FABRICATION OF PLANAR AND TUBULAR SOLID OXIDE FUEL CELLS

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

Nader Hedayat

May, 2015
ABSTRACT

The production of SOFCs is usually cost-intensive and time-consuming. Thus, coupling a low cost technique like tape casting or dip coating with co-firing of several layers would be very advantageous. A reproducible co-tape casting technique for the mass production of the planar fuel cells is described. A method for the fabrication of tubular anode-supported solid oxide fuel cells using dip coating technique is developed. Cathode was added to the co-fired half cells by screen printing. A cellulose rod was prepared as a sacrificing core for dipping into anode support, anode interlayer, and electrolyte slurries, and co-firing of the tubular SOFC was advantageously performed in one sintering cycle.

Structural flaws including a variety of curling and cracking behaviors observed in dried tape casts, and the effect of different fabrication parameters on the successful fabrication rate of SOFCs are investigated. The compositional and structural study of the different layers was performed to improve the electrochemical performance of the SOFCs. The electrochemical performance of the fuel cells were improved through fine-tuning the anode interlayer thickness, finding the optimum cathode sintering temperature, and optimizing the pore-former content in the cathode interlayer and cathode current collector layer.

Polyaniline was synthesized using in situ polymerization by the rapid mixing method. A thin film of conductive polyaniline deposited uniformly on the PE membrane,
and also on the slide glass. In situ polymerization of aniline in liquid phase and vapor phase was done. PANI deposited on PE membrane and the conductivity of deposited PANI measured and compared with the data in the literature. An in-situ IR study was carried out to study the in situ polymerized polyaniline by rapid mixing in liquid phase.
ACKNOWLEDGEMENTS

I would like to express my sincerest gratitude to my research advisor Dr. Steven Chuang for his guidance, support and encouragement toward the development of my research abilities. I like to thank Dr. Scott Lillard, Dr. Mesfin Tsige, Dr. Homero Castaneda-Lopez, and Dr. Hamid Bahrami for serving as my committee members and providing valuable insights to elevate the quality of my research. I would like to thank my friends in fuel cell group. Thanks to all my colleagues for their help, and Tom Quick from the Geology Department at The University of Akron for his expertise on XRD characterization. I would like to dedicate this work to the spirit of my father and to my family for their endless encouragement, deep love, and continuous support.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>iii</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>xv</td>
</tr>
</tbody>
</table>

## CHAPTER

### I INTRODUCTION

1.1 Fuel Cell Definition ................................................................. 1
1.2 Fuel Cell Efficiency ............................................................... 2
1.3 Fuel Cell Types ............................................................................ 2
1.4 Solid Oxide Fuel Cells ............................................................... 3
1.5 Outline ......................................................................................... 4

### II BACKGROUND

2.1 Anode supported SOFCs ............................................................. 7
2.2 Components Requirements .......................................................... 8
  2.2.1 Electrolyte .............................................................................. 8
  2.2.2 Anode ................................................................................... 10
  2.2.3 Cathode ................................................................................ 13
2.3 SOFC fabrication techniques ........................................................ 14
3.3 Strategy of Experimentation ................................................................. 52

IV DEVELOPMENT OF CO-TAPE CASTING AND CO-FIRING ....................57

4.1 Introduction ............................................................................................. 57
4.2 Casting of the slips .................................................................................. 59
4.3 Cell fabrication .......................................................................................... 60
4.4 Results and Discussion .......................................................................... 61
4.5 Structural flaws ....................................................................................... 65
4.6 Sinter plates ............................................................................................. 70
4.7 Co-firing .................................................................................................. 72
4.8 Fuel cell performance reproducibility analysis ....................................... 77
4.9 Scraps recycling ...................................................................................... 81
4.10 Conclusion ............................................................................................. 83

V COMPOSITIONAL AND STRUCTURAL STUDY .............................................84

5.1 Introduction ............................................................................................. 84
5.2 Anode support ........................................................................................ 84
   5.2.1 Comparison of 8YSZ and 3YSZ ..................................................... 84
   5.2.2 Pore-former content ...................................................................... 86
5.3 Anode interlayer ...................................................................................... 87
   5.3.1 NiO/YSZ ratio ................................................................................ 87
   5.3.2 Pore-former content ...................................................................... 88
5.3.3 Interlayer thickness ........................................................................................................ 90

5.4 Electrolyte .......................................................................................................................... 94

5.4.1 Comparison of 8YSZ and 10SCZ ................................................................................ 95

5.4.2 Electrolyte thicknesses .................................................................................................. 96

5.5 Cathode ................................................................................................................................ 97

5.5.1 LSM/YSZ ratio .............................................................................................................. 97

5.5.2 Cathode sintering temperature ...................................................................................... 98

5.5.3 Pore-former content of the cathode interlayer ............................................................... 99

5.5.4 Pore-former content of the cathode current collection layer ...................................... 101

5.6 Conclusion .......................................................................................................................... 104

VI FABRICATION OF TUBULAR SOLID OXIDE FUEL CELLS ........................................ 105

6.1 Introduction ........................................................................................................................ 105

6.2 Rolled Tubular SOFC ........................................................................................................ 106

6.3 Dip coating ........................................................................................................................ 107

6.3.1 Slurry preparation .......................................................................................................... 107

6.3.2 Dip coating of carbon rod ............................................................................................. 108

6.3.3 Dip coating of cellulose core ....................................................................................... 110

VII POLYANILINE .................................................................................................................. 115

7.1 Introduction ........................................................................................................................ 115

7.2 Literature review ................................................................................................................. 116
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2.1 Polyaniline membranes</td>
<td>117</td>
</tr>
<tr>
<td>7.2.2 Kinetics of aniline Polymerization</td>
<td>119</td>
</tr>
<tr>
<td>7.2.3 Synthesis of PANI</td>
<td>121</td>
</tr>
<tr>
<td>7.2.4 Deposition of PANI by in situ polymerization</td>
<td>122</td>
</tr>
<tr>
<td>7.3 Experimental</td>
<td>123</td>
</tr>
<tr>
<td>7.3.1 In situ polymerization in liquid phase</td>
<td>123</td>
</tr>
<tr>
<td>7.3.2 In situ polymerization in vapor phase</td>
<td>127</td>
</tr>
<tr>
<td>7.3.3 Dipping</td>
<td>129</td>
</tr>
<tr>
<td>7.3.4 Conductivity</td>
<td>130</td>
</tr>
<tr>
<td>7.3.5 In situ FTIR-ATR spectroscopic study</td>
<td>131</td>
</tr>
<tr>
<td>7.4 Conclusions</td>
<td>134</td>
</tr>
<tr>
<td>VIII CONCLUSIONS</td>
<td>135</td>
</tr>
<tr>
<td>8.1 Development of co-tape casting and co-firing</td>
<td>135</td>
</tr>
<tr>
<td>8.2 Compositional and structural study of the SOFCs</td>
<td>135</td>
</tr>
<tr>
<td>8.3 Development of the tubular SOFC fabrication</td>
<td>136</td>
</tr>
<tr>
<td>8.4 Polyaniline</td>
<td>137</td>
</tr>
<tr>
<td>8.5 Future Studies</td>
<td>137</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>138</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>155</td>
</tr>
<tr>
<td>APPENDIX A. SELECTIVE DEPOSITION OF CERIA</td>
<td>156</td>
</tr>
</tbody>
</table>
APPENDIX B. COMPARATIVE STUDY OF SUCCESSFUL FABRICATION RATE OF SOFC
................................................................................................................................. 164
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1 Technical characteristics of different fuel cells.</td>
<td>3</td>
</tr>
<tr>
<td>1-2 Efficiency of SOFCs operating with different fuels and O₂/Air as oxidant.</td>
<td>4</td>
</tr>
<tr>
<td>2-1 A comparison of SOFC fabrication techniques.</td>
<td>15</td>
</tr>
<tr>
<td>2-2 Tubular and micro-tubular SOFC fabrication and performance as reported in the literature.</td>
<td>16</td>
</tr>
<tr>
<td>2-3 Performance of SOFCs with various impregnated anodes.</td>
<td>26</td>
</tr>
<tr>
<td>2-4 Performance of SOFCs with various impregnated cathodes.</td>
<td>27</td>
</tr>
<tr>
<td>2-5 Durability and performance of Ni-YSZ SOFCs with additional catalyst layer or additive for anode in methane fuel.</td>
<td>28</td>
</tr>
<tr>
<td>2-6 Properties of different pore-formers for the fabrication of SOFCs.</td>
<td>36</td>
</tr>
<tr>
<td>3-1 Typical electrolyte slips composition.</td>
<td>44</td>
</tr>
<tr>
<td>3-2 Typical NiO-YSZ interlayer slips composition.</td>
<td>45</td>
</tr>
<tr>
<td>3-3 Typical formulation for the NiO-YSZ anode support slips.</td>
<td>46</td>
</tr>
<tr>
<td>3-4 Typical formulation for a sinter plate tape casting slip.</td>
<td>48</td>
</tr>
<tr>
<td>4-1 Variety of defects and cracks observed in dry tape-casts.</td>
<td>68</td>
</tr>
<tr>
<td>4-2 Tape casting problems and troubleshooting.</td>
<td>69</td>
</tr>
<tr>
<td>4-3 Performance data of the fuel cells batch No. 120120 at 750 °C in H₂/He (100 sccm, 50 vol% H₂).</td>
<td>79</td>
</tr>
<tr>
<td>4-4 Recipe for anode support slip from recycled scraps and low-quality tapes.</td>
<td>81</td>
</tr>
<tr>
<td>5-1 Characteristics of 8YSZ, 3YSZ, 10SCZ, and 6SCZ powder.</td>
<td>85</td>
</tr>
</tbody>
</table>
5-2 Typical properties of sintered ceramics of 8YSZ, 3YSZ, 10SCZ, and 6SCZ .......... 85

5-3 Current density and open circuit voltage of the cells with 8YSZ anode support, 70% 8YSZ / 30% 3YSZ, and 3YSZ ................................................................. 85

5-4 Porosity (after reduction of the cells), open circuit voltage and maximum current
density of the cells from batches with different pore-former content .................... 86

5-5 Optimized thickness of anode interlayer (anode functional layer) as reported in the
literature ..................................................................................................................... 92

5-6 Current density of the fuel cells with different electrolyte thicknesses ............... 96

5-7 Maximum current density and open circuit voltage (OCV) of the cells with cathodes
sintered at 1100 °C and 1150 °C ............................................................................. 99

5-8 Summary of the compositional and structural modification and results .............. 104

6-1 Dip coating and drying conditions for anode support, anode interlayer, electrolyte 111

7-1 Summary of kinetic data for aniline polymerization ....................................... 121

7-2 Results of the conductivity measurement for the polymeric substrate coated with
PANI .......................................................................................................................... 131

8-1 Specifications of the fuel cell with optimized composition and structure .......... 136

A-1 Crystal size of different samples .................................................................. 159

B-1 Specification of fabricated fuel cells with 24 and 10 h mixing time of slips (green
diameter: 22 mm) ................................................................................................. 164

B-2 Average maximum current density of fuel cell batches prepared with different 8YSZ
interlayer and composite interlayer (8YSZ+10SCZ). .............................................. 166

B-3 Specifications and successful fabrication rate of fuel cell batches (10SCZ electrolyte,
8 µm) prepared with different pore-former content of 10 µm anode interlayer
(NiO/10SCZ : 63/37). ............................................................................................. 166

B-4 Specifications and successful fabrication rate of fuel cell batches prepared with 4
wt% ball milled and 4 wt% non ball milled pore-former of 10 µm interlayer .......... 167

B-5 Specifications and successful fabrication rate of fuel cell batches prepared with
different particle size of former for the interlayer ............................................. 167
B-6 Specifications and successful fabrication rate of fuel cell batches prepared with different pore-former content of anode support. .......................... 168

B-7 Specifications and successful fabrication rate of fuel cell batches with 8YSZ interlayer prepared with different interlayer thicknesses. ......................................................... 168

B-8 Specifications and successful fabrication rate of fuel cell batches prepared with different anode support thicknesses. ................................................................. 168

B-9 Summary of the comparative study on successful fabrication rate......................... 169
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1 Visualization of dissertation.</td>
<td>6</td>
</tr>
<tr>
<td>2-1 Schematics of the principle of SOFC operation.</td>
<td>8</td>
</tr>
<tr>
<td>2-2 Conductivity of yttria and scandia stabilized zirconia in air at 1000 °C.</td>
<td>10</td>
</tr>
<tr>
<td>2-3 Variation of electrical conductivity measured at 1000 °C as a function of nickel content of Ni/YSZ sintered at different temperatures.</td>
<td>12</td>
</tr>
<tr>
<td>2-4 Schematic of dip coating.</td>
<td>16</td>
</tr>
<tr>
<td>2-5 Schematic of screen Printing.</td>
<td>20</td>
</tr>
<tr>
<td>2-6 A screen printing squeegee with polyurethane blade that is abrasion resistant, solvent and ink resistant.</td>
<td>20</td>
</tr>
<tr>
<td>2-7 Different profile edges provide sufficient mechanical behavior and restrain the transmitted force.</td>
<td>21</td>
</tr>
<tr>
<td>2-8 Sharper edge shape increases the image resolution and decreases the paste thickness.</td>
<td>22</td>
</tr>
<tr>
<td>2-9 Roller squeegee provides constant contact angle that promotes constant paste thickness.</td>
<td>22</td>
</tr>
<tr>
<td>2-10 Typical process for the impregnation of metal salt nitrate solution or nanoparticle suspension into sintered porous electrode: (a) Sintered electrode porous structure; (b) formation of nanoparticles at 500-800 °C; (c) nanostructured electrode.</td>
<td>24</td>
</tr>
<tr>
<td>2-11 Planetary ball mill.</td>
<td>30</td>
</tr>
<tr>
<td>2-12 Schematic depicting the grinding jar and ball motion.</td>
<td>30</td>
</tr>
<tr>
<td>2-13 Particle size contribution after dry ball milling durations.</td>
<td>34</td>
</tr>
<tr>
<td>3-1 SEM image of the raw material used in SOFC fabrication.</td>
<td>40</td>
</tr>
</tbody>
</table>
3-2 Flow chart of the fabrication process of SOFCs via tape casting anode-supported electrolyte via tape casting................................................................. 42

3-3 De-airing setup to remove the extra solvent of slips. ........................................ 46

3-4 (a) vacuum chamber used for the de-airing of slips; (b) pouring of solution/doctor blade set up; (c) casted slip; (d) pinned layers; (e) spraying gun deposition of ethanol/α-terpineol; (f) tape before lamination; (g) laminating the tape; (h) pressing of the tape.... 49

3-5 (a) Outside of laser cutter; (b) inside of laser cutter after completion of circular sinter plate cutting; (c) scraps; (d) circular and rectangular sinter plates after laser cutting..... 50

3-6 Sinter plates after firing ..................................................................................... 50

3-7 Experimental apparatus for the fuel cell testing. ........................................... 51

3-8 Compositional and structural study of the SOFCs. ........................................... 52

3-9 Experimental plan for the improvement of anode support.............................. 53

3-10 Experimental plan for the improvement of anode interlayer.......................... 54

3-11 Experimental plan for the improvement of electrolyte................................. 55

3-12 Experimental plan for the improvement of cathode interlayer and cathode current collection layer................................................................. 56

4-1 principle of the tape casting technique, in which the raw materials (i.e., ceramic oxide powders) are loaded in the reservoir of a doctor blade in the form of organic slip, and are casted on either a moving or a stationary carrier film. ............................................. 58

4-2 Processing steps used to produce SOFCs....................................................... 62

4-3 Co-tape casting process and co-sintering of multilayer’s variables and affected parameters....................................................................................... 64

4-4 Anode support tapes with (a) 5 and (b) 10 min de-airing duration at 30 mmHg. ..... 67

4-5 Dry anode support tape with crow’s foot cracks on it. ..................................... 67

4-6 flexible, leather-like sheet, called green tape is produced after the drying of tape-cast. ........................................................................................................ 69

4-7 Anode-supported SOFCs with different sizes fabricated via co-tape casting, co-sintering, and screen printing............................................................. 69
4-8 Schematic of the fuel cells arrangement on the sinter plates for compressive sintering. .................................................................................................................................................................................. 71

4-9 Sticking of fuel cells to the sinter plates during the firing............................................. 71

4-10 Microstructure of electrolyte sintered at two step co-firing cycle pre-sintered at 1000 °C, and co-sintered at different temperatures ranging from 1300 °C to 1550 °C: surface morphology: (a):1300 °C, (b):1400 °C, (c): 1500 °C, and (d): 1550 °C. ................................................................................ 75

4-11 Microstructure of electrolyte surface morphology co-fired at (a) one step co-firing cycle at 1400 °C; (b): two step co-firing cycle at1400 °C. ........................................................................................................ 75

4-12 X-ray diffraction patterns of ScCeSZ samples. ........................................................... 76

4-13 Raman spectra of the ScCeSZ fuel cells co-fired in on cycle and two cycles........... 77

4-14 Fuel cells from batch No. 120120. ........................................................................... 78

4-15 Pie chart for the acceptable, and non-acceptable cells of batch No. 120120. ........ 79

4-16 Cross-sectional SEM micrograph of the fuel cell with 15 µm thick interlayer....... 80

4-17 Flow chart for the recycling of scraps from tape casting. ........................................ 81

4-18 Recycling procedure (a) Low quality dried tape cast; (b) scraps from the preparation of solid oxide fuel cells; (c) cutting of low quality tapes into strips; (d) pieces of tape to be ground; (e) loaded tape grinder; (f) grinder in use; (g) ground scraps ; (h) ball mill... 82

5-1 V-I curves of fuel cells with different anode support pore-former contents of 9, 11, and 13 wt% recorded at 750°C flowing Ar/H₂ (100 sccm, 50 vol% H₂); seal-less reactor. ........................................................................................................................................... 87

5-2 Maximum current density of fuel cells with 63% and 55% Ni content in the interlaye. ........................................................................................................................................... 88

5-3 Effect of interlayer pore-former content on the maximum current density and survival rate of SOFCs........................................................................................................................................... 89

5-4 (a) Cross sectional SEM of the SOFC with 4 wt.% pore-former in the interlayer; (a) Cross sectional SEM of the SOFC with 6 wt.% pore-former in the interlayer.............. 90

5-5 Cross-sectional SEM micrograph of the cells with 12, 15, and 18 µm thick interlayer. ........................................................................................................................................... 91

5-6 V-I curves of fuel cells with 12, 15, and 18 µm anode interlayer thickness at 750 °C in H₂/Ar (100 sccm, 50 vol% H₂). ........................................................................................................................................... 93
5-7 V-I curves of fuel cells with 12, 15, and 18 µm anode interlayer thickness at 750 °C in CH₄/Ar (100 sccm, 50 vol% CH₄) ................................................................. 93

