Figure 54: Load vs. Time curves of fracture toughness testing (A) and Fracture toughness vs. temperature plots (B) of N65 (RT) and N65m (high temperatures)
The toughness dropped dramatically when the temperature rose from 800 ºC to 900 ºC, the rate of which is much larger than that from room temperature to 800 ºC. In the view of the testing curves (Figure 54A), the specimens still experienced an elastic deformation before fracture at 800 ºC, but the non-linear testing curves of the specimen tested at 900 ºC indicated the plastic behavior of the material without the increase of the fracture toughness of the cermets. This phenomenon coincides with the results of high temperature four-point bending described in Section 5.3.3. It is probably a result of the occurrence of a brittle-to-ductile transition between 800 ºC and 900 ºC.

Based on Griffith’s solids theory, the fracture toughness $K_{Ic}$ has a positive relation with failure stress $\sigma_f$. The toughness dropping at 900 ºC gives evidence of the failure stress decreasing, and thus in consideration of both Figure 52B and Figure 54B, the N65 cermet failed at a lower stress at 900 ºC before fracture. It can be concluded that the changes occurring in the anode cermets between 800 ºC and 900 ºC weaken the material in strength and in toughness, but extend the life time to fracture.

The fracture surfaces of the N65m anode specimens tested at 800 ºC and 900 ºC are shown in Figure 55. The fracture surface of the specimen tested at 800 ºC (Figure 55A) is very similar to the fracture surface of the specimen tested at room temperature. Mostly intergranular fracture mode is detected with few transgranular larger grains. However, at 900 ºC, different microstructural features are detected at the fracture surface near the tip of the notch (Figure 55B–D). Larger grains
are detected with a mostly plastic deformation in the specimens tested at 900 °C in an H₂ reducing atmosphere. It was reported [140,141] that the Ni coarsening in Ni-cermet anodes, such as Ni/YSZ and Ni/GCO, occurs when the cermet materials were exposed to the forming gas at 950 °C for up to 2500 h. Along with grain coarsening, plastic behavior was also observed during testing of the anodes at 900 °C.

Figure 55: SEM micrographs of fracture surfaces of Ni/SCSZ cermets anode after testing at 800 °C (A) and 900 °C (B–D) in reducing atmosphere. The dimples (C and D) indicate the ductile fracture of the Ni grains.
The rough and irregular surfaces with caves where observed Figure 55B) rather than brittle cleavage or faceted surfaces. The dimples have been formed in larger Ni grains (Figure 55C and D), indicating the presence of ductile fracture. Since the specimen is highly porous, the dimples are distributed within individual large Ni grains. Thus, in the Ni/SCSZ cermets at 900 °C, the ductile Ni contributed to the non-linear deformation. The specific microstructural features related to the exhibited plasticity can be seen at the fracture surface near the tip of the notch, where the tensile stress is the highest during the bending of the specimen. When the crack started to propagate through the whole cross section rapidly, the brittle fracture dominated.

5.4 Conclusion

Ni/SCSZ cermets N65, N50 and N65m were completely reduced in the flow of 95% N₂ – 5% H₂ forming gas at 800 °C for 24 h. After reduction, the porosity and the size of pores increased. X-ray diffraction showed stabilization of SCSZ and the shrinkage of SCSZ lattice by doping Ni while Raman spectra indicated the existence of a low symmetric phase of ZrO₂.

Mechanical properties, such as Young’ moduli and the flexural strengths, were measured. The results of Young’s moduli showed strong linear dependence on density or porosity of the specimen in both N50 and N65. N50 has a higher E value than N65, and the machined N65m is even lower because of defects induced by machining. The flexural strengths were tested via the four-point bend method, and Weibull distributions at room temperature were built. The Weibull moduli were
in the range of 4.5 – 6.0, and the strength of N50 is higher than that of N65. Flexural strengths of N65m specimens were tested at the 700 – 900 °C temperature range, and the testing curves implied that while at 700 °C and 800 °C the anode specimens exhibited purely elastic deformation and brittle fracture like those at room temperature, the material presented a plastic behavior and a lower yield stress when tested at 900 °C, but it brought a delayed time to failure. The fracture toughness testing also showed a rapid decrease when temperature went from 800 °C to 900 °C. The cermets weakening between 800 °C and 900 °C is probably due to the nickel grains coarsening and a brittle-to-ductile transition. The fracture surfaces of the specimens tested at 900 °C provided evidence of the plastic deformation and ductile fracture of coarse Ni grains.
CHAPTER SIX: REVISIT THE PHASE STRUCTURES OF THE TWO SOFC MATERIALS