5-8 V-I curves of fuel cells with 12, 15, and 18 µm anode interlayer thickness at 750 °C in CH₄/Ar (100 sccm, 50 vol% CH₄) in the presence of 3% H₂O. ........................................ 94

5-9 Figure 3.22 V-I curves of fuel cells with 12, 15, and 18 µm anode interlayer thickness at 750 °C in CH₄/CO₂ (100 sccm, 50 vol% CH₄). ............................................................ 94

5-10 Maximum current density of the fuel cells from batches No. 2 and 3 as a function of electrolyte material............................................................................................................. 95

5-11 XRD patterns of the cathode interlayers with different LSM/YSZ ratio. .............. 98

5-12 XRD patterns of the cathode interlayer sintered at different temperatures. ......... 99

5-13 V-I curves of fuel cells with various pore former amount in cathode interlayer operated at 750 °C in H₂/Ar (100 sccm, 50 vol% H₂)................................................................. 101

5-14 Figure 3.30 V-I curves of fuel cells with various pore former amount in cathode interlayer operated at 750 °C in CH₄/Ar (100 sccm, 50 vol% CH₄)................................. 101

5-15 curves of fuel cells with various pore former amount in cathode current collection layer operated at 750 °C in H₂/Ar (100 sccm, 50 vol% H₂)......................................................... 102

5-16 V-I curves of fuel cells with various pore former amount in ................................... 103

5-17 V-I curves of the cells with various pore former amount in cathode current collection layer operated at 850 °C in H₂/Ar (100 sccm, 50 vol% H₂). ......................... 103

6-1 Rolled tubular cell and planar cell................................................................. 106

6-2 Half cell prepared in one cycle co-firing......................................................... 108

6-3 Schematic for the fabrication process of tubular cell using a carbon rod as template ..................................................................................................................... 109

6-4 Fabricated cellulose rod to use as a sacrificing core for dip coating.................. 111

7-1 (a) film-cast with no dopant ions; (b) after heavily doping in a strong acid solution; (c) after de-doping in basic medium; and (d) after re-doping in a mild acid solution.... 118

7-2 Aniline polymerization with ammonium persulfate (APS) in HCl medium........ 119
7-3 Conventional synthesis of PANI with the addition rate of 1 cc/min for APS; SEM shows the synthesized PANI after 100 min. ................................................................. 122

7-4 Rapid mixing reaction for the synthesis of PANI; SEM shows the synthesized PANI after 30 min. ................................................................. 122

7-5 The model of film formation: (a) aniline oligomers (open circles) are adsorbed at the available interfaces and (b) they stimulate the growth of a PANI chain (thick curve). A nucleus is produced. (c) Other PANI chains grow due to the auto-acceleration mechanism close to the nucleus. The film spreads along the surface. ............................................ 123

7-6 In-situ polymerization of aniline: the reaction times are (a) 0 s, (b) 60 s, (c) 90 s, (d) 120 s, and (e) 180 s. ........................................................................................................ 124

7-7 Photograph of a slide glass coated with transparent PANI thin film compared to a bare slide glass. The green color indicates the emeraldine state......................... 125

7-8 (a) PE membrane before coating with PANI; (b) PE membrane coated with PANI by liquid phase polymerization (polymerization time: 10 min, temperature: 4 °C). ........ 125

7-9 SEM micrograph of PE membrane before coating with PANI. ........................................ 125

7-10 SEM micrograph of PE membrane coated with PANI by liquid phase polymerization (polymerization time: 30 min, temperature: 4 °C)............................. 126

7-11 XRD pattern of the PANI powder collected from the aniline polymerization after 30 min. ........................................................................................................... 126

7-12 (a) PE membrane coated with PANI by vapor phase polymerization (polymerization time: 5 min, temperature: 75 °C); (b) PE membrane coated with PANI by vapor phase polymerization (polymerization time: 15 min, temperature: 75 °C)....................... 127

7-13 SEM micrograph of PE membrane coated with PANI by vapor phase polymerization (polymerization time: 5 min, temperature: 75 °C).......................... 128

7-14 SEM micrograph of PE membrane coated with PANI by vapor phase polymerization (polymerization time: 15 min, temperature: 75 °C)....................... 128

7-15 (a) PE membrane dipped in PANI solution for 6 h; (b) Dipped PE membrane in PANI solution after doping by 1M HCl....................................................... 129

7-16 SEM micrograph of the PE membrane dipped in PANI solution for 6 hr.............. 130

7-17 Schematic of four-point probe for the measurement of electrical conductivity of PANI on the polymeric substrate ......................................................... 131
7-18 (a) Experimental setup for the FTIR-ATR study of PANI; (b) photograph of ZnSe crystal after the experiment; (c) optical micrograph of the growth of polyaniline film on the ZnSe crystal surface. ................................................................. 132

7-19 Absorbance spectra of ATR before pouring the reaction mixture inside the reactor, after pouring the reaction mixture inside the reactor, and after polymerization for 45 min. ......................................................................................................................... 133

7-20 Absorbance spectra of aniline and APS collected by in situ FTIR-ATR. Absorbance spectra (A) were obtained by \( A = - \log \left( \frac{I}{I_{ATR}} \right) \), in which \( I_{ATR} \) is the single beam spectrum of the empty ATR cell and \( I \) is the single beam spectra of the reaction mixture at the specified times. ........................................................................................................... 133

A-1 Adsorbed acetate anion on the nickel surface........................................................... 157

A-2 XRD patterns of Ni-YSZ anode and impregnated samples................................. 159

A-3 (a) SEM of the CeAcAce impregnated cell; (b) SEM of the Ce(NO_3)_2 impregnated cell.................................................................................................................................. 159

A-4 EDX mapping of the surface of impregnated anode with 0.1M cerium (iii) acetylacetonate impregnated solution ................................................................. 160

A-5 EDX mapping of the cross section of 0.1M cerium (iii) acetylacetonate........ 161

A-6 EDX mapping and SEM of deep cross section (40 µm) of anode...................... 161

A-7 XRF mapping of the surface of impregnated cell with 0.1M cerium (iii) acetylacetonate solution ................................................................................................. 162

B-1 Crack-free fuel cells fabricated with NiO/8YSZ+10SCZ Interlayer fabricated in one batch. ................................................................................................................. 165
CHAPTER I
INTRODUCTION

1.1 Fuel Cell Definition

The history of fuel cells goes back to 1839 when William Robert Grove tried to reverse the electrolysis process [1]. Ludwig Mond and Charles Langer until 50 years later introduced the term fuel cell and used coal as fuel obtaining 20 Am$^{-2}$ at 0.73 V [2]. In recent years people have realized the huge potential of fuel cells and many experimental researches have been performed to improve the fuel cell performance by applying new fabrication methods and materials. A fuel cell is an electrochemical device that directly converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent. Hydrogen is the most common fuel and hydrocarbons such as natural gas can also be used as fuel [3]. A fuel cell is comprised of an anode (negative side), a cathode (positive side), and an electrolyte that allows ion mobility between the anode and the cathode. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. The electrolyte layer is sandwiched between the anode and cathode.
1.2 Fuel Cell Efficiency

Fuel cell operation is a chemical process involves the changes in Gibbs free energy ($\Delta G$) and enthalpy or heat ($\Delta H$). The Gibbs free energy is related to the fuel cell voltage via $\Delta G = -nF\Delta U_0$, where $n$ is the number of electrons in the reaction, $F$ the Faraday constant, and $\Delta U_0$ is the cell voltage for thermodynamic equilibrium in the absence of a current flow, which can be derived by $\Delta U_0 = (-\Delta G)/(nF)$ [4]. The fuel cell maximum efficiency can be calculated based on $\Delta G$ and $\Delta H$ as maximum fuel cell efficiency $= \Delta G/(-\Delta H)$.

1.3 Fuel Cell Types

There are five major types of fuel cells according to the types of electrolyte employed: polymer electrolyte membrane fuel cell (PEMFC); phosphoric acid fuel cell (PAFC); alkaline fuel cell (AFC); molten carbonate fuel cell (MCFC), and the solid oxide fuel cell (SOFC) [5]. The main characteristics of fuel cell are listed in Table 1-1.
Table 1-1 Technical characteristics of different fuel cells [5].

<table>
<thead>
<tr>
<th>Type of fuel cell</th>
<th>Electrolyte</th>
<th>Operating T</th>
<th>Fuel</th>
<th>Efficiency</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline (AFC)</td>
<td>Potassium hydroxide (KOH)</td>
<td>50-200 °C</td>
<td>Pure hydrogen, or hydrazine</td>
<td>50-55%</td>
<td>Platinum</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>40-50%</td>
<td>Platinum</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>40-50%</td>
<td>Platinum</td>
</tr>
<tr>
<td>Molten carbonate (MCFC)</td>
<td>Molten salt such as nitrate, sulfate, ...</td>
<td>630-650 °C</td>
<td>Hydrogen, carbon monoxide, natural gas, propane, marine diesel</td>
<td>50-60%</td>
<td>Electrode material</td>
</tr>
<tr>
<td>Solid oxide (SOFC)</td>
<td>Ceramic as stabilized zirconia and doped perovskite</td>
<td>600-1000 °C</td>
<td>Natural gas or propane</td>
<td>45-60%</td>
<td>Electrode material</td>
</tr>
</tbody>
</table>

1.4 Solid Oxide Fuel Cells

SOFCs operate at high temperatures ranging from 600-1000°C. The high operating temperatures have both minor disadvantages and some unique advantages. The disadvantage of the SOFCs are that they have to be constructed from relatively expensive metallic and ceramic materials to comply with certain criteria, and sealing problems [6]. The deposition of carbonaceous material and sulfur poisoning at the Ni-YSZ anode tend to decrease performance due to decreased reaction sites. The advantage of the SOFCs is that it has more fuel flexibility than the other types of fuel cells. The main applications of SOFC technology are combined cycle power plant, cogeneration/tri-
generation for residential building etc. and transportation [7]. SOFC efficiency is 50-60% when electricity alone is value, but when both electricity and high quality waste heat are valued the efficiency is 70-90% [8]. SOFC system efficiency varies for different fuels as reported in the literature [9, 10]. Table 1-2 presents the efficiency of SOFCs operating with different fuels.

Table 1-2 Efficiency of SOFCs operating with different fuels and O₂/Air as oxidant.

<table>
<thead>
<tr>
<th>Type of fuel cell</th>
<th>Fuel</th>
<th>SOFC system efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane-SOFC</td>
<td>Methane</td>
<td>96%</td>
<td></td>
</tr>
<tr>
<td>Ethanol-SOFC</td>
<td>Ethanol</td>
<td>94%</td>
<td></td>
</tr>
<tr>
<td>Methanol-SOFC</td>
<td>Methanol</td>
<td>91%</td>
<td>[9]</td>
</tr>
<tr>
<td>Gasoline-SOFC</td>
<td>Gasoline</td>
<td>83%</td>
<td></td>
</tr>
<tr>
<td>Carbon-SOFC</td>
<td>Carbon</td>
<td>52.90%</td>
<td>[10]</td>
</tr>
</tbody>
</table>

1.5 Outline

The objective of this thesis is to develop a fabrication method that allows the production of planar and tubular half cells including electrolyte, anode interlayer, and anode support within one step for co-firing. Manufacturing problems occurred during the co-tape casting, multi layer dip coating and co-firing for the fabrication of the SOFCs and also solution for the problems are addressed. The structure of the dissertation is outlined in this section. CHAPTER I gives a brief introduction on fuel cells, especially solid oxide fuel cells, and the scope of this study. CHAPTER II provides information about the operating principle of SOFCs, techniques for the fabrication of SOFCs, required components and material processing. Co-tape casting, co-firing, and screen printing are introduced as low-cost and simple techniques for the fabrication of fuel cells.
Chapter III presents the experimental techniques, instruments and characterization techniques used in this research project. CHAPTER IV presents the development of co-tape casting and co-firing techniques for the fabrication of SOFCs. CHAPTER V discusses the results of compositional and structural studies performed toward improvement of the electrochemical performance of SOFCs. CHAPTER VI presents the development of multilayer dip coating and co-firing techniques for the fabrication of tubular SOFCs. CHAPTER VII includes the introducing of inherently conducting polymers, the filled conducting polymers, synthesis of polynilene as an inherently conducting polymer, literature review of polyaniline membranes, coating of PET substrate with polyaniline and characterization by infrared spectroscopy. CHAPTER VIII presents the conclusions of this research dissertation and summarizes the significant findings. Figure 1-1 demonstrates a visualization of the research methodology for this dissertation.
Figure 1-1 Visualization of dissertation.
CHAPTER II
BACKGROUND

2.1 Anode supported SOFCs

The use of anode supported SOFCs as a suitable option for power generation has more advantages in comparison with the electrolyte or cathode supported SOFCs including lower cost, higher mechanical strength, and higher power density especially at intermediate temperatures that results from thinner electrolyte and lower ohmic resistance [11]. The basic operational principle for the solid oxide fuel cell is illustrated in Figure 2-1. The charge carrier in the SOFC is the oxygen ion. At the cathode, the oxygen molecules from the air decompose into oxygen ions by reacting with electrons from the external circuit. The oxygen ions transport through the electrolyte and combine with hydrogen at anode to form water and release electrons. The electrons travel an external circuit providing electric power and producing by-product heat. For unit mole of hydrogen, the number of electrons generation is 2. Therefore, the overall reaction and the half reactions at both anode and cathode can be written as the following:

Anode: \[ \text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \] (1.1)

Cathode: \[ \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-} \] (1.2)

Overall: \[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \] (1.3)
The electrochemical reactions in anode interlayer and electrolyte occur at the interface or three phase boundary (TPB) where the electronic conducting phase (e.g. Ni), ionic conducting phase (e.g. YSZ), and the gas phase coexist.

2.2 Components Requirements

The SOFC can be described as three layered ceramics, comprising of anode, electrolyte, and cathode, respectively. An interlayer is required to improve the interface between the main layers. Each layer of the SOFC has its own function. Thus, there are different requirements for each component. The requirements of each layer are explained below.

2.2.1 Electrolyte

The electrolyte materials for SOFCs are generally oxygen ion conductors, in which ion conduction occurs by the movement of oxygen ions through the crystal lattice. This movement is a result of thermally activated hopping of the oxygen ion, moving from one crystal lattice to its neighbor site. The crystal must contain unoccupied sites.
equivalent to those occupied by the lattice oxygen ions. ZrO$_2$ ceramics show a monoclinic to tetragonal phase transformation at 1170 °C, tetragonal to cubic phase transition at 2370 °C, and cubic to liquid phase transformation at 2680 °C [12]. A reversible transformation from monoclinic to tetragonal occurs in pure zirconia during cooling, associated with a large shear strain due to a volume change of 5–10%. This transformation leads to the formation of cracks. Doping of oxides stabilizes the high-temperature cubic and tetragonal phases that results in an enhancement in the density of the oxygen vacancies and the oxygen-ion conductivity [13].

Yttria-stabilized zirconia (YSZ) is the common electrolyte materials for SOFCs. YSZ is created by doping ZrO$_2$ with a certain percentage of Y$_2$O$_3$ to achieve this movement. The doping concentration is typically around 8 mol% because it has been reported that the ion conductivity reaches peak at that yttria content [14]. In the crystal structure two zirconium cations (Zr$^{4+}$) are replaced by two yttrium cations (Y$^{3+}$), thus one oxygen site (O$^{2-}$) will be left vacant to maintain charge balance. One way to lower the operation temperature of SOFC is replacing YSZ with alternative electrolyte materials showing similar characteristics at relatively low temperatures.

Scandium stabilized zirconia (ScSZ) is considered as a good electrolyte material alternative to YSZ for intermediate temperature SOFCs. Scandia stabilized zirconia (ScSZ) has a higher conductivity and at 780°C its value is comparable to that of YSZ at 1000°C. Taking into account the costs of different dopants yttria-stabilized zirconia is used for most practical applications up to now [15]. Figure 2-2 shows that the conductivity of YSZ increases for the yttria additions of up to about 8 mole% and then decreases for higher yttria contents. The decrease at higher dopant contents is due to the
association of point defects that leads to a reduction in defect mobility and conductivity [16].

Figure 2-2 Conductivity of yttria and scandia stabilized zirconia in air at 1000 °C [16].

2.2.2 Anode

Porous Ni-YSZ composite, patented in the 1970s [17], is the most commonly used anode in the SOFC fabrication for various reasons including low cost, high catalytic activity for hydrocarbon reforming, thermo-mechanical compatibility with YSZ electrolyte, high stability in reducing environments, and high electrical conductivity [18]. In a porous Ni-YSZ anode, the Ni serves both as an electro catalyst and electronic conductor, and the relatively low thermal expansion of YSZ ceramic prevents the Ni from coarsening. Furthermore, YSZ also provides ionic conductivity to the electrode and broadening the triple phase boundary (TPB). The electrical conductivity is dependent on the Ni composition. Figure 2-3 shows the conductivity as a function of nickel measured
at 1000 °C for different sintering temperatures of the Ni/YSZ [19]. “Sintering” is defined as “The coalescence of powders at an elevated temperature via extensive solid-state diffusion” [20].

The percolation threshold plays an important role in the conductivity of composite materials. Percolation threshold of a SOFC means the critical configuration of same type of particles connecting with each other to form a bridge through the electrodes. It relies on composition, porosity, particle sizes and other physical parameters of electrode. In this particular case, the percolation threshold for nickel is about 30 volume percent. Below the threshold, the Ni-YSZ exhibits predominantly ionic conduction behavior. Above this threshold, the electrical conductivity increases by about three orders of magnitude [21].

Figure 2-3 shows that higher sintering temperature, in the range given, will result in higher conductivity. In general, the anode and electrolyte are co-sintered in the range of 1300 °C and 1400 °C to achieve a dense electrolyte and an anode with desirable mechanical strength, electrochemical properties and thermal conductivity [22-24]. The percolation threshold is revealed to be influenced by many variables such as the porosity, pore size, size distribution and size of raw powders as well as contiguity of each constituent component.

Applying a thin anode interlayer between the anode and electrolyte has shown that the anode interlayer improved the anode supported SOFCs performance due to increased electrochemical reaction zones or three-phase boundaries (TPBs) as well as intimate contact between the anode interlayer and electrolyte [25-30]. High performance anode supported SOFCs consist of a dual layer structured anode as following: (i) a highly
porous anode substrate with 200–1500 µm in thickness that fulfills mechanical stability, electrical properties, and the diffusion pathways for fuel and exhaust gases and, (ii) an anode interlayer with 5–30 µm in thickness that provides TPBs [31].

Figure 2-3 Variation of electrical conductivity measured at 1000 °C as a function of nickel content of Ni/YSZ sintered at different temperatures [19].

Several methods have been used to fabricate the interlayer, including drop coating [32], brush painting [33, 34], dry pressing [35], dip coating [36], wet powder spraying (WPS) [37], vacuum slip casting (VSC) [37, 38], spin coating [39, 40], and tape casting and lamination [25, 41, 42]. Tape casting is a simple and cost-effective technique that can be used to fabricate electrolyte, anode interlayer, and anode support within one step [43]. Most of the studies in the literature are concentrated on YSZ-based anode interlayers. The electrochemical reactions in SOFCs takes place in a reactive layer approximately 10 µm thick adjacent to the anode–electrolyte interface [44, 45].
2.2.3 Cathode

The total oxygen reduction reaction on a solid oxide fuel cell (SOFC) cathode can proceed as follows (Kroger-Vink notation) [46]:

\[ O_2(g) + 2V_{O,electrolyte}^{**} \rightarrow 2O_{O,electrolyte}^\delta + 4h_{electrode}^* \]

where \( V_{O}^{**} \) and \( O_{O}^\delta \) symbolize an oxide ion vacancy and an oxide ion in the crystal lattice of the electrolyte. \( h^* \) is an electron hole in the electrode crystal lattice. Oxygen-ion conductivity is very low in LSM. An effective approach for enhancing the electrochemical performance is to mix another material of higher ionic conductivity, such as YSZ, with LSM. Moreover, the incorporation of an YSZ component in the LSM layer may improve the long term stability of the electrode by preventing the coalescence of LSM grains. Thus, LSM-based cathodes are typically mixed with YSZ to form a LSM-YSZ composite cathode, where the YSZ can provide high ionic conductivity in order to possess mixed electronic and ionic conductivity and expand the reaction zone.

LSM reacts with YSZ at temperatures higher than 1100 °C to form secondary phases of \( \text{La}_2\text{Zr}_2\text{O}_7 \) and \( \text{SrZrO}_3 \) at the interface [47, 48]. These reaction products are detrimental to the performance of the cathode, probably due to their low electrical conductivities. With increasing sintering temperature the composite–current collector interface is assumed to become more important, as gas access to the composite–electrolyte interface and to LSM–YSZ contacts in the composite structure may be obstructed if the composite structure becomes too dense [49].
2.3 SOFC fabrication techniques

Powder metallurgy includes four main steps [20]:

(i) Blending

The purposes of powder blending are listed as following: improving the packing ratio by mixing powders of different size distributions, tailoring the final composition of the materials, and adding enough additives to hold the structure together for the forming processes.

(ii) Compaction

The compaction of powder blends is done to increase the density and strength of the compact.

(iii) Forming

The forming of the powder is carried out because the powders have to end up in the desired shape prior to firing.

(iv) Firing

The firing process results in the sintering of powders so that a rigid product with higher quality will be fabricated.

Several ceramic processing techniques have been used for the production of SOFC including screen printing, dip-coating, spin coating, spraying, and tape casting. Table 2-1 compares a variety of fabrication processes [50]. Table 2-1 compares the different SOFC fabrication techniques.
Table 2-1 A comparison of SOFC fabrication techniques [50].

<table>
<thead>
<tr>
<th>Process</th>
<th>Thickness</th>
<th>Components made</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screen printing</td>
<td>&gt;5 µm</td>
<td>Electrodes, electrolyte</td>
<td>Cheap, co-sintering</td>
</tr>
<tr>
<td>Extrusion/co-extrusion</td>
<td>&gt;100 µm</td>
<td>Electrodes, supports</td>
<td>Large, complex shapes</td>
</tr>
<tr>
<td>Tape casting</td>
<td>&gt;10 µm</td>
<td>Whole cell</td>
<td>Cheap, co-sintering</td>
</tr>
<tr>
<td>Dip coating</td>
<td>&gt;1 µm</td>
<td>Whole cell</td>
<td>Cheap</td>
</tr>
<tr>
<td>Atmospheric plasma spraying</td>
<td>&gt;20 µm</td>
<td>Electrolyte, electrodes</td>
<td>Dense electrolyte</td>
</tr>
<tr>
<td>Wet powder spraying</td>
<td>&gt;10 µm</td>
<td>Electrolyte, electrodes</td>
<td>Cheap</td>
</tr>
<tr>
<td>Impregnation/infiltration</td>
<td>N/A</td>
<td>Electrodes</td>
<td>Nanostructured surfaces</td>
</tr>
</tbody>
</table>

Table 2-2 presents the tubular and micro-tubular SOFC fabrication and performance as reported in the literature. It can be seen from Table 1 that extrusion process is the most typical approach to manufacture the micro-tubular anode supports, and the conventional used method for the coating of electrolyte on the anode support is dip coating. There exist certain mechanical requirements for extrusion to occur, including the enough flow-ability of the material during the extrusion process, and enough strength of the extruded material to resist deformation during the firing [2].

2.3.1 Dip coating

Dip coating is a technique to deposit a uniform thin film of slurry as a coating onto a substrate by withdrawing the substrate into the slurry. Figure 2-4 shows the schematic of dip coating. Among commonly used fabrication methods for the production of tubular cells, the dip coating is most attractive due to the following reasons: (i) low cost and easy process; (ii) a homogeneous product composition; (iii) the capability of producing thinner layers (>1 µm compared to >100 µm in extrusion) [50].
Table 2-2 Tubular and micro-tubular SOFC fabrication and performance as reported in the literature.

<table>
<thead>
<tr>
<th>Fabrication technique</th>
<th>Power density (Wcm(^{-2}))</th>
<th>Temp. (°C)</th>
<th>Cell diameter (mm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion, dip coating</td>
<td>0.3</td>
<td>450</td>
<td>1.8</td>
<td>[52]</td>
</tr>
<tr>
<td>Extrusion, dip coating</td>
<td>1.017</td>
<td>550</td>
<td>0.8</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>0.628</td>
<td>500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.273</td>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase inversion, dip coating</td>
<td>0.645-0.848</td>
<td>800</td>
<td>8</td>
<td>[54]</td>
</tr>
<tr>
<td>Extrusion, dip coating</td>
<td>1</td>
<td>570</td>
<td>1.6</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>0.857</td>
<td>550</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extrusion, dip coating</td>
<td>1.1</td>
<td>600</td>
<td>1.9</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>550</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Co-extrusion, slurry coating</td>
<td>0.8</td>
<td>550</td>
<td>1.4</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>0.42</td>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extrusion, vacuum infiltration</td>
<td>0.3</td>
<td>800</td>
<td>7.8</td>
<td>[58]</td>
</tr>
<tr>
<td></td>
<td>0.17</td>
<td>700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extrusion, dip coating</td>
<td>0.415</td>
<td>850</td>
<td>7</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>0.367</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.327</td>
<td>750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-extrusion, slurry coating</td>
<td>2.3</td>
<td>600</td>
<td>1.4</td>
<td>[60]</td>
</tr>
<tr>
<td>Dip coating</td>
<td>0.19</td>
<td>800</td>
<td>1.2</td>
<td>[61]</td>
</tr>
<tr>
<td>Extrusion, dip coating</td>
<td>1.310</td>
<td>550</td>
<td>1.6</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>0.518</td>
<td>500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.263</td>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extrusion, spraying</td>
<td>0.432</td>
<td>800</td>
<td>7</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>0.145</td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extrusion, dip coating</td>
<td>0.26</td>
<td>920</td>
<td>3.8</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>900</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.3.2 Tape-casting

Tape-casting or doctor blade process is a low cost and simple shaping method that is capable of forming thin, flat layers with large area. Glenn Howatt who intended to find a replacement for mica as a capacitor material during the Second World War invented the tape casting process [65]. Howatt founded Glenco Corporation, the first tape casting company, for the production of capacitors. He filed the first patent on tape casting in 1952 [66]. J. L. Park developed a continuous tape casting process for the production of thin sheets of ceramic in 1961 [67]. RCA Corporation developed multilayer ceramics based on the lamination of ceramics fabricated by tape casting that led to the co-firing of ceramics [68]. Tape casting became very popular due to the capability of laminating thin ceramic sheets.

A slip is formed by homogeneous dispersion of desired ceramic powders and organic additives including dispersant, binder, plasticizer, and pore-former (if required) in a solvent system. The ratios of the slip components depend on the grain size of the powders. The organic additives used in the formulation of slips are described below:

(a) Dispersant

Hypermer KD1 (Imperial Chemical Industries PLC, England) is a polymeric cationic surfactant and is recommended as a non-aqueous dispersant (polar continuous phase). The KD1 belongs to a kind of polyester/polyamine condensation polymers with a high molecular weight, which has an estimated MW of about 10000 g/mol. It is composed of anchoring groups that absorb onto the particle surface tightly, and a polymeric chain with a chemical structure designed to give optimum steric stabilization to the dispersion [69]. New dispersants are capable of preventing the formation of
agglomerates in the slip that results in a tape cast without random variation in density [70].

(b) Binder

The binder used in the preparation of green ceramic tape (unfired, but completely dried tape) is probably the most important processing additive of the system. The binder is responsible to make the pre-sintered tape cast structure hold its shape. The most commonly used binder in the tape casting field is (poly)vinyl butyral (PVB) and it is called by the trade name Butvar®, which is a registered trademark of Solutia, Inc. PVB, a polymer with large molecular weight, is very crucial for tape casting to build the network in the anode.

PVB will be burning at high temperature, simultaneously resulting in many pores. These pores pose a negative influence on the electrolyte, lowering the density and the ionic conductivity of electrolyte. Therefore, decreasing the amount of PVB is an effective way to reduce the pores of the electrolyte, resulting in the reducing of the sintering temperature. It supplies the network that holds the entire chemical system together for further processing [21].

(c) Plasticizers

Plasticizers work either on or around the binder polymer chains to improve the binder performance by allowing motion inside the tape matrix without breaking the matrix itself. Type I plasticizers are used to soften the binder polymer chains, allowing them to stretch or deflect under an applied force. These additives can be accurately described as T_g modifiers or binder solvent (e.g. S-160). The ways in which the Type I plasticizer can modify the T_g of a polymer chain are by shortening the polymer chain
length and by partially dissolving the polymer chain. Both of these mechanisms make the tape more flexible at a given temperature. The Type II plasticizer works as a lubricant in the tape matrix. The Type II plasticizer works between the polymer chains, not only allowing them better mobility within the dry tape, but also preventing some of the “cross-linking” between chains (e.g. PEG-200) [69].

(d) Pore-former:

An effective method to optimize the anode substrate is adding a proper amount of pore former into NiO and yttria-stabilized zirconia (YSZ) composite powders to form a highly porous microstructure for gas diffusion. Inorganic or organic sacrificial compounds, such as carbon or cellulose, can be added to the green body and be burned out during firing, leaving behind a ceramic with porous structure.

2.3.3 Screen printing

Figure 2-5 shows the screen printing process. In screen printing, a paste is squeezed through the opening of the mesh and adheres to the substrate. The high-viscosity paste contains particles, binder and solvent. A layer adheres to the substrate after drying, i.e. evaporation of the solvent. Advantages of the screen printing are simplicity and low material consumption. Limitations are evenness of the substrate, size of the screen (mesh opening), and the layer thickness. The thickness of the screen printed layer is given by the screen [71].

Evaporation of the solvents leads to the drying of the ink in the screen and producing uneven printing [71, 72], and variations in the ink viscosity that affects the adjusted parameters of screen printing [72]. Thus, even a highly automated screen printing process is not efficient for the mass production of SOFCs [73]. The squeegee
(Figure 2-6) for screen printing has to perform few tasks that are influenced by many of parameters. First, the squeegee forces the ink into the mesh that is influenced by the ink viscosity and mesh opening. Screen has to be in contact with the substrate to deposit the ink, but high off-contact distance and high screen tension can prevent it. In addition, squeegee removes excess inks from the screen that affects the thickness of next printed layer and the quality of screen printed film.

Figure 2-5 Schematic of screen Printing [51].

Figure 2-6 A screen printing squeegee with polyurethane blade that is abrasion resistant, solvent and ink resistant.
Important factors affecting the quality of screen printed thin films are as following:

1. Squeegee travel speed

   The slower squeegee travel speed gives better prints than the faster one [74]. If the printing speed is too high, the squeegee cannot spin out the paste regularly but a thin paste film is left back in the screen that can lead to paste smearing and the distortion of printed layout [75].

2. Squeegee pressure

   The squeegee force must overcome the force that is necessary to press the paste through the screen. The squeegee has to be only moderately flexible to achieve uniform paste film on the substrate [75].

3. Squeegee shape

   One of the most important variables affecting the quality of screen printed films is the design of the squeegee blade [74]. The important parameters of the right squeegee are hardness, profile, and edge shape. Soft squeegees have higher adaptability to the surface of the substrate, but hard squeegees transmit more force than soft ones. By modifying the profile of the squeegee the value of the force transmitted to the printing surface can be limited (Figure 2-7).

![Figure 2-7 Different profile edges provide sufficient mechanical behavior and restrain the transmitted force [75].](image-url)
Square profile is the most commonly used profile in screen printing that provides medium adaptability and maximum force. Round profile squeegee has low adaptability, transmits minimum force and the effective angle is always very small and hardly affected by the set angle. The sharpness of the squeegee can be set by the edge shape (Figure 2-8). Edge shape establishes the amount of ink delivering to the substrate.

![Figure 2-8](image1.png)

Figure 2-8 Sharper edge shape increases the image resolution and decreases the paste thickness [75].

Sharper edge delivers less ink. Substituting the conventional squeegee by a roller squeegee (Figure 2-9), higher printing speed, and consistent film thickness on the substrate can be achieved [75].

![Figure 2-9](image2.png)

Figure 2-9 Roller squeegee provides constant contact angle that promotes constant paste thickness [75].
4. Squeegee material

Squeegees are usually made of polyurethane or other elastomers. The squeegee material effect is probably because the harder blade is not capable of conforming to the uneven substrate surface leading to thinly printed film. The optimum hardness of the blade would be that, which is just soft enough to guarantee the required yield of good prints. Using softer material would only lead to rapid blade wear. The blunt edge has the advantage that it wears more slowly than does a sharp edged blade [74].

5. Other factors including the mesh open area, paste viscosity, etc

Better results were obtained from the flat substrate, and mesh with more open area. Using a fixed squeegee design and substrate type, it is only necessary to optimize the squeegee speed and pressure separately as there is negligible interaction between them. The conditions that led to the best results were those that produced the heaviest deposit of paste on the substrate [74].

2.3.4 Impregnation

Since high sintering temperatures are required to ensure intimate contact between electrode and electrolyte, for example 1000-1150 °C for LSM cathodes and 1300-1400 °C for Ni/YSZ cermet anodes [76], the conventional approach to introduce nano-particles in the green stage of the electrodes is not very successful for the high temperature SOFC electrodes. Thus, the key consideration in the development of nano-structured SOFC electrodes is to bypass the high processing temperature via the deposition of catalytically and/or electrochemically active nano-particles into a rigid and pre-fired electronic and/or ionic conducting electrode or electrolyte scaffold by impregnation techniques. An
impregnation (infiltration) process involves the precipitation and decomposition of a metal salt solution at 500-800 °C inside a porous electrode or electrolyte structure [77].

Figure 2-10 shows a typical process for impregnation. The significantly reduced phase formation temperature avoids the grain growth, resulting in the deposition of nano-sized particles on the surface of scaffold. Enhancing SOFC performance by surface modification through impregnation is reported in the literature [78-85]. Moreover, prolonging the lifetime of SOFCs is reported in the literature [33, 34, 86-94]. Table 2-3 lists the performance improvement of SOFCs with various impregnated anode. Table 2-4 presents the performance improvement of SOFCs with various impregnated cathode. Table 2-5 lists the durability improvement of SOFCs with impregnated Ni-YSZ anode. The promotion factor ,fp, was calculated by dividing the Faraday resistance of the cell with impregnated anodes by the Faraday resistance of the non-impregnated cell, measured under identical conditions [77].

\[ f_p = \frac{\text{Faraday resistance of impregnated SOFC}}{\text{Faraday resistance of the non-impregnaated cell}} \]

Figure 2-10 Typical process for the impregnation of metal salt nitrate solution or nanoparticle suspension into sintered porous electrode: (a) Sintered electrode porous structure; (b) formation of nano-particles at 500-800 °C; (c) nano-structured electrode (adapted from [77]).

The variations of the promotion factors are because of the differences in the microstructure, ionic and electronic properties of the scaffold, loading and catalytic activities of the impregnated nano-particles. The observed significant promotion effect of
the nano-structured electrodes with discretely distributed nano-particles (i.e., nanoparticles are not interconnected) indicates that there must be significant catalytic effects of the impregnated nano-particles on the electrochemical performance of the electrodes in addition to the obviously enhanced TPB. This is particularly true that in the case of metallic nano-particles (e.g., Pd), the amounts of metallic nano-particles required to provide significant enhancement in electrode performance are so small that the effect must be catalytic. The main advantages of electrodes surface modification through impregnation are as following [95]: (1) it is an effective approach for enhancing electro-catalytic activity and improving electrode stability at low cost because it requires much less material compared to the standard electrode fabrication process; (2) it makes it feasible to use a wide variety of active materials that cannot be otherwise used in a conventional electrode fabrication process; (3) it allows the establishment of nano-sized and/or nano-structured electrodes. The concerns in developing SOFCs through impregnation technique are as following: (1) The long term stability of the impregnated metal nano-particles is a major concern due to the inevitable agglomeration and grain growth of the nano-particles under the high operation temperature of SOFCs [95]; (2) Additional process and sintering step if high oxide loading is required [77].
Table 2-3 Performance of SOFCs with various impregnated anodes.