6.1 Introduction

While the high ionic conductivity is of prime importance to ensure SOFC efficient operation, the stability of phase and crystal structure are playing detrimental role for SOFC durability and longevity. The phase stability of YSZ was studied intensively in the past decades and it was found the 8 mol% Y2O3 stabilized ZrO2 (YSZ) remains in the cubic form from room temperature to 1000 °C or above [42]. Studies of the phase stability of SCSZ revealed that 10 mol% Sc2O3 and 1 mol% CeO2 stabilized ZrO2 (SCSZ) ceramics transforms from cubic to β-rhombohedral phase upon heating at ~300 °C and then back to cubic structure at 500 °C. It remains cubic in 500 – 1000 °C temperature range [76].

Besides phase stability, the mechanical properties of YSZ and SCSZ are also of importance. Upon the investigation of their mechanical behaviors at high temperatures, it was found that very high damping occurred at high temperatures during the Young’s modulus measurement of those materials by impulse excitation technique, as mentioned in CHAPTER FOUR. The damping occurred in 110 – 400 °C temperature range for YSZ ceramics and 200 – 400 °C for SCSZ ceramics (Figure 28). In this temperature range it was not possible to measure Young’s modulus. It
was also reported in the literature that the strong peaks of loss modulus were observed in similar temperature range [48,50]. As SCSZ ceramic exhibits cubic to rhombohedral phase transition in this temperature range, it was hypothesized that the damping occurred due to the atom rearrangement in the lattice and the enhanced atom vibrations during phase transition in 350 – 500 °C temperature range. At the same time, there was no phase transition of YSZ ceramics reported in such temperature range, but instead, the ion-vacancy enhanced interactions were used to explain the damping at low temperature in YSZ [37,50,142]. At the same time it was hypothesized [143] that a non-reported phase transition which might occur during long time annealing of YSZ could be the reason for the damping.

Therefore, the goal of this chapter is to investigate the phase stability of both YSZ and SCSZ ceramics during long-term annealing at constant temperature. The *in situ* X-ray and neutron diffraction as well as Raman spectroscopy are employed to verify/detect any occurrence of phase transition from cubic to lower symmetry phase during annealing.

### 6.2 Experimental

#### 6.2.1 X-ray Diffraction

The high temperature X-ray diffraction was performed on the PANalytical X’pert Pro MPD Diffractometer (PANalytical B.V., Almelo, Netherlands) with a copper anode X-ray source with
Bregg-Brentano geometry equipped with a high temperature stage (XRK 900 Reaction chamber, Anton Paar GmbH, Graz, Austria). The sintered YSZ and SCSZ specimens were ground into powders using agate mortar and pestle. The YSZ and SCSZ powders were heated to 275 °C and 350 °C with heating rate 2 °C/min and they were isothermally annealed at those temperatures for 59 h and for 44 h, respectively. The X-ray diffraction patterns were collected every 12 minutes. The collected X-ray data were refined and analyzed using High Score Plus software.