<table>
<thead>
<tr>
<th>Impregnated nano-particles</th>
<th>Scaffold/skeleton</th>
<th>Performance</th>
<th>Promotion factor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd (5 wt.%) + CeO₂ (5wt.%)</td>
<td>(La₀.₇₅Sr₀.₂₅)(C₀.₅Mn₀.₅)O₃ /YSZ</td>
<td>P=0.52 Wcm⁻² @ 700 °C</td>
<td>5</td>
<td>[81]</td>
</tr>
<tr>
<td>Pd (0.36-0.46 mg cm⁻²) Cu, Ce, and Pd</td>
<td>(La₀.₇₅Sr₀.₂₅)(C₀.₅Mn₀.₅)O₃ /YSZ</td>
<td>P=1.1 Wcm⁻² @ 600 °C</td>
<td>1.9</td>
<td>[82]</td>
</tr>
<tr>
<td>Ni</td>
<td>YSZ</td>
<td>P = 0.3 Wcm⁻² @ 700 °C</td>
<td>-</td>
<td>[79]</td>
</tr>
<tr>
<td>Ni</td>
<td>ST-YSZ</td>
<td>P = 0.57 Wcm⁻² @ 800 °C</td>
<td>2.8</td>
<td>[80]</td>
</tr>
<tr>
<td>NiO-ScSZ</td>
<td>P = 0.12 Wcm⁻² @ 750 °C</td>
<td>1.5</td>
<td>[85]</td>
<td></td>
</tr>
<tr>
<td>CeO₂ NiO-SDC</td>
<td>P = 0.78 Wcm⁻² @ 600 °C</td>
<td>1.4</td>
<td>[83]</td>
<td></td>
</tr>
<tr>
<td>SDC</td>
<td>P = 0.76 Wcm⁻² @ 600 °C</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>P = 0.74 Wcm⁻² @ 600 °C</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 mol% Gd(NO₃)₃ + 90 mol% Ce(NO₃)₃*</td>
<td>NiO-ScSZ</td>
<td>P=1.35 Wcm⁻² @ 700 °C</td>
<td>1.7</td>
<td>[84]</td>
</tr>
<tr>
<td>Mo₀.₁Ce₀.₉O₂⁺δ (MDC)</td>
<td>Ni-YSZ</td>
<td>P=0.58 Wcm⁻² @ 700 °C</td>
<td>1.7</td>
<td>[86]</td>
</tr>
</tbody>
</table>

* Both cathode and anode electrodes were impregnated using the same solution.
<table>
<thead>
<tr>
<th>Impregnated nanoparticles</th>
<th>Scaffold/skeleton</th>
<th>Performance</th>
<th>Promotion factor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mol% Gd(NO$_3$)$_3$ + 90 mol% Ce(NO$_3$)$_3$*</td>
<td>LSF-ScSZ</td>
<td>$P=1.35$ Wcm$^{-2}$ @ 700 °C</td>
<td>1.7</td>
<td>[84]</td>
</tr>
<tr>
<td>La$<em>{0.6}$Sr$</em>{0.4}$CoO$_3$ (30 vol.%)</td>
<td>YSZ</td>
<td>$P=2.1$ Wcm$^{-2}$ @ 800 °C</td>
<td>-</td>
<td>[97]</td>
</tr>
<tr>
<td>SDC</td>
<td>LSM</td>
<td>$P=0.40$ Wcm$^{-2}$ @ 700 °C</td>
<td>2.6</td>
<td>[98]</td>
</tr>
<tr>
<td>GDC (50 wt.%)</td>
<td>LSBM</td>
<td>$P=1.04$ Wcm$^{-2}$ @ 700 °C</td>
<td>2.1</td>
<td>[99]</td>
</tr>
<tr>
<td>GDC (30 wt.%)</td>
<td>LSBM</td>
<td>$P=0.74$ Wcm$^{-2}$ @ 700 °C</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>BSCF (1.8 mgcm$^{-2}$)</td>
<td>LSM</td>
<td>$P=0.58$ Wcm$^{-2}$ @ 700 °C</td>
<td>3.4</td>
<td>[100]</td>
</tr>
<tr>
<td>Ag</td>
<td>LSCF-GDC</td>
<td>$P=0.98$ Wcm$^{-2}$ @ 600 °C</td>
<td>3.3</td>
<td>[101]</td>
</tr>
</tbody>
</table>

* Both cathode and anode electrodes were impregnated using the same solution.
Table 2-5 Durability and performance of Ni-YSZ SOFCs with additional catalyst layer or additive for anode in methane fuel.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Electrolyte/Cathode</th>
<th>Temp. (ºC)</th>
<th>Fuel</th>
<th>Power density (Wcm$^{-2}$)</th>
<th>Operation Period (h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt. % Sn</td>
<td>YSZ/LSM-YSZ</td>
<td>800</td>
<td>3% H$_2$O–CH$_4$</td>
<td>0.08</td>
<td>25</td>
<td>[34]</td>
</tr>
<tr>
<td>3 wt % Ru–Al$_2$O$_3$</td>
<td>YSZ/LSM-YSZ</td>
<td>850</td>
<td>CH$_4$:CO$_2$ (2:1)</td>
<td>0.93</td>
<td>–</td>
<td>[93]</td>
</tr>
<tr>
<td>LiLaNi–Al$_2$O$_3$+Cu</td>
<td>YSZ/LSM-YSZ</td>
<td>850</td>
<td>CH$_4$:O$_2$ (4:1)</td>
<td>1.08</td>
<td>7</td>
<td>[94]</td>
</tr>
<tr>
<td>Cu$^2$</td>
<td>YSZ/LSM-YSZ</td>
<td>800</td>
<td>dry CH$_4$</td>
<td>0.05</td>
<td>25</td>
<td>[33]</td>
</tr>
<tr>
<td>Sn</td>
<td>YSZ/LSM-YSZ</td>
<td>650</td>
<td>3% H$_2$O–CH$_4$</td>
<td>0.41</td>
<td>120</td>
<td>[89]</td>
</tr>
<tr>
<td>1 wt. % Li$_2$TiO$_3$</td>
<td>YSZ/LSM-YSZ</td>
<td>800</td>
<td>25% CH$_4$ + 75% air</td>
<td>0.40</td>
<td>50</td>
<td>[90]</td>
</tr>
<tr>
<td>SZY</td>
<td>YSZ/LSM</td>
<td>900</td>
<td>dry CH$_4$</td>
<td>0.28</td>
<td>–</td>
<td>[87]</td>
</tr>
<tr>
<td>10 wt. % CeO$_2$</td>
<td>YSZ/LSM</td>
<td>800</td>
<td>dry CH$_4$</td>
<td>0.48</td>
<td>5</td>
<td>[92]</td>
</tr>
<tr>
<td>Cu$^3$</td>
<td>YSZ/LSM-YSZ</td>
<td>700</td>
<td>3% H$_2$O–CH$_4$</td>
<td>0.24</td>
<td>200</td>
<td>[91]</td>
</tr>
<tr>
<td>1 wt. % Sn</td>
<td>YSZ/LSM-YSZ</td>
<td>800</td>
<td>3% H$_2$O–CH$_4$</td>
<td>0.39</td>
<td>49</td>
<td>[88]</td>
</tr>
<tr>
<td>SDC</td>
<td>YSZ/LSM</td>
<td>700</td>
<td>25% CH$_4$ + 75% air</td>
<td>0.30</td>
<td>500</td>
<td>[95]</td>
</tr>
</tbody>
</table>

$^1$ Catalyst layer
$^2$ Cu deposited by microwave irradiation process.
$^3$ Cu electroplating
2.3.5 Planetary ball milling

Mixing and grinding of materials are important in the preparation of mixtures or slips because mixing and grinding will lead to “uniform dispersion” and “particle size reduction”. Having a uniform dispersion with a reduced particle size is a prerequisite for having a homogeneous mixture. Dry or wet milling is possible, but the solvents in wet milling must comply with the stringent safety requirements. Figure 2-11 shows a ball mill that is called planetary ball mill because of the planet-like movement of its milling jar that contains the powder to be ground and the grinding balls. The milling jar is arranged on a rotating support disk (sun wheel) and a special drive mechanism causes it to rotate around its own axis. The centrifugal force produced by the milling jar rotating around its own axis and that produced by the sun wheel both act on the jar contents. The high rotational speed of both, the jar and the sun wheel, leads to large impact energies of milling balls inside the jar to achieve an effective grinding performance. The powders under comminuting are located between surfaces and crushed due to the impact and/or frictional forces that are caused by collisions [101]. Figure 2-12 shows the grinding Jar and ball motion inside the grinding jar [51].
Planetary ball-milling variables are not completely independent. The optimum milling time, for instance, depends on the size of the grinding medium, ball-to-powder ratio, etc. Some of the important parameters that have an effect on the final constitution of the powder are as following [101]: milling container, milling speed, milling time, type, size, and size distribution of the grinding medium, ball-to-powder weight ratio, extent of
filling the jar, and process control agent to reduce the excessive cold-welding of the powder at the initial milling stage.

An increase in revolution speed often leads to higher yields or better substrate conversion at constant milling times as a result of the more efficient mixing and the increasing number of collisions. The speed has no influence above a particular number of revolutions or no influence at all for some reactions. On the other hand a lower revolution speed leads to less energy consumption and hence to lower cost and a more energy efficient process [102]. The number of balls depends on the volume of the grinding chamber and is limited by the filling ratio $\rho$. It is known that for dry grinding a ball filling ratio of $\rho = 0.3$ results in the most effective feed grinding [102]. The filling level of the jar is of crucial importance for a successful grinding process in planetary ball mills. For grinding bulk materials a jar filling should consist of about 1/3 sample and 1/3 ball charge. The remaining third is the free jar volume that is necessary for the free movement of the balls [51].

Depending on the size of the milling balls a certain amount of balls is necessary to guarantee a qualitative yield. A higher number of balls at constant density and diameter influence the reaction due to the change in stress number. The restricted movements of the balls inside an overloaded milling jar leads to a low yield. Otherwise in a charge with too few balls strong abrasion can take place and may not be in line with the recommendation of the mill manufacturer [101]. A mixture of balls with different size may randomize the motion of the ball charge in a way that without well-defined trajectories tracks in the pot are avoided.
The collision of balls against each other and the wall of the pot during the grinding process will lead to wear of the container and the balls. The dislodged material gets incorporated into the powder where it contaminates or alters the powder chemistry. The wear is highly affected by the adhesion of the powder material to the ball, whether the material is able to form a layer around the ball respectively. If the ball surface is insufficiently coated due to low adhesion of a free flowing powder the energy is wasted in wearing the balls. This effect is even stronger when not a dry powder but a suspension is processed: the wear in wet grinding is up to 7 times higher than in dry processes due to an un-layered ball surface accompanied with corrosive wear. The amount of dislodged material from balls and the grinding chamber that is incorporated into the powder also depends on time and energy input of milling, stress intensity of milling as well as on the milling atmosphere. Most important for the relative ball wear is the overall energy input into the grinding chamber. The total amount of wear increases with milling time or energy input, respectively, so that the milling process should be carried out just for the required duration. In order to gather information about the influence of the process parameters on the wear, studies were carried out with steel balls in a planetary ball mill without using powder. With an excess number of balls the motion of balls inside the grinding chamber is interrupted and collisions with high enough impact energy to cause wear are emerging less frequent. In addition the contamination can be minimized by using the same material for the milling chamber and milling balls as the feed material so there will be no cross-contamination while the changing chemistry of the product powder still has to be considered. The assessment depends on whether high stress energies for size reduction are needed or the process depends on the total energy input. High stress
energies can be provided by large ball diameters or high ball densities and a high revolution speed [101].

There exists an optimum ball size at a given rotation speed that yields minimum particle size of powder. The optimum ball diameter decreases as the rotation speed increases. This result has been interpreted in light of the competition between the reduced kinetic energy of the smaller balls (a negative source for milling efficiency) and the increased number of contact points of the smaller balls (a positive source), which yields the optimum ball diameter at an intermediate size. As the rotation speed increases, kinetic energy of the balls increases, which, in turn, shifts the optimum ball size toward a smaller value. As the powder loading increases at a given rotation speed and ball size, the milling efficiency decreases monotonically [103]. In many cases high finenesses can be achieved only by wet milling. In dry milling processes an improved fineness of milling can be achieved by the addition of a few drops of stearic acid or acetic acid and use of milling balls with a diameter < 10 mm and a filling level of 70-80% of the milling cup volume [51].

Dry milling increases the particle size, whereas wet milling decreases the size. Wet milling reduces the average particle size by producing fragmented particles [104]. Figure 2-13 shows the particle size distribution after different dry ball mill durations. It can be seen that at milling times less than 10 h, increasing the dry ball mill time greatly reduced the amount of agglomerates. Prolonging the ball mill time did not show a significant effect on the particle size distribution after 10 h. From this study, it was learned that the agglomerates (with an average particle size of 10 mm) could not be completely eliminated, although the amount of the agglomerates could be significantly
reduced through the variation of the grinding techniques (by hand, dry ball mill and wet ball mill), or optimizing the grinding duration [105].

Figure 2-13 Particle size contribution after dry ball milling durations [105].

2.4 Porous structure

The performance of SOFCs strongly depends on the microstructure of the anode, such as the porosity and the pore size distribution, composition and distribution of the constituent phases, and the length of the three phase boundary (TPB). Hu et al. developed a composite pore-former containing flour and activated carbon to provide suitable porosity in the anode support and shrinkage matched well with that of YSZ electrolyte film [106]. The porous material are commonly classified into three groups
according to their pore sizes that are included the micro-porous (<2 nm), meso-porous (2-50 nm), and macro-porous (>50 nm) [107].

Methods for the production of porous ceramics are as following:

- Sintering the powders made up of different particle sizes

A porous structure can be formed by the spaces between the necked powders, and porosities between 40%–50% can be achieved by this method [108].

- In-situ polymerization

In-situ polymerization could generate interconnecting pore channels due to the homogenous distribution of the monomer in the green body, and the fabricated porous ceramics showed a significant improvement in gas permeability over ceramics fabricated using starch as the pore-former [109, 110].

- Leaching out the Ni.

Boaro et al prepared porous yttria-stabilized zirconia by nickel removal from Ni-YSZ using acid leaching [111].

- Using pyrolizable pore formers

Table 2-6 summarizes different pore-formers and fabrication methods used for the production of SOFCs. Mingyi et al. reported that the pores with diameter in the range of 5-10 nm were formed by the pore-formers, but the small pores with diameter less than 1.0 nm were formed by NiO reduction to Ni [22]. Talebi et al. observed that the pore size was 1-10 nm and about 4 nm in average for the Ni-YSZ composite prepared with 33 wt.% starch as pore-former, but no pore larger than 4 nm was observed in the composite prepared with 9 wt.% starch. They also reported that the number of macro pores in the anodes increased with the content of pore former [112]. Hu et al. reported that more
micro pores surrounded by the Ni and YSZ particles will be formed after the reduction of
NiO to Ni [113]. The Ni metal is capable of expanding into the pores, which lowers the
coefficient of thermal expansion (CTE) of the composite. The CTE was varied with the
content of pore-formers. It indicates that not only the pore size and porosity, but also the
interfaces between Ni and YSZ particles were affected by the pore-former [114].

<table>
<thead>
<tr>
<th>Pore-former</th>
<th>Fabrication Method</th>
<th>Amount</th>
<th>Porosity range (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>Uni-axial pressing</td>
<td>35-60 wt. %</td>
<td>20-65</td>
<td>[115]</td>
</tr>
<tr>
<td>Carbon balck</td>
<td>Tape casting</td>
<td>0-4.5 wt. %</td>
<td>24-33</td>
<td>[116]</td>
</tr>
<tr>
<td>PMMA</td>
<td>Extrusion</td>
<td>10-40 vol.%</td>
<td>36-51</td>
<td>[117]</td>
</tr>
<tr>
<td>Rice starch</td>
<td>Dry-pressing</td>
<td>10-30 wt. %</td>
<td>N.A</td>
<td>[118]</td>
</tr>
<tr>
<td>Potato starch</td>
<td>Uni-axial pressing</td>
<td>5-30 wt. %</td>
<td>14-58</td>
<td>[22]</td>
</tr>
<tr>
<td>Flour</td>
<td>Precipitation</td>
<td>10-30 wt. %</td>
<td>18-37</td>
<td>[119]</td>
</tr>
<tr>
<td>CMS*</td>
<td>Uni-axial pressing</td>
<td>1-5 wt.%</td>
<td>32-40</td>
<td>[120]</td>
</tr>
</tbody>
</table>

* PMMA: polymethyl methacrylate
** CMS: Carbon microspheres

The pore size can be controlled by varying the following variables: pore-former
size [121]; thermal decomposition/oxidation behavior of the pore-former [122]; volume
ratio of pore-former/ceramic particles [121, 123]; and sintering temperature. Experience
has shown that the process of inducing porosity by burning out the pore-formers is
difficult to control because the pore sizes in the sintered ceramic and the particle sizes of
the pore formers are not related in a simple manner [124]. Tang et al fabricated porous
ceramic materials with controlled pore size and porosity via a hetero-coagulation
template processing [123]. The modification of the oppositely charged polymer and
ceramic suspensions is the key for the fabrication of such closely packed structures with
high porosity and well-defined pore structure. Berson et al. showed that a relationship
exists between porosity and average pore size where average pore size increases linearly as porosity increases [125]. It is shown that decreasing the co-sintering temperature of the tubular cells from 1400 °C to 1250 °C led to the significant improvement of electrochemical performance of the cell due to the reduction of constituent particles size (Ni particle size below 100 nm) and the formation of a highly porous microstructure [56].

2.5 Wetting properties

The contact angle of a water drop placed on a smooth surface can characterize the degree of hydrophobic properties. This method cannot be applied for porous materials due to the distortion of the contact angle caused by the surface roughness. In addition, it cannot reflect the wetting properties of the internal surface of the porous material [126]. Considering the range of pore sizes present in the porous structure of a SOFC, the effect of the contact angle is minor [127]. Gorte et al. used \((\text{NH}_4)_2\text{Ce(NO}_3)_6\) in ethanol for the impregnation on one cell, and used \(\text{Ce(NO}_3)_3\) in water for the impregnation on another cell. The cell made using ethanol solvent exhibited a greater performance, with a maximum power density that was about 20% higher. Changing the morphology of ceria affects anode performance, but the mechanism of improvement is not clear yet [78].

2.6 Porosity

Bulk density is defined as the weight of the particle divided by the volume occupied by the entire particle. The following formulas (Archimedes relations) can be used to calculate open porosity \(P_o\), and bulk density \(D_b\) of composites. \(w_a, w_b\) and \(w_c\)
are weight of dry, weight of saturation and weight of immersed in distilled water (D water = 1 g cm\(^{-3}\)), respectively [112].

\[
\begin{align*}
P_o & = \frac{w_b - w_a}{w_b - w_c} \times 100 \\
D_b & = \frac{w_a}{w_b - w_c}
\end{align*}
\]

Theoretical density (skeletal density) is defined as the density of a single particle excluding the pores [128].

\[
D_{th} = \frac{D_{Ni} D_{3YSZ}}{wD_{3YSZ}+(1-w)D_{Ni}}
\]

, where \( w \) is the weight fraction of Ni:

\[
w = \frac{m_{Ni}}{m_{3YSZ}+m_{Ni}}
\]

Relative density is defined as the ratio of bulk density to theoretical density.

\[
D_r = \frac{D_b}{D_{th}}
\]

There are two types of pores: open pores and closed pores. The closed pores are ineffective, so should be decreased. Higher porosity may lower the closed pores; however, the strength and electrical conductivity would be decreased. The total porosity (summation of the open and the closed porosities) is related to the by relative density by [120]:

\[
P_t = 1 - D_r
\]

, where and \( P_t \) and \( D_r \) are the total porosity and relative density.