6.2.2 Neutron Diffraction

The neutron diffraction of YSZ powder was carried out using POWGEN beam line at Spallation Neutron Source in Oak Ridge National Laboratory, Oak Ridge, TN, USA. The powder was heated to 275 °C with a heating rate of 5 °C/min and then annealed at this temperature for 26 h using 80 wt% N₂ – 20 wt% O₂ flowing gas as the environment. To perform this heating experiment, the YSZ powder was placed in a quartz cylindrical can with vents on both ends for free gas flow, the wool clothes were placed on both ends of the quartz tube to keep the powder inside. Every high resolution diffraction pattern was collected for 64 minutes, one after another. The diffraction patterns were analyzed with Rietveld refinements using General Structure Analysis System package (GSAS) [144] and the graphical user interface (EXPGUI) [145].
6.2.3 Raman Spectroscopy

The vibrational properties of both SCSZ and YSZ were studied with a Renishaw InVia Raman microscope (Renishaw Inc., Gloucestershire, UK). The Raman microscope system comprises a laser (532 nm line of solid Si) to excite the sample, a single spectrograph fitted with holographic notch filters. Before collecting the spectrum, the spectrometer was calibrated with a standard silicon wafer using a Si band position at 520.3 cm$^{-1}$. The SCSZ raw powders were heated up to 350 °C at a rate of 2 °C/min, and then the temperature were dwelled for 108 h with the collection of Raman spectrum every 20 min. The average collection time for a single spectrum was 300 s. The Raman spectra of YSZ raw powders were collected with a similar process, and the dwelling temperature and dwelling time were 275 °C and 216 h, respectively. During the experiment, the samples were mounted inside a heating/cooling stage (TS1500, Linkam, UK) with a water circulation cooling system.

6.3 Result and Discussion

6.3.1 X-ray Diffraction

The X-ray diffraction patterns of SCSZ and YSZ ceramics at the isothermal heating are presented in Figure 56 and Figure 57. The dwell temperatures 350 °C and 275 °C were chosen for SCSZ and YSZ, respectively, at which temperature Young’s modulus damping is well pronounced.
Figure 56: XRD patterns of YSZ and SCSZ at the beginning and the end of annealing (A); (4 0 0) profile of SCSZ (B) and YSZ (C)
Figure 57: Selected peaks in the X-ray diffraction of SCSZ (A, C and E) and YSZ (B, D and F) during the annealing. (A–B): diffraction pattern. (C–F): intensity mapping with time. (Pseudo-cubic coordinates are used for indexing)
As shown in Figure 56A, only fluorite or pseudo-fluorite structure without impurity was detected by XRD. Before annealing, both SCSZ and YSZ have a pure cubic phase since all peaks are singlet obeying FCC-type extinction. The XRD patterns of YSZ after annealing for 59 h show little difference, and it indicates the same cubic phase as before annealing without phase transition occurring. Differently, the SCSZ has its diffraction peaks spitting after the 44 h annealing, which is evidence of occurrence of a phase transition. The (4 0 0) diffraction profiles (Figure 56B–C) characterize the lattice distortion along [0 0 1] direction, such as a tetragonal phase transition. The unchanging (4 0 0) peaks of YSZ confirm the cubic phase, and there is no detectable t or t′ phase. The SCSZ also shows a single (4 0 0) peak after annealing, which certainly denies the existence of tetragonal phase, and the changed intensity indicates the cubic-to-rhombohedral phase transition.

As it was reported before [76], cubic to \( \beta \)-rhombohedral phase transition started in SCSZ upon isothermal dwell. At the beginning of dwell only cubic phase can be detected, however the amount of rhombohedral phase progressively increases with time (Figure 57). As the amount of the rhombohedral phase is increasing, the amount of the cubic phase is decreasing. The refinement suggested the cubic phase and the rhombohedral phase reached 56.7 wt% and 43.3 wt%, respectively, after 44 h dwelling at 350 °C. The phase transition rate obviously became lower after the annealing, and the two phases would probably coexist with equilibrium at 350 °C if annealed for a longer period rather than the complete c \( \rightarrow \) \( \beta \) transition occurring.

Using the pseudo-cubic coordinates (in this dissertation, the pseudo-cubic coordinates (Figure
6) are used for all indexes of c, t and β phases if without particular notes), the selected (1 1 1) and (2 2 0) characteristic diffraction peaks of the SCSZ at the beginning of dwell (time = 0 hour) and at the end of dwell (time = 44 hours) are shown in Figure 57C and E. At the same time, while cubic to β-rhombohedral phase transition was detected in SCSZ, only a single cubic phase remained stable during the annealing of YSZ for total 59 hours. Figure 57D and F show the (1 1 1) and (2 2 0) diffraction peaks of the YSZ ceramics at the beginning of the dwell time (time = 0 h) and at the end of the dwell (time = 59 h).

The changes in lattice parameters of the two ceramics as a function of annealing time are shown in Figure 58. While the lattice parameter of the SCSZ cubic phase did not change during the beginning of the annealing, it started to decrease slowly after 700 min of dwelling (Figure 58B). In the β-rhombohedral phase, the lattice parameters (in Hexagonal coordinates) \( a_R \) and \( c_R \) changed significantly (Figure 58B), where \( a_R \) and \( c_R \) represent 1/2[1 1 0]_c and [1 1 1]_c of pseudo-cubic lattice, respectively, with rhombohedral distortion along [1 1 1]_c direction. As the rhombohedral phase appeared, \( a_R \) had a lower value than 1/2[1 1 0]_c of the cubic phase, and it was increasing to 3.5787 Å within the starting 800 min. In the rest of annealing, \( a_R \) was almost kept as constant. In contrast, the parameter \( c_R \), which shows a higher value than [1 1 1]_c of the cubic phase due to the rhombohedral distortion, was dropping in the first 800 min and then slowly decrease in the rest annealing time like the behavior of \( a_c \) in cubic phase. The discontinuity of lattice parameters (\( a_R \) and 1/2[1 1 0]_c, \( c_R \) and [1 1 1]_c) indicates a first order phase transition between cubic and β phase.
Figure 58: Weight percentages (A), lattice parameters (B) and volumes of pseudo-cubic cell (C) of cubic and rhombohedral phases in SCSZ during annealing at 350 °C by X-ray diffraction
The lattice distortion was also reflected by the unit cell (pseudo-cubic lattice) volume change as a function of the dwelling time (Figure 58C). The volume of cubic SCSZ, that is three-cubed $a_c$, exhibited a constant and then slowly decreasing. In the case of $\beta$-SCSZ, the volume was close to the cubic phase at the beginning ($V = 133.22 \ \text{Å}^3$) but rapidly increasing within 1000 min dwelling time ($V = 133.32 \ \text{Å}^3$). After that, the volume was gradually decreasing until it became 133.30 Å$^3$ after 49 hours of annealing. There is no phase transition in YSZ detected by XRD, so the lattice parameter and the unit cell volume of cubic YSZ were measured as $5.15032 \pm 0.00002 \ \text{Å}$ and $136.616 \pm 0.002 \ \text{Å}^3$, respectively. They remained almost constant for the whole duration of the annealing. As a comparison, the low standard deviation of the parameters in YSZ suggests that the variation in the parameters of SCSZ, though quite slight, is beyond the experimental error.

The cubic-to-$\beta$ phase transition in scandia stabilized zirconia was considered as a first-order martensitic transition [61]. The transitional process from cubic to rhombohedral was not observed. The rhombohedral phase was present with abrupt lattice distortion from cubic: the elongation of [1 1 1]$_C$ and the area shrinkage of (1 1 1)$_C$ are both about 1.9%. Then, the new rhombohedral has little mismatch of the unit cell volume with the cubic phase. At the beginning of annealing, the nucleation probably occurred in the cubic grain with strong constraint of the volume. The cubic phase which acted as a matrix limited the lattice expansion of the new small amount of rhombohedral phase during growth, and thus the strain energy was generated in the rhombohedral phase. After further annealing, the strain energy was released during the crystallization and grain
growth, accompanying the presence of the defects such as twining boundary and stacking faults, which are common in the rhombohedral scandia stabilized zirconia. Since the rhombohedral phase was gradually accommodated with cubic phase, the lattice parameters and the unit cell volume were recovered. It took about 1000 min to finish this kinetic procedure. Although $a_R$ was maintained as constant through 1000 min to 2700 min dwelling time, the lattice parameter $c_R$ and the unit cell volume both experienced a slow decreasing. At the same time, the parameters in the cubic phase were also slightly dropping. The decreases are probably results from the redistribution of the doped Sc$^{3+}$ and Ce$^{4+}$ ions. The phase transition led to nonstoichiometric SCSZ, and more oxygen vacancy might be introduced in the both phases as to result in the slight lattice shrinkage.