The following formula can be used to calculate closed porosity (\( P_c \)):

\[
P_c = P_t - P_o
\]
2.7 Sealant materials

Development of suitable sealant materials to separate the air and fuel compartments of the SOFC constitutes a challenging research area that could play a key role on the advancement of this technology into commercialization stage [129, 130]. Consequently, extensive efforts have been focused on the study of sealant materials exhibiting the necessary adherence, mechanical integrity, stability and compatibility with other fuel cell components [131, 132].

The majority of SOFC sealant materials can be classified as rigid or compressive seals [131]. Rigid seals such as ceramic cements, rigid glass, and glass-ceramics provide a gas tight environment by adhering (i.e. chemically bonding) to the surface of fuel cell housing and interconnect materials. The properties of rigid seals can be tailored by adjusting their chemical composition. However, these materials are inherently brittle and can undergo mechanical failure at high temperatures due to mismatch in the coefficient of thermal expansion (CTE) with respect to other cell components [133].

Compressive seals provide the advantage of accommodating the different thermal expansion between components, deforming under the applied load to provide a gas tight environment. Ductile metals such as gold or silver have been extensively studied as cathode and anode sealant materials due to their mechanical properties and their resistance to degradation by the formation of oxide scale [134, 135]. However, their cost, and long-term stability has limited their widespread use. Alternatively, research efforts have been focused on the use of lower cost mica seals [136].
3.1 Planar Fuel cell fabrication

Figure 3-1 shows the SEM of typical raw materials for the fuel cell fabrication. The starting materials of the anode support layer were composed of NiO (AEE Atlantic Engineers Equipment, USA), 3YSZ (TZ-3Y, Tosoh Co., Japan) or 8YSZ (TZ-8Y, Tosoh Co., Japan), SCZ(10% ScCeSZ, Daiichi, Japan), and microcrystalline cellulose (PH-301, Avicel, USA). The maximum particle size is estimated 55 µm for 3 YSZ, 50 µm for 8 YSZ, 65 µm for SCZ, and 15 µm for NiO.

Figure 3-1 SEM image of the raw material used in SOFC fabrication.
In the first step of fabrication, the materials were mixed with the solvents and dispersant, and ball-milled for 3 h. Secondly, the binder and plasticizers were added to the slip and ball-milled again for 20 h to produce the slip for tape casting. The slips were de-aired in vacuum prior to tape casting. Tape casting was performed using a Lab scale continuous tape caster (Lab Cast TC-71-LC, HED international), in which slip was casted onto a polyethylene carrier film (Mylar sheet).

The doctor blade uses a scraping blade to remove the excess slurry from a moving carrier. The carrier is usually a Mylar sheet that is a silicone coated polyethylene film. The doctor blade available in our lab is a rectangular-shaped tool 10 inches in length, 7.5 inches in width, and 4 inches in height. It is used for the manufacturing of planar SOFCs in our laboratory. The doctor blade has two cylindrical screws in order to adjust the thickness of the casted slurry. By adjusting the height of the blade, we can form a thin layer of slip with a favorable thickness for the manufacturing of thin ceramic sheets. The adjusting screws are graded by dividing the surface area of each screw. The surface area of each screw is divided to 25 grades using 25 vertical lines. Each vertical line is equal to 0.001 inch. In other words, each complete rotation of the screws is equal to 0.025 inch height for the blade.

The doctor blade is stationary while the Mylar sheet moves straightforwardly, powered by a variable speed drive. The tape cast is formed by moving the Mylar sheet under the doctor blade. The precision of the doctor blade allows the operator to control the thickness of the tape being cast. Three layers were casted one by one from electrolyte to anode support. The thickness of each layer was controlled by adjusting the height of “doctor blade”. Three tapes with different anode interlayer thicknesses were casted. The
tapes were dried at 25 °C for 48 h and cut into disc of 28 mm in diameter, and sintered at 1400 °C for 2 h. The thickness of anode support and electrolyte were 800 µm and 10 µm, and the thicknesses of anode interlayer in different cells were 12, 15 and 18 µm. A 25 µm LSM/YSZ cathode interlayer (60 wt % LSM, Heraeus CL86-8706A) and a 35 µm LSM cathode layer (Heraeus CL86-8706) with the active area of 0.25 cm² were screen printed and fired for 1 hr at 1150 °C. Figure 3-2 shows the flow chart of fabrication process for SOFCs.

![Flow chart of the fabrication process](image)

Figure 3-2 Flow chart of the fabrication process of SOFCs via tape casting anode-supported electrolyte via tape casting.
3.2 Tape casting of slips

Slips containing Yttria Stabilized Zirconia (YSZ, TZ-3Y Tosoh) or SCZ (10% Scandia Ceria Stabilized Zirconia, Daiichi Kigenso Kagaku Kogyo Co. Ltd.) and Nickel oxide (NiO, Atlantic Equipment Engineers) powders were prepared with the purpose of fabricating anode supported fuel cells. The composition of the slips was adjusted for the casting of the key components of the anode supported fuel cells: a pure SCZ electrolyte layer, a NiO-SCZ interlayer (60 wt% NiO), and a NiO-YSZ anode support layer (65 wt% NiO). The preparation of the slips involved: (i) dispersing the powders in a mixture of ternary solvents and dispersant, (ii) ball-milling the resulting mixture for 3 h at 60 rpm, (iii) adding a binder, plasticizer and additional mixture of solvents, and (iv) ball milling for 20 h. The slips were casted on a Mylar film connected to a variable speed drive and acting as the moving carrier film. The height of the doctor blade was fixed at 50, 75, and 3000 µm for electrolyte, interlayer and anode support layers, respectively.

3.2.1 SCZ electrolyte layer slip

The particle size of SCZ powder was reduced in a wet planetary ball mill using a mixture of binary solvents as wet milling agents. The electrolyte slip was prepared by loading the milling jar (125 ml, Retsch, Haan, Germany) with 60 g of SCZ powder (100-200 nm), 1.1 g of dispersant, 29.1 g of solvents and ball milling the mixture for 30 min at 200 rpm using 21 spherical grinding media (YSZ, 10 mm in diameter, inframat advanced materials), 1.8 g of plasticizer I, 2.3 g of plasticizer II, and 4.5 g of binder were added to the milling jar and the mixture was ball milled for 5.5 h at 200 rpm. Table 3-1 lists the composition of the electrolyte slip.
Table 3-1 Typical electrolyte slips composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>(wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>57.6</td>
</tr>
<tr>
<td>Solvent I</td>
<td>13.1</td>
</tr>
<tr>
<td>Solvent II</td>
<td>19.7</td>
</tr>
<tr>
<td>Dispersant</td>
<td>1.0</td>
</tr>
<tr>
<td>Plasticizer I</td>
<td>1.7</td>
</tr>
<tr>
<td>Plasticizer II</td>
<td>2.6</td>
</tr>
<tr>
<td>Binder</td>
<td>4.3</td>
</tr>
</tbody>
</table>

3.2.2 NiO-SCZ interlayer slips

Table 3-2 lists the composition of the interlayer slip. The interlayer slip containing nickel oxide and 8YSZ powders was prepared through the following steps:

1. Reducing the particle size by wet milling

The particle sizes of NiO and 8YSZ powders were reduced via a wet planetary ball milling process. The 125 ml milling jar (125 ml, Retsch, Haan, Germany) was loaded with 47.18 g of NiO (< 44 µm), 27.82 g of SCZ (100-200 nm), 0.75 g of dispersant, and 30 g of a wet milling agent. The mixture was ball milled for 2 hr at 400 rpm using 21 spherical grinding media (YSZ, 10 mm in diameter, inframat advanced materials).

2. Dry milling of the powder

The wet milled powder was dried at 140ºC for 5 hr. The agglomerates obtained were broken using a spatula, and a dry planetary ball milling process was performed for 1 h at 400 rpm using 21 spherical grinding media (YSZ, 10 mm in diameter, Inframat advanced materials).

3. Dispersing the powder with tape casting additives in binary solvents system

The dry milled powders were dispersed in a 250 ml LDPE bottle containing solvent I, solvent II, binder, pore former and dispersant using cylindrical grinding media
(3YSZ, 10 mm long, inframat advanced materials). The grinding media filled about one-third of the LDPE bottle. The slip was prepared by mixing the above materials for 24 h at 60 rpm.

Table 3-2 Typical NiO-YSZ interlayer slips composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>(wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>23.2</td>
</tr>
<tr>
<td>NiO</td>
<td>34.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>13.8</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone (MEK)</td>
<td>19</td>
</tr>
<tr>
<td>Dispersant</td>
<td>1.2</td>
</tr>
<tr>
<td>Plasticizer I</td>
<td>1.8</td>
</tr>
<tr>
<td>Plasticizer II</td>
<td>2.7</td>
</tr>
<tr>
<td>Binder</td>
<td>3.5</td>
</tr>
</tbody>
</table>

3.2.3 NiO-YSZ anode support layer slip

Table 3-3 lists the composition of the anode support slip. The slip was prepared via the following steps: the nickel oxide and 3 mol% Y$_2$O$_3$ stabilized ZrO$_2$ (3YSZ, Tosoh) powders were dispersed in ternary solvents system using dispersant. The mixture was ball milled for 3 h at 60 rpm with cylindrical grinding media (10 mm long, inframat advanced materials) in a 1000 ml LDPE bottle using a horizontal rotary ball mill. The slip was prepared by adding the binder, pore former and plasticizer to the above mixture after 3 h, and ball milling the materials for 24 h. The microcrystalline cellulose was used as the pore-former, which burned out during the firing process, increasing the porosity of the anode support without the formation of ash residues.
Table 3-3 Typical formulation for the NiO-YSZ anode support slips.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>19</td>
</tr>
<tr>
<td>NiO</td>
<td>35.4</td>
</tr>
<tr>
<td>Pore former</td>
<td>6.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11.8</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone (MEK)</td>
<td>17.8</td>
</tr>
<tr>
<td>Dispersant</td>
<td>1.2</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>4.1</td>
</tr>
<tr>
<td>Binder</td>
<td>4.6</td>
</tr>
</tbody>
</table>

3.2.4 De-airing of slips

The slip consisting of powder, solvents and organics must be de-aired before casting. De-airing under a mechanical vacuum is inevitable to prevent the formation of air bubbles during the casting. A mechanical vacuum pump and a vacuum chamber was used to perform the de-airing on a stir plate. Figure 3-3 shows the de-airing setup including a vacuum pump, a vacuum chamber, and a stir plate.

Figure 3-3 De-airing setup to remove the extra solvent of slips.
3.2.5 Fuel cell co-firing

The fuel cell discs obtained after cutting the dried tape cast by laser were fired in a high temperature furnace. The discs were heated to 450 °C at a heating rate of 0.1 °C /min, and were kept at 450 °C for 4 h in order to remove the organic components. Then the discs were heated to 1000 °C at a heating rate of 1 °C/min, kept at 1000 °C for 4 h, and heated to 1400 °C at a heating rate of 2 °C /min, and were kept at 1400 °C for 2 h in order to achieve electrolyte densification.

3.2.6 Fuel cell screen printing

A 25 μm LSM/YSZ cathode interlayer (70 wt % LSM, Heraeus CL86-8706B) and a 35 μm LSM cathode layer (Heraeus CL86-8706) with the active area of 1 cm² were incorporated to the densified electrolyte of the solid oxide fuel cell discs by the screen printing technique, and fired for 2 h at 1150 °C.

3.2.7 Sinter plates fabrication

YSZ sinter plates were fabricated by tape casting and lamination of high purity YSZ powders. YSZ tapes were prepared by casting viscous slips containing YSZ powders (Tosoh and Unitec Ceramics), polyester-polyamine copolymer dispersant (hypermer KD1, Uniqema), polyvinyl butyral binders (Butvar B-76, and B-98, Solutia), benzyl n-butyl phthalate plasticizer (S-160, 98% Alfa Aesar), polyethylene glycol plasticizer (PEG-200, Sigma Aldrich) and organic solvents including absolute ethanol (Pharmco Aaper), and methyl ethyl ketone (MEK, Fisher Scientific). Table 3-3 lists the composition of the sinter plates slips. The slips were de-aired, casted using a doctor blade assembly (6 inch wide, 1000 μm casting thickness), dried at room temperature, and

47
laminated (to increase the sinter plate thickness) as it is shown in Figure 3-4. Figure 3-5 shows that the laminated sinter plates were cut by a laser cutter before firing. Figure 3-6 shows the sinter plates fired at 1400 °C for 2 h.

Table 3-4 Typical formulation for a sinter plate tape casting slip.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>48.5</td>
</tr>
<tr>
<td>Pore former</td>
<td>7.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11.7</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone (MEK)</td>
<td>17.5</td>
</tr>
<tr>
<td>Dispersant</td>
<td>1.9</td>
</tr>
<tr>
<td>Plasticizer I</td>
<td>6.6</td>
</tr>
<tr>
<td>Binder</td>
<td>6.1</td>
</tr>
</tbody>
</table>
Figure 3-4 (a) vacuum chamber used for the de-airing of slips; (b) pouring of solution/doctor blade set up; (c) casted slip; (d) pinned layers; (e) spraying gun deposition of ethanol/α-terpineol; (f) tape before lamination; (g) laminating the tape; (h) pressing of the tape.
Figure 3-5 (a) Outside of laser cutter; (b) inside of laser cutter after completion of circular sinter plate cutting; (c) scraps; (d) circular and rectangular sinter plates after laser cutting.

Figure 3-6 Sinter plates after firing.
3.2.8 Fuel cell testing and characterization

The SOFCs were sealed to the iron based tube (ID=3.5 cm and H=25 cm) serving as fuel cell housing and anode current collector via Al$_2$O$_3$ based ceramic seal. A silver strip was attached to SOFC cathodes to serve as the cathode current collector. The experimental apparatus included a gas manifold with flow controllers (5850E, Brooks), high temperature furnace, cell test unit with impedance spectrometer (Solartron 1470E CellTest System). The cells were heated to 750 °C with heating rate of 3 °C/min and reduced in He/H$_2$ stream (100 sccm, 50 mol% H$_2$). Figure 3-7 shows the experimental apparatus. The SEM images and EDX mappings of the samples were taken by scanning electron microscopy (SEM, TM-3000 Hitachi, Tokyo, Japan) and energy-dispersive X-ray (EDX, Bruker, Ewing, NJ, USA). The crystalline structure of the samples were analyzed by X-ray diffractometer (XRD) using a Philips APD 3700 diffractometer equipped with Cu Kα (wavelength 1.5406 Å).

![Experimental apparatus for the fuel cell testing.](image)
3.3 Strategy of Experimentation

Figure 3-8, 3-9, 3-10, 3-11, and 3-12 illustrate the strategy of experimentation to optimize the (i) anode support, (ii) anode interlayer, (iii) electrolyte, and (iv) cathode of SOFCs. The strategy of experimentation involves identifying primary factors and the region of interest for the primary factors, conducting the experiment, analyzing and confirming the results.

Figure 3-8 Compositional and structural study of the SOFCs.
Figure 3-9 Experimental plan for the improvement of anode support.
Figure 3-10 Experimental plan for the improvement of anode interlayer.
Figure 3-11 Experimental plan for the improvement of electrolyte.
Figure 3-12 Experimental plan for the improvement of cathode interlayer and cathode current collection layer.
CHAPTER IV
DEVELOPMENT OF CO-TAPE CASTING AND CO-FIRING

4.1 Introduction

Fabrication of planar solid oxide fuel cells requires generating multilayer ceramics that comprise a dense electrolyte layer, a porous anode, and cathode electrode. Each of the layers of an SOFC must be thermally, chemically, and mechanically stable at the operating conditions. An interlayer is required to improve the interface between the main layers. The anode supported SOFCs performance improved by employing a thin anode interlayer due to increased electrochemical reaction zones or three-phase boundaries as well as intimate contact between the anode and electrolyte [25-30]. Such multilayer substrates can be produced by several ceramic processing techniques including screen printing, dip-coating, spin coating, spraying, and tape casting [137].

Tape-casting, a process to fabricate the thin (10 µm up to 1000 µm) flat layers of SOFCs, possesses the following attractive features [69]: (i) forming reproducible layers with uniform thickness and structure; (ii) controlling the thickness of anode and electrolyte; (iii) casting multilayer tapes in one batch; and (iv) mass production, if automated. The disadvantage of this process is the limitation in the thickness of the layer. Figure 4-1 illustrates the basic principle of the tape casting technique. Casting electrolyte and anode within one batch is called co-tape casting, and sintering electrolyte and anode within one step is called co-sintering.
Figure 4-1 principle of the tape casting technique, in which the raw materials (i.e., ceramic oxide powders) are loaded in the reservoir of a doctor blade in the form of organic slip, and are casted on either a moving or a stationary carrier film.

Owing to the large number of variables affecting the quality of the tapes, and the stringent requirements of fuel cell components, implementing a tape casting process for fuel cell fabrication involves performing a large number of experimental runs. Tape-cast thickness can be controlled by a combination of slip viscosity, doctor blade gap and casting speed [138]. Porous ceramics can be prepared through the use of pyrolyzable pore-formers. The anode support porous microstructure should provide the appropriate levels of porosity to exhibit desirable mechanical strength, electrochemical properties, thermal conductivity and polarization resistance [22-24, 139].

Implementing the co-tape casting and co-sintering of the SOFC components consisting of highly porous and fully dense microstructures is complicated. Different adjacent layers undergo high processing temperatures, and high thermal stresses would be generated because of the different thermal expansion coefficients of the layers. It may lead to crack formation that can be minimized by closely matching the coefficient of thermal expansion (CTE) for the composite materials. The stress caused by shrinking and CTE mismatch may produce cracks in the electrolyte film [140].
The successful development of co-tape casting process requires fine tuning the composition of slips with the adequate amounts of additives such as dispersants, plasticizers and organic binders to cast homogeneous tapes free from defects (i.e., pinholes, and cracks). In addition, the exact controlling of drying profiles is required to prevent tape flaws formation. Co-sintering must occur at a slow rate at low temperatures to evacuate the combustion gases through the porosity that the combustion has just created. Increasing the temperature at a high rate decreases the porosity that can result in the accumulation of combustion gases and increasing the gas pressure inside the layers leading to crack formation. The present study has focused on the fabrication of the tri-layers components of solid oxide fuel cells by co-tape casting and co-firing techniques, screen printing of the cathode, and the problems encountered in the manufacturing steps.