Therefore, a kinetic processing with crystallization and defects’ moving accompanying the change of lattice parameters lasted for up to 1000 min after the instantaneous displacive phase transition. The slow diffusion of ions did not finish after 2700 min. The cubic and rhombohedral lattices of SCSZ hardly had definite phonons in the Young’s modulus measurement by a dynamic method. It can be hypothesized that the mixed two phases can both contribute to a definite response of the pulse after a long enough time when the equilibrium is reached. However it is longer than 44 h. Thus, damping was observed in the Young’s modulus measurement by the dynamic method with limited measuring time. Similar situation would be met at higher temperatures unless 450 °C was reached, where the phase transition was complete, and the specimen was able to respond a definite frequency.
Unlike the case of SCSZ, the YSZ ceramic shows a different situation. Rather than a rhombohedral-to-cubic phase transition as in SCSZ, there was no evidence of a phase transition by XRD. The cubic YSZ phase was maintained during the heating and annealing. Since X-ray diffraction is not sensitive to the light atom such as oxygen, the structural changes due to the displacement of oxygen would not be reflected by X-ray technique. If the vibration damping was caused by a phase transition similar as that in SCSZ but not detectable using X-ray, the neutron technique might be employed to determine the position and occupancy of oxygen and thus to indentify the phase transition.

6.3.2 Neutron Diffraction

A hypothesis was raised that YSZ experienced a similar phase transition in the temperature range where the damping of Young’s modulus was observed. To verify the structural stability of the cubic YSZ upon long term isothermal annealing, the YSZ powder was annealed at 275 °C for 26 hours with continuous collection of neutron diffraction data. The high resolution neutron diffraction patterns of YSZ annealed at 275 °C were refined and analyzed using GSAS.

The diffraction patterns do not show any obvious change as a function of the annealing time. Similar to the results of XRD, a single pure phase was present from the beginning to the end. The typical neutron diffraction pattern of YSZ during annealing at 275 °C is shown in Figure 59. Although strong peaks in the YSZ pattern coincide with the peaks present in the X-ray diffraction
pattern based on $Fm\bar{3}m$ cubic symmetry, a set of forbidden peaks of FCC structure were
detected by the neutron diffraction technique. Those peaks are weak but suggest the loss the cubic
symmetry; instead, the tetragonal structure with space group $P4_2/nmc$ is better fit for the YSZ
neutron diffraction pattern. For example, the (112) peak belonging to the tetragonal ($P4_2/nmc$)
structure was detected, as shown in Figure 59(insert).

The lattice parameters of the tetragonal phase were determined as $a = 5.1452 \pm 0.0003 \ \text{Å}$ and
$c = 5.1624 \pm 0.0005 \ \text{Å}$ using Rietveld refinement (Figure 60). The $c/a$ is equal to 1.0033, which is
very close to 1 indicating only very small lattice distortion from the cubic structure. The volume of
the tetragonal unit cell is $68.332 \pm 0.003 \ \text{Å}^3$. The low standard deviation of lattice parameters
measured during annealing indicates the high stability of the tetragonal structure.