4.2 Casting of the slips

Powders of NiO (Novamet, USA), and 3YSZ (TZ-3Y, Tosoh Co., Japan) were used to obtain anode support slip. Powders of NiO (Novamet, USA), and 8YSZ (TZ-8Y, Tosoh Co., Japan) were used to prepare anode interlayer slip, and 8YSZ (TZ-8Y, Tosoh Co., Japan) was used to obtain electrolyte slip. The slips were ball milled using a horizontal rotary ball mill (Warehouse, USA) with zirconia 5-mm grinding media from Tosoh Europe. The slips consisting of powder, solvents and organics were sieved to remove the grinding media and were de-aired at 30 inHg for 20 min before casting. De-airing under a mechanical vacuum is necessary to prevent the formation of air bubbles during the casting. Lab scale tape caster Procast TC-71-LC (HED international, NJ, USA) was used for the tape-casting experiments. Slips were cast on a silicone coated
Mylar, 12 inch wide x 0.003 inch thick as a carrier: The casting speed was kept constant at 9 mm/s for the electrolyte and the anode interlayer, but the casting speed was decreased to 1.5 mm/s for anode support. Preparation of the electrolyte/anode half-cell includes the tape casting of three layers: (a) the electrolyte; (b) the anode interlayer; (c) the anode support layer. They are cast one by one from electrolyte to anode support successively after 20 minutes. The thickness of each layer can be controlled by adjusting the height of doctor blade. Tape casters often incorporate a drying chamber with adjustable speed career drive, airflow, air heaters, and under-bed heaters that facilitate setting up the desired temperature profile in the machine. The tape-cast was dried in the drying chamber of the tape-casting machine under controlled conditions for 48 h before being cut into disks.

4.3 Cell fabrication

The multilayer disks obtained after cutting the dried tape-cast by laser were sintered in a high temperature furnace. The temperature was increased to 450 °C at a rate of 0.1 °C/min, followed by a dwelling step of 4 h to remove the organic components introduced during the slip preparation. Then, the temperature was increased to 1000 °C at a rate of 1 °C/min and hold for 4 h to crystallize YSZ. Finally, the furnace was heated up at a rate of 5 °C/min to 1400 °C and hold for 2 h for grain growth and achieving dense electrolyte. The furnace was cooled down to room temperature at 10 °C/min after the sintering. A 25 μm LSM/YSZ cathode interlayer (60 wt % LSM, Heraeus CL86-8706A) and a 15 μm LSM current collecting layer (Heraeus CL86-8706) were fabricated by screen-printing and fired for 1 h at 1150 °C.
4.4 Results and Discussion

Figure 4-2 shows the different steps of anode supported SOFC fabrication including tape casting, calcinations, and cathode sintering. Figure 4-3 shows the variables and affected parameters of tape casting. Rheological behavior of the tape-cast slip highly depends on solid loading and ambient temperature. Due to changes in ambient temperature and relative humidity, it is possible that some error be introduced to the system and make batch-to-batch variation. It is important to make sure that carrier speed, ambient temperature, doctor blade gap, and de-aring time is fixed for all batches to prevent batch-to-batch variation. The most important step in the fabrication of SOFCs by co-tape casting and co-sintering techniques is slip development because without a proper slip formulation multi-layered half cells would crack during the drying or sintering of the tape. In addition, slip formulation determines the performance of the SOFCs. In our experience, slip development can be best achieved by using a base formulation comprising the basic slip components including NiO, yttria-stabilized zirconia, dispersant, binder, plasticizer, pore-former (if needed) and a solvent system, and adjusting the tape casting conditions.
Figure 4-2 Processing steps used to produce SOFCs.

The slip composition, i.e., the type of additives used in the slip and their relative concentration, have a direct impact on the physical properties such as viscosity and density that in turn control the casting of homogeneous tapes free from defects (i.e., pinholes, and cracks). Therefore, the development of slips for tape casting involves the preparing slips with adequate amounts of additives such as dispersants, plasticizers and organic binders to achieve a homogeneous tape-cast with favorite microstructure, and to reach a reproducible fabrication process. The slip has to be adjusted for tape casting, drying, cutting, compression between sinter plates, pyrolysis of organic components and sintering. Powder characteristics including surface area, particle density, and surface moisture content are the most important parameters in determining the amount of components that is required for the preparation of a slip. The surface area determines the solids loading and organic content. Higher surface area particles need more organic
additives to disperse and bind. The surface area of the powders used for tape casting is usually between 5-10 m²/g [69].

An azeotropic mixture of methyl ethyl ketone (MEK) and ethanol (EtOH) (40/60 vol%) that combines the dissolving capabilities of both solvents and evaporates as a single liquid during the drying process was used as a binary solvent system. The solvent quantity needs to be precisely adjusted to achieve a good dispersion of the powders. A high solid loading leads to limited dissolution of the binder and high viscosity slip that cannot be casted as a flawless tape, but a low solid loading leads to low viscosity slip that flows under the gap of doctor blade very fast without thickness adjustment.

A dispersant or deflocculant is a surfactant (literally SURFace ACTive AgeNT) that modifies the surface properties of the powder by steric repulsion (organic solvent) or ionic repulsion (aqueous solvent). Hypermer KD1 (Imperial Chemical Industries PLC, England) was used as dispersant to obtain a stable solution of well-dispersed particles in the solvent system that leads to a homogeneous microstructure. The KD1 is a polyester/polyamine condensation polymer with a high molecular weight, which has an estimated MW of about 10000 g/mol. It is composed of anchoring groups that absorb onto the particle surface tightly, and a polymeric chain with a chemical structure designed to give optimum steric stabilization to the dispersion [141]. Binder has to be added to increase the strength of the dried tape-cast for further processing. The binder used is polyvinyl butyral (PVB), which is the most commonly used binder in the tape casting field. The PVB has a burnout temperature range from 350 °C to 450 °C [142]. A higher content of binder results in a tape-cast with lower flexibility. Thus, plasticizer is required to make the tape-cast more plastic or bendable. A mixture of the two types of
plasticizer was used in the slip recipe. Type I plasticizers (e.g. n-butyl phthalate) soften the binder polymer chains and lower the glass transition temperature of the binder, but type II plasticizers (e.g. poly ethylene glycol) work as internal lubricant in the dried tape-cast and can prevent cracking by promoting plastic deformation. [69].

Figure 4-3 Co-tape casting process and co-sintering of multilayer’s variables and affected parameters.
The preparation of slips for tape casting was a two-step ball-milling process. In the first step, all the powders were homogeneously dispersed in ethanol/MEK solvent, with KD1 as the dispersant. Secondly, polyvinyl butyral (PVB) was added as binder, and a mixture of polyethylene glycol (PEG) and n-butyl phthalate was added as plasticizer to adjust the viscosity of the slip. Homogenization of low-viscosity slip (i.e. without binder and plasticizers) to obtain well-dispersed particles in the solvent system is more efficient than that of a high-viscosity slip. Moreover, simultaneous addition of the binder and dispersant prevents the adsorption of dispersant on the surface of particles. Thus, the sequence of components addition is critical. In other words, the dispersant must be added before the binder to prevent the competitive adsorption and maximize the effectiveness of the dispersant [143]. Table 2 summarizes common flaws occurred during the slip development experiments along with possible causes and solutions. The most effective solution to avoid cracking is increasing the binder content, but an extra amounts of binder resulted in very high slip viscosity, ineffective de-airing, and formation of the pinholes in the tape-cast. Solid loading of the de-aired slip will lead to the control of a 1-2 μm size interconnected porosity that can be extremely useful for increasing the length of triple phase boundaries [144].

4.5 Structural flaws

The developed stresses during solvent removal can cause different defects in the tape. In a drying tape, the lower layer is bounded laterally to the carrier film. Exterior unbounded top layer shrinks more than the carrier-bounded interior layer, which results in edge curling. Regardless of the surface shrinkage allowed by curling, some of the
stresses will be stored in the tape polymer matrix. The amount of stress that can be stored in the polymer matrix depends on the polymer type, polymer content, and effect of the type I plasticizer. Type I plasticizer increases the reversible strain and affect the amount of energy that can be stored in the tape matrix. The lateral shrinkage in drying tape is accommodated by the combination of stored energy in the matrix, edge curling, and plastic deformation. If the lateral shrinkage exceeds what can be tolerated, the excess stress will be alleviated in different ways. The tape will disengages itself from the carrier surface, freeing the bottom from constrain and allowing the bottom to shrink, if the tape adhesion to the carrier (substrate) is less than the particle-to-particle compression forces.

In the case that the adhesion to the carrier is stronger than the inter-particular adhesion forces, the tape will crack and separate itself from carrier to relieve the tensile stress. If both the inter-particular adhesion forces and adhesion to the carrier are high, the tape will continue to curl. The addition of type II plasticizer can increase the level of stress storage and avoid cracking by promoting plastic deformation. Increasing the binder content is the most effective solution to avoid cracking. Additional binder increases not only the inter-particulate adhesion but also the level of plastic deformation and stress storage in the polymer matrix [69].

Improving the slip de-airing procedure enhanced the survival rate of co-fired multilayer tapes [145]. The effect of de-airing on anode support tape was studied for 5 min and 10 min de-airing duration. The de-airing of anode support was performed at 30 mmHg in a vacuum chamber, while the anode support slip was stirred at 30 rpm with magnetic stirrer. Figure 4-4 shows the photograph of anode support tapes with 5 and 10 min de-airing process. Small dents are observed in anode support tape with 5 min de-
airing duration (Figure 4-4 (a)). Small dents created by air bubbles can lead to “crow’s foot” cracking (cracks that originate from a dent) upon drying, as shown in Figure 4-5. Table 4-1 summarizes common flaws originated from improper stress relief in the drying tape cast films along with possible causes and solutions. Table 4-2 lists the structural flaws of fired cells and troubleshooting.

Figure 4-4  Anode support tapes with (a) 5 and (b) 10 min de-airing duration at 30 mmHg.

Figure 4-5 Dry anode support tape with crow’s foot cracks on it.
During the cooling process the compressive stresses generated by thermal mismatch may cause de-lamination of layers. An example of blister de-lamination occurred during the fabrication process at the interlayer-electrolyte interfaces is shown in Table 4-2. The surface of interlayer can be seen because the electrolyte layer is very thin (~20 µm), and it is damaged due to de-lamination. Figure 4-6 shows the dried tape-cast, called green tape. Figure 4-7 shows the fabricated screen printed SOFCs with different sizes.

Table 4-1 Variety of defects and cracks observed in dry tape-casts.

<table>
<thead>
<tr>
<th>Flaw</th>
<th>Shape</th>
<th>Potential causes</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holes in electrolyte</td>
<td>![Holes in Electrolyte]</td>
<td>De-aired slip was not in equilibrium with the atmospheric pressure</td>
<td>Waiting enough after de-airing of slip to reach equilibrium with atmospheric pressure.</td>
</tr>
<tr>
<td>Small dents in anode support</td>
<td>![Small Dents in Anode Support]</td>
<td>High viscosity slip due to high solid loading</td>
<td>Decreasing the solid loading.</td>
</tr>
<tr>
<td>Center cracking</td>
<td>![Center Cracking]</td>
<td>Particle-to-particle adhesion lower than carrier adhesion</td>
<td>Slowing down the drying rate</td>
</tr>
<tr>
<td>Crow’s foot cracking</td>
<td>![Crow’s Foot Cracking]</td>
<td>Low binder content</td>
<td>Increasing the binder content</td>
</tr>
<tr>
<td>Lateral sheeting</td>
<td>![Lateral Sheetling]</td>
<td>Reorientation of forces along casting direction into the cross-cast direction</td>
<td>Increasing the binder content</td>
</tr>
</tbody>
</table>
Table 4-2 Tape casting problems and troubleshooting.

<table>
<thead>
<tr>
<th>Flaw</th>
<th>Solution</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blister delamination</td>
<td>Casting the interlayer after complete drying of the electrolyte will impede the formation of blister delamination at the interlayer-electrolyte interface</td>
<td></td>
</tr>
<tr>
<td>Orange crusted electrolyte</td>
<td>Casting the anode interlayer and anode support must be carried out successively after drying the interlayer. Otherwise, a pattern that resembles to orange crust will be formed on the electrolyte.</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4-6 flexible, leather-like sheet, called green tape is produced after the drying of tape-cast.

Figure 4-7 Anode-supported SOFCs with different sizes fabricated via co-tape casting, co-sintering, and screen printing.
4.6 Sinter plates

The elevated fuel cell sintering temperatures that ensure the formation of high strength sintered NiO-YSZ anodes and fully densified electrolytes impose stringent requirements for those materials serving as fuel cell sinter plates for sandwiching the tape-cast during the sintering. Sinter plates have to possess high chemical resistance to the fuel cell materials (i.e., chemical inertness at the firing temperature under highly oxidizing environments), high porosity to allow the removal of processing additives during sintering, rigidity to avoid warping and deformation at high temperature, and low thermal mass to reduce power consumption during firing cycle [144].

The driving force for the observed anisotropic shrinkage is densification or the disappearance of porosity. The planar shrinkage of tape-cast during co-sintering was about 15%, and the shrinkage in the thickness of tape-cast was about 25%. If the tape-cast sandwiched between sinter plates topped by a substrate to maintain the flatness, then the deformation transforms into stresses. The weight of substrate has to be fine tuned to allow the planar deformation to occur, and to prevent the vertical deformation [144]. The deformation of planar cell has a detrimental effect on current collection and leads to decrease the contact area between the interconnect and adjacent electrode [146].

Compressive sintering is a method that can release the internal stress during co-firing and can lead to the fabrication of flat planar SOFCs [147]. Compressive sintering is using enough loads on the green tape sandwiched between two sinter plates, and used to prevent shape distortion or warping during co-firing. Figure 4-8 shows the Schematic of the fuel cells arrangement for compressive sintering. High organic content (i.e.
dispersant, plasticizers, organic pore-former, and binder) results in the sticking of fuel cells to the sinter plates during sintering operation as shown in Figure 4-9.

Figure 4-8 Schematic of the fuel cells arrangement on the sinter plates for compressive sintering.

Figure 4-9 Sticking of fuel cells to the sinter plates during the firing.
4.7 Co-firing

The co-firing temperature depends on the sintering temperature or densifying temperature of the zirconia-based electrolyte, which is over 1300 °C [148, 149], but the unfavorable reaction between LSM cathode and electrolyte occurs about 1200 °C [150]. Thus, the cathode was screen printed and sintered after the co-firing of half cells including electrolyte, anode interlayer, and anode support. Co-firing of the half cells is one of the critical issues in the fabrication of the SOFCs because during the co-firing of half cells due to the different shrinkage rate and CTE of the layers many flaws and defects such as cracks, de-lamination, and warpage can occur during the sintering [151].

Fabrication of a multilayered ceramic or solid oxide fuel cell (SOFC) by co-tape casting technique requires the matching of different layers shrinkage to prevent cracking and de-lamination due to possible stress induced by the co-firing process. The higher shrinkage rate of the electrolyte than that of the anode support, results in a cracked electrolyte, and the lower shrinkage rate of the electrolyte than that of the anode support, results in de-lamination of layers. Shrinkage and cracking that occurs during the reduction of the SOFCs make the fabrication process further complicated. The oxygen gas generated during the reduction of the SOFCs must be capable of diffusing out from the structure, leaving a porous and partially bonded substrate. As oxygen vacancies are consolidated the structure begins to shrink, but the metal is constrained from shrinking by the ceramic. Thus, the reduction process can lead to crack the SOFCs.
The slow sintering of the SOFC to 450 °C (0.1 °C/min) completely removes the organic materials without cracking of the fuel cell. The high sintering temperature of the anode needs to form the percolation paths that make possible the densification and neck formation between particles [152]. A low sintering rate would suppress the cracking of the cells because the combustion gases can be evacuated through still highly open porosity just created by sintering, and the gas pressure inside the layers will not be increased. The sintering of YSZ or ScCeSZ is a two-step process including the crystallization at low temperature (about 800 °C –1000 °C), and the grain growth at high temperature (more than 1100°C) [153].

There are two conflicting effects for the sintering temperature: a relatively low sintering temperature for the anode prevents the particles from agglomeration and results in obtaining large three phase boundaries, but to obtain a dense electrolyte a high sintering temperature is required. Polyvinyl Butyral (PVB), a polymer with large molecular weight, is used to build the network in the electrolyte. PVB would be burnt at high temperature that results in many pores. Thus, the fuel cells are sintered at different temperatures to achieve optimum processing conditions. A two cycle co-firing process, with pre-sintering and co-sintering, is used.

The pre-sintering process is conducted to evaporate solvents and burn-out binder. The pre-sintering process is designed to require 55 h to reach 450 °C, at a rate of 0.1 °C min⁻¹. After finishing the burn-out process at 450 °C, the final pre-sintering process is carried out until the processing temperature reached 1000 °C. Then the cells were cooled down and the second co-sintering cycle started. The second cycle is conducted at 1400
°C using a temperature ramp rate of approximately 2.9 °C min⁻¹. The whole fabrication process especially co-firing is time consuming. Thus, a one cycle co-firing process, with pre-sintering and co-sintering, is designed. The pre-sintering process is designed to require 24 h to reach 450 °C, at a rate of 0.23 °C min⁻¹. The final pre-sintering process is carried out until the processing temperature reached 1000 °C, and the co-sintering process is performed at 1400 °C. The two cycle co-firing and the one cycle co-firing were compared. As mentioned above, the two cycle co-firing is including the sintering of half cells at low temperature (i.e. 1000 °C), and cooling down the half cells. Then, the pre-sintered half cells were co-sintered at different temperatures ranging from 1300 °C to 1550 °C to figure out the appropriate co-sintering temperature for the densification of the electrolyte.

Figure 4-10 shows the microstructure of the electrolyte surfaces that were sintered at a two cycle co-firing process with different co-sintering temperatures at the range of 1300 °C to 1500 °C. As can be seen, the density of electrolyte increased gradually when the sintering temperature increased. The electrolyte was porous after sintering at the range of 1300 °C to 1500 °C and quite dense at 1550 °C. A half cell heated to 1400 °C in one co-firing cycle to compare the impact of heating cycle on the electrolyte densification. Figure 4-11 shows that the electrolyte sintered in one sintering cycle was quite dense after sintering, but the electrolyte sintered in two sintering cycles was very porous after sintering at 1400 °C.
Figure 4-10 Microstructure of electrolyte sintered at two step co-firing cycle pre-sintered at 1000 °C, and co-sintered at different temperatures ranging from 1300 °C to 1550 °C: surface morphology: (a):1300 °C, (b):1400 °C, (c): 1500 °C, and (d): 1550 °C.