Since the ratio of $c/a$ is near 1, the Zr$^{4+}$/Y$^{3+}$ cations are distorted little from face-centered cubic
sublattice in the fluorite structure, but there is a displacement of oxygen ions from their tetrahedral
sites in the anion’s sublattice, which results in the loss of the cubic $Fm\bar{3}m$ symmetry. It was
determined that the coordinate of the oxygen at 4$c$ sites was $(0, 0, z)$ with $z = 0.0251 \pm 0.0003$ in the
tetragonal unit cell with space group of $P4_2/nmc$, that is an oxygen displacement of $0.1298 \pm
0.0015 \ \text{Å}$ along $c$-axis in comparison with the position in the cubic phase. As a reference, the
displacement of Zr$^{4+}$/Y$^{3+}$ cations is approximately the difference of the lattice parameters: $c - a =
0.0172 \ \text{Å}$, but it is almost one order less than the displacement of oxygen. Therefore, the tetragonal
distortion is likely induced by the displacement of oxygen ions rather than the Zr$^{4+}$/Y$^{3+}$ cations.
Figure 59: Neutron diffraction pattern of YSZ when annealing at 275 °C
Figure 60: The lattice parameters (A), volume of unit cell (B), coordinates of oxygen ions (C) and occupancy of oxygen ions (D) of YSZ during annealing at 275 °C by neutron diffraction.
The occupancy of oxygen was found to be 0.937 ± 0.005, which is smaller than the theoretical values of 0.963 in 8 mol% Y₂O₃ – ZrO₂. The values of those parameters as a function of annealing time are plotted in Figure 60. Though a non-cubic symmetry was found, the phase maintained without structural changing during annealing at 275 °C for up to 26 h.

As the tetragonal distortion is very small with cla closed to 1, this tetragonal phase is identified as t′ phase [31]. The t′ phase in the raw YSZ powders existed since room temperature. During the ramping, the lattice parameters as long with the volume were linear increasing due to the thermal expansion, as shown in Figure 61. In the view of lattice parameters and the oxygen occupancy, there was no abnormal change when the temperature increased from room temperature to 275 °C. However, the position of oxygen ions changed. As the temperature was increasing, the coordinate z kept dropping until 125 °C. In the rest ramping to 275 °C and the further annealing, this value of z are almost maintained without large variation (Figure 5.5C and Figure 5.6C). The decreasing of z indicates the trends back to cubic, but the movement of the oxygen ions halts at 125 °C. This slight coordinate change is not consistent with the temperature range that Young’s modulus damping occurs. Therefore, the hypothesis that a structural transition in YSZ results in the dynamic damping is not well-founded because of insufficient evidence so far.

As an additional calculation, lattice thermal expansion measured by neutron diffraction can be used to verify the coefficient of thermal expansion by dilatometer. Using the slope of the line in Figure 61B, the coefficient of volume thermal expansion is thus calculated as 2.75 × 10⁻⁵ °C⁻¹.
Figure 61: The lattice parameters (A), volume of t unit cell (B), coordinates of oxygen ions (C) and occupancy of oxygen ions (D) of YSZ during temperature ramping by neutron diffraction.
Since the coefficient of line thermal expansion of the lattice is approximately one third of that of volume, it is calculated as $9.16 \times 10^{-6} \, ^\circ\text{C}^{-1}$. It can be seen that the coefficient of lattice thermal expansion calculated by neutron diffraction of YSZ coincides with the CTE value of YSZ in Figure 29 at low temperature range in CHAPTER FOUR.

6.3.3 Raman Spectroscopy

In addition to X-ray and neutron diffraction, *in situ* Raman spectroscopy was employed to explore any imperceptible phase transition and lattice distortion in SCSZ and YSZ during annealing.

The Raman spectra during temperature ramping are shown in Figure 62. The phase transition from cubic phase to rhombohedral phase occurred in this step, and it can be characterized by the broadening of the peak near 315 cm$^{-1}$. As the $\beta$-rhombohedral phase was produced, a Raman vibration band of $\beta$ at 311 cm$^{-1}$ became stronger [77]. This band is added to the 315 cm$^{-1}$ band of cubic and attributes to the broadening. However, the broadening did not continue in the annealing step. Figure 63A presents the spectra at the annealing time between 0 h and 26 h, where no obvious change was detected. Even after a longer time annealing for up to 108 h, the Raman spectrum maintained identical as those at the beginning of annealing. It can be concludes that the $c \rightarrow \beta$ phase transition finished before the temperature reached 350 °C, and from then on, the powders are in the equilibrium of the cubic and $\beta$ mixture. The conclusion of Raman does not agree with the
result of X-ray diffraction, because the XRD indicates the phase transition were taking place after a certain time of annealing. One possible explanation is the laser irradiation and heating. As mentioned in the Section 6.3.1, the phase transition in SCSZ takes a dynamic process, and the laser is likely to supply extra energy to accelerate the process. Thereby, the phase transition occurred earlier than expected.

Figure 62: Raman spectra of SCSZ during the temperature ramping from 25 °C to 350 °C
Figure 63: Raman spectra of SCSZ during annealing. (A) 0 – 26 h ; (B) 24 – 108 h
It is also proved that the cubic phase will not completely transit to β phase. The equilibrium was reached quickly, and it did not move even after a 108 h annealing. The XRD results show the deceleration of the phase transition as well. The higher temperature is needed to complete the phase transition.

In addition, there are some bands such as 150 cm\(^{-1}\) and 465 cm\(^{-1}\) stands for the tetragonal phase, and they are also present in the reference [77]. It does not mean the large amount of tetragonal phase exists in the sample, but those bands may be due to the defects from the powder processing.

Similar to SCSZ, the YSZ Raman spectra at temperature ramping suggest slight change of lattice (Figure 64). One of the characteristic bands for tetragonal phase [44,137] locating near 465 cm\(^{-1}\) was weakening when the temperature increased from RT to 175 °C. This trend indicates the recovery of the tetragonal distortion from cubic, and it has good agreement with the oxygen displacement detected by neutron diffraction in Figure 61C. As the temperature was further increased to 275 °C and the annealing started, the main bands maintained the same, as shown in Figure 65. During annealing at 275 °C for up to 25.8 h, the YSZ sample did not exhibit phase transition while two weak bands were present at 950 cm\(^{-1}\) and 1014 cm\(^{-1}\), as pointed by the arrows in Figure 65. The annealing continued till 216 h, but the main bands were still unchanging while those two bands were stronger. By my knowledge, no report has discussed the relation between such bands and cubic or tetragonal YSZ. They may be the results of the change of defects configuration in YSZ, or they are probably due to the congregation and crystallization of the small
amount of impurities in the YSZ raw powder.

The Raman spectroscopy still cannot detect any structural transition in YSZ that is responsible to the damping phenomenon of dynamic tests. It is considered that the defects coupling and the reorientation of the defect dipole are probably the reason for the damping.

Figure 64: Raman spectra of YSZ during the temperature ramping from 25 °C to 275 °C
Figure 65: Raman spectra of YSZ during annealing. (A) 1.9 – 25.8 h; (B) 26 – 216 h
6.4 Conclusion

As a result of the performed experiments, it was shown that while cubic to β-rhombohedral structural phase transition occurs in SCSZ ceramics upon isothermal annealing, both cubic and t′ tetragonal structures of YSZ sintered ceramics and raw powder remain stable upon isothermal heating at 275 °C for rather long period of time, and no changes in the structure were detected by in situ X-ray diffraction, neutron diffraction or Raman scattering. Therefore, the damping and high loss modulus of YSZ ceramics in 200 – 400 °C temperature range can hardly be explained by the phase transition due to the lack of evidence.
CHAPTER SEVEN: CONCLUSION AND FUTURE WORK

Three-, four- and six-layered $Y-\lambda SC-Y$ electrolytes ($x = 1 \rightarrow 4$) with outer $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (YSZ) layers and inner $(Sc_2O_3)_{0.1}(CeO_2)_{0.01}(ZrO_2)_{0.89}$ (SCSZ) layers were designed and produced, so that the advantages of both YSZ (phase stability and reliability) and SCSZ (superior conductivity) were combined in the layered electrolytes. They were manufactured via tape casting, laminating and pressureless co-sintering. The thickness per layer was about 30 – 35 μm. The linear scanning via EDS verified the layered structure after sintering and suggested the inter-diffusion regions with a width of about 5 μm. The SEM images showed well-joint interfaces between layers without delamination, but there were larger pores sitting at the grain boundary in the outer YSZ layers. The SIMS detected some unwanted impurities such as Al and Mg in the electrolytes, which might be related to the pores at the grain boundary.