Figure 4-11 Microstructure of electrolyte surface morphology co-fired at (a) one step co-firing cycle at 1400 °C; (b): two step co-firing cycle at1400 °C.
Figure 4-12 shows the X-ray diffraction patterns of ScCeSZ samples. All the diffractions seem to be characteristics of the cubic structure. The samples also analyzed by Raman spectroscopy that allows for a better identification of the structural phases in zirconia matrices. Figure 4-13 shows Raman spectra of the ScCeSZ samples. The Raman spectrum of cubic zirconia displays a single band at ~620 cm\(^{-1}\). As can be seen, an additional band at ~485 cm\(^{-1}\) reveals the presence of the tetragonal phase in these samples. The Raman band at approximately 700 cm\(^{-1}\) was detected in scandia-stabilized zirconia with tetragonal symmetry, and was attributed to some type of disorder due to formation of the solid solution and consequent generation of oxygen vacancies.
4.8 Fuel cell performance reproducibility analysis

The reproducibility of fuel cell electric current output was tested on the fuel cell batch number 120120. The fuel cells of batch No. 120120 comprise a Ni/YSZ (Yttria Stabilized Zirconia) anode support (65 wt% Ni), a Ni/YSZ/SCZ anode interlayer (63/18.5/18.5 wt %), a SCZ electrolyte, a YSZ/LSM cathode layer (40/60 wt %), and a pure LSM cathode current collector layer. Tape casted slips were cut into circular cells with 15 mm diameter. The fuel cell diameter decreases to 12.5 mm after shrinkage during co-firing. Fabricated fuel cells of batch No. 120120 are shown in Figure 4-14.

Figure 4-13 Raman spectra of the ScCeSZ fuel cells co-fired in on cycle and two cycles.
Table 4-3 shows the performance and testing condition of 28 fuel cells from batch No. 120120. The maximum current density and OCV of the fuel cells in Table 4-3 were categorized into high performance, i.e., producing maximum current density higher than 400 mA/cm$^2$ and OCV higher than 900 mV, and low performance fuel cells, which do not meet the criteria. Figure 4-15 shows 75% of the fuel cells meet the criteria of high performance fuel cell. Analysis of the low performance fuel cells reveals that 93% of these fuel cells produced OCV higher than 900 mV, indicating high reproducibility of the catalytic activity on the electrodes. These results highlight the reproducibility of the fabrication and testing procedure.
Table 4-3 Performance data of the fuel cells batch No. 120120 at 750 °C in H₂/He (100 sccm, 50 vol% H₂).

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Cathode current collector</th>
<th>Leak</th>
<th>OCV (mV)</th>
<th>Max. I (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sealed</td>
<td>Ag strip</td>
<td>-</td>
<td>1000</td>
<td>560</td>
</tr>
<tr>
<td>Sealed</td>
<td>Ag strip</td>
<td>-</td>
<td>550*</td>
<td>740</td>
</tr>
<tr>
<td>Sealed**</td>
<td>Ag coated FeCr</td>
<td>12%</td>
<td>3000</td>
<td>400</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>973</td>
<td>974</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>920</td>
<td>716</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>946</td>
<td>412</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>991</td>
<td>318*</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>997</td>
<td>576</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>1010</td>
<td>544</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>994</td>
<td>370*</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>992</td>
<td>830</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>954</td>
<td>1110</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>737*</td>
<td>1528</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag strip</td>
<td>-</td>
<td>965</td>
<td>1342</td>
</tr>
<tr>
<td>Sealed**</td>
<td>Ag coated FeCr</td>
<td>32%</td>
<td>3000</td>
<td>500</td>
</tr>
<tr>
<td>Sealed**</td>
<td>Ag coated FeCr</td>
<td>-</td>
<td>3070</td>
<td>960</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag coated FeCr</td>
<td>-</td>
<td>960</td>
<td>240*</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag coated FeCr</td>
<td>-</td>
<td>958</td>
<td>156*</td>
</tr>
<tr>
<td>Seal-less</td>
<td>Ag coated FeCr</td>
<td>-</td>
<td>965</td>
<td>365*</td>
</tr>
<tr>
<td>Sealed**</td>
<td>Ag coated FeCr</td>
<td>-</td>
<td>2645</td>
<td>495</td>
</tr>
</tbody>
</table>

* indicating low performance fuel cells.
** indicating 3 Cells in Series.

Figure 4-15 Pie chart for the acceptable, and non-acceptable cells of batch No. 120120.
Figure 4-16 shows the cross-sectional SEM micrograph of the tested anode supported SOFC. The multilayer structure of the fuel cell consisting of anode support, anode functional layer, electrolyte, cathode interlayer, and cathode current collection layer is visible. The anode is comprised of two distinguishable layers including a dense anode interlayer with fine particles adjacent to the electrolyte layer and a porous anode support with coarse particles. The porous structure of the anode support was formed by burning out the pore-former and could help to facilitate gas diffusion. The porosity of anode support and anode interlayer after reduction was determined to be 49% and 26% using Archimedes method.

![Cross-sectional SEM micrograph of the fuel cell with 15 µm thick interlayer.](image)
4.9 Scraps recycling

Low-quality casted tapes and scraps were cut, grinded, and mixed with proper amounts of the solvents for recycling. Figure 4-17 shows the flow chart for the recycling of scraps from tape casting. The recycling materials include scraps shown in Fig. 4-18,a and low quality casted tapes in Figure 4-18,b. Using a cutter (Figure 4-18, c), scraps and previously casted unusable low quality casted tapes were cut into small pieces (Figure 4-18, d). These small pieces were loaded into a tape grinder (Figure 3-18, e) and ground for 3 minutes (Figure 4-18, f). The specific amount of uniformly ground scraps (Figure 4-18, g) and solvents including ethanol, acetone, and amylacetate, following the recipe in Table 4-5, were added into a bottle filled one-third full with grinding media. The prepared mixture was placed on the rotary ball mill (Fig. 4-18, h) for twenty-four hours to make a homogeneous slip that can be casted after de-airing as a fresh anode support tape.

Figure 4-17 Flow chart for the recycling of scraps from tape casting.

<table>
<thead>
<tr>
<th>Components</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Scrap</td>
<td>69 %</td>
</tr>
<tr>
<td>Ethanol</td>
<td>15 %</td>
</tr>
<tr>
<td>Acetone</td>
<td>9 %</td>
</tr>
<tr>
<td>Amylacetate</td>
<td>7 %</td>
</tr>
</tbody>
</table>

Table 4-4 Recipe for anode support slip from recycled scraps and low-quality tapes.
Figure 4-18 Recycling procedure (a) Low quality dried tape cast; (b) scraps from the preparation of solid oxide fuel cells; (c) cutting of low quality tapes into strips; (d) pieces of tape to be ground; (e) loaded tape grinder; (f) grinder in use; (g) ground scraps; (h) ball mill.
4.10 Conclusion

Compressive sintering of the dried tape cast prepared by the co-tape casting of slips with proper compositions resulted in the production of flat half cells. Then, the cathode layer was added by screen printing and sintering. Co-tape casting and co-firing techniques that allow the fabrication of multiple layers in one step can be regarded as a promising manufacturing technology with high reproducibility and low cost for mass production in industry. De-lamination or cracking was not observed after testing. The recycling of scraps to cast as anode support performed successfully.
CHAPTER V
COMPOSITIONAL AND STRUCTURAL STUDY

5.1 Introduction

Compositional and structural variations have as much influence on the microstructure as the fabrication techniques selected. Compositional and structural study of the fuel cells was conducted toward the improvement of mechanical properties and electrochemical performance. Improving the structure of the cell to decrease mass transport restriction and decrease the contact resistance is significant. Improving the composition of different layers to increase the ionic conductivity and the electrical conductivity is significant to fabricate SOFCs with high electrochemical performance.

5.2 Anode support

The material of anode support changed from NiO/8YSZ to NiO/3YSZ, and the pore-former content of the anode support varied from 9 to 11, and 13 wt.%.

5.2.1 Comparison of 8YSZ and 3YSZ

Table 5-1 presents the characteristics of YSZ powders. Table 5-2 lists the typical properties of sintered ceramics of 8YSZ and 3YSZ. The use of 3YSZ anode-supported SOFCs could improve the mechanical properties of the fuel cell due to the higher bending strength and higher density of 3YSZ comparing to those of 8YSZ. Table 3 summarizes
the performance of SOFC for (i) a batch with NiO/8YSZ anode support; (ii) a batch comprising NiO/3YSZ/8YSZ : 65/10.5/24.5 wt% anode support; and (iii) a batch with NiO/3YSZ anode support. Testing results are summarized in Table 5-3. The replacing of 8YSZ with 3YSZ in anode support layer improves fuel cell mechanical strength, avoids cell cracking, and results in a similar performance as fuel cells with 8YSZ anode support.

Table 5-1 Characteristics of 8YSZ, 3YSZ, 10SCZ, and 6SCZ powder.

<table>
<thead>
<tr>
<th>Powder Characteristics</th>
<th>8YSZ</th>
<th>3YSZ</th>
<th>10SCZ</th>
<th>6SCZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$ (mol%) or Sc$_2$O$_3$</td>
<td>8</td>
<td>3</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Specific Surface Area (m$^2$/g)</td>
<td>13.6</td>
<td>14.7</td>
<td>11.1</td>
<td>12.5</td>
</tr>
<tr>
<td>Crystallite Size</td>
<td>210 Å</td>
<td>260 Å</td>
<td>0.53 µm</td>
<td>0.60 µm</td>
</tr>
</tbody>
</table>

Table 5-2 Typical properties of sintered ceramics of 8YSZ, 3YSZ, 10SCZ, and 6SCZ.

<table>
<thead>
<tr>
<th>Typical Properties of Sintered Ceramic</th>
<th>8YSZ</th>
<th>3YSZ</th>
<th>10SCZ</th>
<th>6SCZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>5.90</td>
<td>6.05</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Bending Strength R.T. (MPa) $^1$</td>
<td>300</td>
<td>1200</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Electric Resistance (Ω·cm) at 800°C $^2$</td>
<td>19.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Electric Conductivity log$_{10}$ (S/cm) at 800°C $^2$</td>
<td>-1.30</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>TEC X 10$^6$ (1/°C) $^3$</td>
<td>10.5</td>
<td>--</td>
<td>9.9</td>
<td>10.3</td>
</tr>
<tr>
<td>Ionic Conductivity (S/cm)</td>
<td>0.02</td>
<td>--</td>
<td>0.156</td>
<td>0.11</td>
</tr>
</tbody>
</table>

$^1$: Three-point bending test  
$^2$: 4-terminal method by direct current  
$^3$: Thermal expansion coefficient

Table 5-3 Current density and open circuit voltage of the cells with 8YSZ anode support, 70% 8YSZ / 30% 3YSZ, and 3YSZ.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Anode (NiO/8YSZ/3YSZ)</th>
<th>Current density (mA/cm$^2$)</th>
<th>OCV (mv)</th>
<th># Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>8YSZ</td>
<td>65/35/0</td>
<td>450 745 365</td>
<td>970</td>
<td>10</td>
</tr>
<tr>
<td>3YSZ / 8YSZ</td>
<td>65/10.5/24.5</td>
<td>470 520 420</td>
<td>920</td>
<td>2</td>
</tr>
<tr>
<td>3YSZ</td>
<td>65/0/35</td>
<td>510 560 450</td>
<td>965</td>
<td>3</td>
</tr>
</tbody>
</table>
5.2.2 Pore-former content

Table 5-4 summarizes the porosity of the cells with different pore-former content, and the V–I performance results of the mentioned cells. Porous structure is required for the anode support to supply fuel as well as for the removal of reaction products. The used pore-forming material was microcrystalline cellulose (PH-301). The cells were reduced in Ar/H\_2 stream (100 sccm, 50 vol. % H\_2) at 750 °C, and Archimedes relation was used for calculating porosity. The Archimedes method for measuring the porosity of ceramics is Appendix A.

<table>
<thead>
<tr>
<th>PF content (wt. %)</th>
<th>Porosity</th>
<th>Avg. Max. current density (mA/cm^2)</th>
<th>OCV (mV)</th>
<th># tested Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>9%</td>
<td>43 %</td>
<td>550</td>
<td>930</td>
<td>1</td>
</tr>
<tr>
<td>11%</td>
<td>50 %</td>
<td>365</td>
<td>960</td>
<td>2</td>
</tr>
<tr>
<td>13%</td>
<td>53 %</td>
<td>215</td>
<td>835</td>
<td>2</td>
</tr>
<tr>
<td>25%</td>
<td>70 %</td>
<td>10</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>

Comparison of the results in Table 5-4 shows that by increasing the pore-former content of anode support, the maximum current density of the cells has decreased significantly. Decreasing in maximum current density can be ascribed to the removal of active three-phase boundary region by replacement of the anode material with porous structure. The higher the porosity, the less material there is to form a conduction pathway, and the less contact area between the particles [23].

In these experiments, the highest maximum current density was obtained from an anode support fabricated using 9 wt% PH-301 as a pore-former. Highly porous structure is required for anode support to increase the diffusion of gases, but an additional effect of increasing porosity can be the loss of active three-phase boundary area. The cell with 25% pore-former did not produce measurable current because of short circuit inside the
cell. The silver paste had penetrated through the electrolyte of the cell, giving the visible Ag layer on the surface of the electrodes. Figure 5-1 shows the voltage-current curves of fuel cells with different anode support pore-former content.

![Figure 5-1 V-I curves of fuel cells with different anode support pore-former contents of 9, 11, and 13 wt% recorded at 750°C flowing Ar/H₂ (100 sccm, 50 vol% H₂); seal-less reactor.]

5.3 Anode interlayer

The anode interlayer was studied by changing the NiO/YSZ ratio from 65/35 wt.% to 55/45 wt.. In addition, the thickness and pore-former content of anode interlayer varied to improve the electrochemical performance.

5.3.1 NiO/YSZ ratio

The effect of NiO/YSZ content in the interlayer, on the fuel cell performance was investigated. Decreasing the NiO content from 63 to 55 wt%, decreased the maximum current density by 45%. Lower current density of the cells with 55 wt% NiO can be attributed to the suppressed thermal compatibility of the interlayer and anode support
Layer. Lowering Ni content in the interlayer decreased the thermal compatibility between the interlayer and anode support layer that increased the resistance of the cells and as a result decreased the current density. Figure 5-2 shows the maximum current density of fuel cells with 63% and 55% NiO content in the interlayer. More than 88% of the cells with 63% NiO content, exhibited current densities higher than 250 mA/cm², but only 55% of the cells with 55% NiO content, showed current densities higher than 250 mA/cm².

![Figure 5-2 Maximum current density of fuel cells with 63% and 55% Ni content in the interlayer.](image)

5.3.2 Pore-former content

Figure 5-3 shows the effect of interlayer pore-former content on the average maximum current density and successful fabrication rate of the cells. Increasing the pore-former content in the interlayer from 1 wt.% to 2 wt.% increased the average maximum current density of the cells from 900 mA/cm² to 1150 mA/cm², but increasing the pore-former content of interlayer up to 6 wt.% decreased the average maximum current density of the cells from 1150 mA/cm² to 450 mA/cm². Figure 5-4 (a) and Figure
5-4 (b) show the cross sectional SEM of the SOFC with 4 wt.% and 6 wt. % pore-former in the interlayer.

Increasing the pore-former content in the interlayer from 2 wt.% to 6 wt.% decreased the successful fabrication rate from 85% to 40%. Figure 5-4 (b) shows that using 6 wt.% pore-former has decreased the contact between the electrolyte and interlayer, and large pores can be seen in the interlayer that can lead to the low ionic conductivity of interlayer. Adding higher amounts of pore-former to the interlayer increases the diffusion rate of gases across the interlayer, but decreases the ionic conductivity of interlayer and the contact between the electrolyte and interlayer. Thus, an optimum pore-former content in interlayer exists. The cell with 2 wt.% pore-former exhibited a higher maximum current density than the cells with 1 wt.%, 4 wt.%, and 6 wt.% pore-former content in the interlayer.

Figure 5-3 Effect of interlayer pore-former content on the maximum current density and survival rate of SOFCs.
5.3.3 Interlayer thickness

Figure 5-5 shows the cross-sectional SEM micrographs of the fuel cells with different interlayer thicknesses. A good contact is observed between the layers at all thicknesses. In the literature given in table 1, the optimum anode interlayer thickness was in the range of 1 µm [9] to 135 µm [11]. The difference in the optimum interlayer thickness is ascribed to the difference in the microstructure and ionic conductivity of interlayers, and also the thickness of anode supports that limits the rapid diffusion of gases across the interlayer [13].

Figures 5-6 to 5-9 show the voltage – current curves of the fuel cells with different interlayer thicknesses recorded at 750°C in H₂/Ar, dry and wet CH₄/Ar and CH₄/CO₂. The cell with 15 µm thick interlayer showed a higher current density than the cells with 12 and 18 µm interlayer in all feed streams. Increasing the anode interlayer thickness increases the three phase boundary length, but limits the rapid diffusion of
gases across the interlayer. Thus, an optimum interlayer thickness of 15 is a trade-off between increasing the TPB length and decreasing the gas diffusion.

Figure 5-5 Cross-sectional SEM micrograph of the cells with 12, 15, and 18 μm thick interlayer.
Table 5-5 Optimized thickness of anode interlayer (anode functional layer) as reported in the literature.

<table>
<thead>
<tr>
<th>Interlayer Thickness (µm)</th>
<th>Interlayer fabrication technique</th>
<th>Power Density (W/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5+4 (fine)</td>
<td>VSC</td>
<td>0.59 @ 800 °C</td>
<td>[38]</td>
</tr>
<tr>
<td>5</td>
<td>VSC or WPS</td>
<td>0.7 @ 800 °C</td>
<td>[37]</td>
</tr>
<tr>
<td>12</td>
<td>Lamination and impregnation</td>
<td>0.86 @ 800 °C</td>
<td>[154]</td>
</tr>
<tr>
<td>20</td>
<td>Tape casting and lamination</td>
<td>0.73 @ 700 °C</td>
<td>[42]</td>
</tr>
<tr>
<td>5</td>
<td>Spin coating</td>
<td>2.63 @ 800 °C</td>
<td>[39]</td>
</tr>
<tr>
<td>8</td>
<td>Spin coating</td>
<td>3.41 @ 650 °C</td>
<td>[40]</td>
</tr>
<tr>
<td>15</td>
<td>Tape casting and lamination</td>
<td>2 @ 800 °C</td>
<td>[25]</td>
</tr>
<tr>
<td>9.8</td>
<td>Electrophoretic deposition</td>
<td>1.15 @ 800 °C</td>
<td>[28]</td>
</tr>
<tr>
<td>1 ≤ T_{Int.} ≤ 7</td>
<td>Deposition</td>
<td>-</td>
<td>[155]</td>
</tr>
<tr>
<td>*</td>
<td>Lamination</td>
<td>-</td>
<td>[156]</td>
</tr>
<tr>
<td>135</td>
<td>Tape casting and lamination</td>
<td>1.06 @ 800 °C</td>
<td>[41]</td>
</tr>
<tr>
<td>15</td>
<td>Co-tape casting</td>
<td>0.34 @ 800 °C</td>
<td>This Study</td>
</tr>
</tbody>
</table>

* The SOFCs with different AFL thicknesses (8 µm, 19 µm, and 24 µm) exhibit similar power densities at the measured current density range (0–2 A cm⁻²), but show different impedance responses.
Figure 5-6 V-I curves of fuel cells with 12, 15, and 18 µm anode interlayer thickness at 750 °C in H₂/Ar (100 sccm, 50 vol% H₂).