The effect of thermal residual stresses on mechanical performance of layered $Y-\lambda SC-Y$ electrolytes is clarified. Based on the slight mismatch of the coefficient of thermal expansion of YSZ and SCSZ, the layered $Y-\lambda SC-Y$ electrolytes were designed by an approach that compressive residual stress was present in the outer YSZ layers and tensile residual stress was present in the inner SCSZ layer. The presence of the compressive stress in the outer layer contributed to the increase of the biaxial strength of the composite both for the room temperature experiments and for the testing performed at 800 °C. Additionally, the Weibull statistics were built,
and it helped to verify the calculation of residual stresses. Therefore, the residual stress effects on the mechanical behavior were demonstrated for the layered Y–xSC–Y electrolytes for intermediate temperature solid oxide fuel cells.

The ionic conductivities of the electrolytes with different layered designs were measured at 500 – 800 °C, and the electrolyte with Y–4SC–Y design maintained high ionic conductivity in the intermediate temperature range. The ionic conductivities of layered electrolytes basically obey the series-type mixing rule; however, 4% – 17% improvements were present in comparison with the calculation without consideration of the stress/strain effects. The temperature with highest improvements was found to nearly coincide with that with the largest residual compressive in-plane strain in the outer YSZ layer. The compressive stress/strain in YSZ due to the layered structure was considered as one of the important reasons for the improvement of ionic conductivity of the layered electrolytes.

As another application of SCSZ in anode for SOFC, porous Ni/SCSZ anode cermets were produced by completely reduced in the flow of 95% N₂ – 5% H₂ forming gas at 800 °C for 24 h. The phase structure and the mechanical properties of porous Ni/SCSZ cermets were studied. After reduction, the porosity and the size of pores increased. X-ray diffraction showed stabilization of SCSZ and the shrinkage of SCSZ lattice by doping Ni while Raman spectra indicated the existence of a low symmetric phase of ZrO₂. Young’s moduli of the anodes showed a strong dependence on the density or porosity of the specimen. The flexural strengths were tested via the four-point bend
method. The Weibull distributions were built, and the Weibull moduli were in the range of 4.5 – 6.0. Flexural strengths were also tested at the 700 – 900 °C temperature range in reducing atmosphere, and the testing curves implied that while at 700 °C and 800 °C the anode specimens exhibited purely elastic deformation and brittle fracture like those at room temperature, the material presented a plastic behavior and a lower yield stress when tested at 900 °C, but it brought a delayed time to failure. The fracture toughness testing also showed a rapid decrease when temperature went from 800 °C to 900 °C. The cermets weakening between 800 °C and 900 °C might be due to the nickel grains coarsening and a brittle-to-ductile transition. The fracture surfaces of the specimens tested at 900 °C of the fracture surfaces of those specimens provided evidence of the plastic deformation and ductile fracture of coarse Ni grains.

The Young’s moduli of SCSZ and YSZ damped at the temperature range of 110 – 400 °C and 200 – 400 °C, respectively. The phase structures of the two materials were characterized by in situ X-ray diffraction, neutron diffraction and Raman scattering while SCSZ and YSZ were annealed at 350 °C and 275 °C for a long term, respectively. The cubic to β-rhombohedral phase transition during annealing was detected by X-ray diffraction. The phase transition led to the damping of Young’s modulus in SCSZ. The neutron diffraction confirmed the t’ phase in YSZ raw powders, and the oxygen displacement at the temperature ramping, which was also detected by Raman spectroscopy. However, there is still not sufficient evidence of the structural relationship with the damping of Young’s modulus in YSZ. It is considered that the defects coupling and the
reorientation of the defect dipole are the reason for the damping.

Based on the present work, the potential further work or the direction is suggested as following:

(1) SCSZ/YSZ interface in the multi-layered electrolytes;
(2) Duration or long-term properties of SCSZ/YSZ layered electrolytes;
(3) Processing of coating electrodes and manufacturing the whole single cell;
(4) Residual stress state and its effects on the performance of the whole single cell;
(5) Electrochemical testing and characterization of the whole single cell.
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