Figure 5-7 V-I curves of fuel cells with 12, 15, and 18 µm anode interlayer thickness at 750 °C in CH₄/Ar (100 sccm, 50 vol% CH₄).
The electrolyte was studied by fabricating and comparing the cells with 10SCZ electrolyte and 8YSZ electrolyte. In addition, the thickness of electrolyte decreased from 15 µm to 10 µm to improve the electrochemical performance.

5.4 Electrolyte

The electrolyte was studied by fabricating and comparing the cells with 10SCZ electrolyte and 8YSZ electrolyte. In addition, the thickness of electrolyte decreased from 15 µm to 10 µm to improve the electrochemical performance.
5.4.1 Comparison of 8YSZ and 10SCZ

The ohmic resistance of the electrolyte can be reduced by enhancing the ionic conductivity of the electrolyte. Replacing 8YSZ with 10SCZ in electrolyte precursor increases the fuel cell maximum current density by 43 % (from 471 to 673 mA/cm$^2$). The increase in the fuel cell maximum current density can be attributed to the high ionic conductivity of the SCZ electrolytes. The ionic conductivity of 10SCZ at 780°C is comparable to that of 8YSZ at 1000°C. Figure 5-10 shows the plot of maximum current density of the fuel cells with 8YSZ electrolyte and 10SCZ electrolyte.

![Figure 5-10](image)

**Figure 5-10** Maximum current density of the fuel cells from batches No. 2 and 3 as a function of electrolyte material.

The ohmic resistance is the summation of resistance to the (i) flow of ions through the solid electrolyte and (ii) flow of electrons through the electrodes and current collectors [157]. Resistance (i) can be decreased by using highly ionic conductive materials, decreasing the thickness of electrolyte, and increasing the fuel cell operating temperature. Resistance (ii) can be reduced by using highly electrical conductive materials for cathode and anode, enhancing connection between the electrodes and current collectors (low contact resistance) [15], and implementing highly electrical
conductive materials for current collectors. The ohmic resistance resulted from flow of ions was decreased by replacement of 8YSZ with 10SCZ in electrolyte. Ionic conductivity of 8YSZ at 800°C is about 0.02 S cm\(^{-1}\) compared to 0.08 S cm\(^{-1}\) of 10SCZ [158, 159].

5.4.2 Electrolyte thicknesses

Two batches of SOFCs with different electrolyte thicknesses of 10 and 15 µm were prepared. The average current density and ohmic resistance of the cells are summarized in Table 5-6. Eight cells were tested from each batch and the average ohmic resistance of the cells with 15 µm electrolyte is 1.72 Ω cm\(^2\) compared to 2.76 Ω cm\(^2\) of the cells with 20 µm electrolyte. Ohmic losses resulted from the resistance against flow of ions through the electrolyte and flow of electrons through the electrodes and current collectors. Decreasing the electrolyte thickness from 15 to 10 µm lowered the average ohmic resistance by 38% and increased the average current density by 105% (from 180 to 370 mA/cm\(^2\)).

Table 5-6 Current density of the fuel cells with different electrolyte thicknesses.

<table>
<thead>
<tr>
<th>Batch#</th>
<th>Electrolyte/Thickness</th>
<th>Avg. current density (mA/cm(^2))</th>
<th>Avg. ohmic resistance (Ω cm(^2))</th>
<th>Tested cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>120717</td>
<td>6SCZ - 10 µm</td>
<td>370</td>
<td>1.72</td>
<td>8</td>
</tr>
<tr>
<td>120320</td>
<td>6SCZ - 15 µm</td>
<td>180</td>
<td>2.76</td>
<td>8</td>
</tr>
</tbody>
</table>
5.5 Cathode

The cathode was improved by finding the optimum LSM/YSZ ratio for cathode interlayer, and optimizing the cathode sintering temperature. In addition, the pore-former content of cathode interlayer and cathode current collection layer was optimized.

5.5.1 LSM/YSZ ratio

Figure 5-11 shows the X-ray diffraction (XRD) patterns of the LSM/YSZ cathode interlayers with 50 wt.% LSM, 60wt.% LSM, and 70 wt.% LSM. The cathode interlayers with different LSM/YSZ ratios were sintered at 1150 °C for 1 hr resulted in the formation of La₂Zr₂O₇ (LZO) and SrZrO₃ (SZO) ternary phases. Lower ionic conductivity of LZO and SZO compared to that of YSZ could decrease the cathode electric and ionic conductivity. XRD patterns showed that the formation of LZO and SZO for the LSM/YSZ (60 wt.% LSM) cathode was less than that of LSM/YSZ cathode interlayers with 50 wt.% LSM, and 70wt.% LSM. Thus, the LSM/YSZ (60 wt.% LSM) paste was selected to be used as cathode interlayer.
5.5.2 Cathode sintering temperature

Figure 5-12 shows the X-ray diffraction (XRD) patterns of the cathode interlayer at different sintering temperatures. Sintering of the cathode interlayer at higher temperatures (1200 and 1250°C) resulted in the formation of higher amounts of La$_2$Zr$_2$O$_7$ (LZO) and SrZrO$_3$ (SZO) ternary phases. The cathode interlayer sintered at 1100 °C, and 1150 °C formed lower amount of LZO, and SZO than the cathode interlayer sintered at 1200 °C and 1250 °C.
Table 5-7 lists the current densities and open circuit voltages of fuel cells with the cathodes sintered at 1100 °C and 1150 °C. Fuel cells with the cathode sintering temperature of 1150 °C have exhibited a higher average current density than that of the cells sintered at 1100 °C. The 1150 °C is an optimum sintering temperature resulting in a dense oxygen membrane while forming a low amount of undesired LZO and SZO phases.

Table 5-7 Maximum current density and open circuit voltage (OCV) of the cells with cathodes sintered at 1100 °C and 1150 °C.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Sintering temp.</th>
<th>OCV (mV)</th>
<th>$I_{\text{max}}$ (mA/cm$^2$)</th>
<th># tested cells</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Avg.  Max.  Min.</td>
<td></td>
</tr>
<tr>
<td>121218A</td>
<td>1100°C</td>
<td>954</td>
<td>356  560  230</td>
<td>9</td>
</tr>
<tr>
<td>121218B</td>
<td>1150°C</td>
<td>1064</td>
<td>774  948  600</td>
<td>2</td>
</tr>
</tbody>
</table>

5.5.3 Pore-former content of the cathode interlayer

The cathode interlayers with 0, 2, 5, 10, 20, 30 and 40 wt% pore-former content were prepared. Stickiness of the cathode interlayers with pore former content more than 20 wt% to the electrolyte was poor and testing of those cells was impossible. Figures 5-
13 and 5-14 show the voltage - current curves of fuel cells operated at 750 °C in H\textsubscript{2}/Ar (100 sccm, 50 vol% H\textsubscript{2}) and in CH\textsubscript{4}/Ar (100 sccm, 50 vol% CH\textsubscript{4}).

Results showed that the cell with cathode interlayer containing 2 wt% pore-former has the highest current density at 750 °C in H\textsubscript{2}/Ar and in CH\textsubscript{4}/Ar. This improvement can be ascribed to the rapid gas diffusion through a porous cathode interlayer structure with a reasonable ionic and electronic conductivity. Adding 5 wt.% pore-former to the cathode interlayer has decreased the fuel cell maximum current density, indicating the decreased ionic and electronic conductivity.
5.5.4 Pore-former content of the cathode current collection layer

Cells with cathode current collection layers with 0, 5, 10, 20, 30, and 40 wt% pore-former content were prepared, screen printed, and sintered. The resistance of cells containing more than 10 wt% pore-former in the cathode current collection layer was increased significantly. Figures 5-15 to 5-17 show the voltage - current curves of fuel cells operated at 750 °C, 800 °C, and 850 °C in H2/Ar (100 sccm, 50 vol% H2),
respectively. Results exhibited that the current collection layer containing 5 wt% pore-former had the highest current density.

The properties of the cathode current collection layer are governed not only by the connection of the electrical conducting path, but also by that of the gas-diffusion path. Thus, controlling the porous structure of cathode current collection layer could help to obtain better electrical conductivity and gas permeability. The Faraday resistance was the main contributor to the loss of cell voltage, and it decreased from 0.85 $\Omega$.cm$^2$ to 0.2 $\Omega$.cm$^2$ by increasing the temperature from 750 °C to 850 °C for the cell with 5 wt% of pore-former in the cathode current collection layer.

Figure 5-15 curves of fuel cells with various pore former amount in cathode collection layer operated at 750 °C in H$_2$/Ar (100 sccm, 50 vol% H$_2$).
Figure 5-16 V-I curves of fuel cells with various pore former amount in cathode current collection layer operated at 800 °C in H₂/Ar (100 sccm, 50 vol% H₂).

Figure 5-17 V-I curves of the cells with various pore former amount in cathode current collection layer operated at 850 °C in H₂/Ar (100 sccm, 50 vol% H₂).
5.6 Conclusion

The results of the compositional and structural modification are summarized in Table 5-8.

<table>
<thead>
<tr>
<th>Component</th>
<th>Modification</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode support</td>
<td>3YSZ instead of 8YSZ</td>
<td>Improved fuel cell mechanical strength, and resulted in the same performance.</td>
</tr>
<tr>
<td>- Pore-former</td>
<td></td>
<td>The highest maximum current density was obtained from the cell with 9 wt. % PH-301 in the anode support.</td>
</tr>
<tr>
<td>Interlayer</td>
<td>NiO/YSZ ratio</td>
<td>Decreasing the NiO content from 63 to 55 wt%, decreased the average maximum current density by 45%.</td>
</tr>
<tr>
<td>- Pore-former</td>
<td></td>
<td>Cell with 2 wt. % pore-former in the interlayer exhibited a higher maximum current density than that of the cells with 1 wt.%, 4 wt.% and 6 wt.% pore-former content in the interlayer.</td>
</tr>
<tr>
<td>- Thickness</td>
<td></td>
<td>The highest maximum current density was obtained from the cell with 15 µm thick interlayer.</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>10SCZ instead of 8YSZ</td>
<td>Replacing 8YSZ with 10SCZ in electrolyte increased the fuel cell maximum current density by 43 %.</td>
</tr>
<tr>
<td>- Thickness</td>
<td></td>
<td>Decreasing the electrolyte thickness from 15 to 10 µm increased the average current density by 105%</td>
</tr>
<tr>
<td>Cathode</td>
<td>LSM/YSZ ratio</td>
<td>LSM/YSZ (60 wt.% LSM) paste was selected to be used as cathode interlayer.</td>
</tr>
<tr>
<td>- Sintering temperature</td>
<td></td>
<td>Fuel cells with the cathode sintering temperature of 1150 ºC have exhibited a higher average current density than that of the cells sintered at 1100 ºC. Adding 2wt. % pore-former to the cathode interlayer improved the electrochemical performance.</td>
</tr>
<tr>
<td>- Pore-former (cathode interlayer)</td>
<td></td>
<td>Adding 5wt. % pore-former to the current collection layer improved the electrochemical performance.</td>
</tr>
</tbody>
</table>
CHAPTER VI

FABRICATION OF TUBULAR SOLID OXIDE FUEL CELLS

6.1 Introduction

Compared with planar cells the tubular cells have advantages such as following: (1) easier to seal and make into stacks; (2) higher capability of coping with thermal stresses; (3) greater potential for stationary power generation applications [160-162].

Several methods for preparing the tubular anode supports have been used, including gel casting [163-165], extrusion [59, 166], tape casting [167, 168], and slip casting [169]. The commonly used method for the coating of electrolyte on tubular anode support is dip coating [59, 164-169]. The thermal stress of the cells can be reduced by the use of cells with smaller diameter. In addition, the decrease in the diameter of the tubular cells improves the surface-to-volume ratio of the SOFCs, and thus the volumetric power density. This observation has led to the invention of the micro-tubular SOFC (mSOFC) with the cell diameters less than 2 millimeters [62].

Among various fabrication methods, dip coating is the most attractive method due to the following reasons: (i) low cost, (ii) simplicity, and (iii) the capability of producing a homogeneous layer with a thickness of less than 10 µm [3].
6.2 Rolled Tubular SOFC

The tape-cast was rolled around a tube, and a 60/40 wt.% mixture of ethanol and alpha trepineol was used to stick and to seal the edges of the rolled tape. The rolled tape was put vertically in the furnace for co-firing, and the cathode was added by screen printing. The tubular cells fabricated by rolling the tape-cast were not in a perfect cylindrical shape. In addition, due to the hardships in rolling the tape-cast fabricating the rolled tubular cells with the diameters smaller than 10 mm is not feasible. Thus, multilayer dip coating was used within one step to fabricate tubular cells. Figure 6-1 shows a rolled tubular cell with 20 mm outer diameter and 25 mm length, and a planar cell with 13 mm diameter.

Figure 6-1 Rolled tubular cell and planar cell.
6.3 Dip coating

Multilayer dip coating and co-sintering techniques were used within one step to decrease the fabrication cost of tubular half-cells. De la Torre et al. reported the fabrication of mSOFCs by applying multi-layer dip coating technique to produce the anode support, electrolyte, and cathode using water-based slurries [61, 170]. In this study organic solvents were used for the preparation of dip coating slurries because the organic solvents are very volatile, dry much more rapidly than water, and the drying rate is closely tied to fabrication rate.

6.3.1 Slurry preparation

An anode support slurry (thin slip) was prepared in a binary solvent system by ball milling 22 wt.% NiO and 12 wt.% 3YSZ powders. 4 wt.% microcrystalline cellulose, 3 wt.% binder, 1 wt.% dispersant, and 3 wt.% plasticizer were added. An anode interlayer slurry was prepared in a binary solvents system by ball milling 22 wt.% NiO and 13 wt.% SCZ powders. Then 3 wt.% binder, 1 wt.% dispersant and 3 wt.% plasticizer were added. The electrolyte slurry consisted of 38 wt.% ScCeSZ powder along with 3 wt.% binder, 1 wt.% dispersant, and 3 wt.% plasticizer dispersed in a binary solvents system. Ball milling was continued for 24 h to prepare homogeneous slips.
6.3.2 Dip coating of carbon rod

Mechanical pencil lead (carbon rod) was used as a sacrificing core for dip coating, and three layers were dip coated successively as following: (a) the anode support layer; (b) the interlayer; (c) the electrolyte. Figure 6-2 shows the half cell prepared using pencil lead in one cycle co-firing heated to 1400 °C. The half cell was damaged due to the melting of the core. Two cycles co-firing process was applied. The dip coated core was heated to 1000 °C in the first cycle and the residue of the sacrificing core was removed at the end of the first co-firing cycle. The pre-sintered half cell was heated up to 1400 °C in the second co-firing cycle. Figure 6-3 shows the schematic of tubular cell fabrication process by dip coating a carbon rod as a sacrificing core.

Figure 6-2 Half cell prepared in one cycle co-firing.
Figure 6-3 Schematic for the fabrication process of tubular cell using a carbon rod as template.
6.3.3 Dip coating of cellulose core

Two cycles co-firing process is time consuming, and as per the discussion in section 4-7 it requires higher temperature to achieve electrolyte densification. Moreover, carbon rods are only available in specific sizes in the market. Thus, a home-made dye was fabricated for the production of cellulose rods as sacrificing material by pressing a cellulose paste. The paste prepared by ball milling 45 wt.% microcrystalline cellulose, 3 wt.% binder, 1 wt.% dispersant and 3 wt.% plasticizer in a binary solvents system. The paste was shaped as a cylinder with a diameter of 5.5 mm by pressing at 4000 psi pressure for 2 minutes. The cellulose rod was dried at 75 °C for 1 h. Figure 6-4 shows the fabricated cellulose rod. The rod cut into the required lengths and dip coated with the anode support slip. Dip coated rod was dried in air for 10 min and this was repeated several times until achieving the required anode support thickness. The cellulose rod dip coated with anode support, anode interlayer, and electrolyte slurries successively at a withdrawing rate of 3 mm s\(^{-1}\). Table 6-1 lists the dip coating and drying conditions used to fabricate the tubular SOFCs. The dip coated cellulose rods were co-sintered in air. The furnace was heated to 1000 °C, followed by a dwelling step for 1 h to burn out the pore-former and sacrificing core. Then the furnace was heated up to 1400 °C for 2 h. Sintered half-cells were screen printed using a LSM/YSZ cathode and LSM current collector. The samples were then sintered in air at 1150 °C for 1 h. The Final fabricated tubular cell is shown in Figure 6-5. Figure 6-6 shows the temperature profile of co-firing of the dip coated ceramic for the preparation of half cell. Figure 6-7 shows the schematic of tubular cell fabrication process by dip coating a cellulose rod as a sacrificing core. Table 6-2 summarizes the failure cases occurred during the development of fabrication
process for the tubular anode supported SOFCs. Figure 6-8 shows the SEM of different parts of the fabricated tubular cell.

![Figure 6-4 Fabricated cellulose rod to use as a sacrificing core for dip coating.](image)

Table 6-1 Dip coating and drying conditions for anode support, anode interlayer, electrolyte.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Dips</th>
<th>Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>°C</td>
</tr>
<tr>
<td>Anode support</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>Anode interlayer</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

![Figure 6-5 Tubular SOFC fabricated by dip coating method (l = 25 mm, OD = 7mm).](image)
Figure 6-6 Temperature profile for co-firing.

Figure 6-7 Schematic for the fabrication process of tubular cell using a cellulose rod as sacrificing core.
Figure 6.8 SEM of the tubular cell for (a) tubular cell cross section; (b) cathode surface (c) electrolyte surface; (d) anode support surface; and (e) anode support cross section.
Table 6-2 Summary of the failure cases occurred during the development of fabrication process for the tubular anode supported SOFCs.

<table>
<thead>
<tr>
<th>No</th>
<th>#dip.</th>
<th>Core</th>
<th>Core dia.</th>
<th>Problem</th>
<th>Reason</th>
<th>Picture</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35</td>
<td>Quartz glass</td>
<td>10 mm</td>
<td>Cracked during firing</td>
<td>Expansion of quartz glass during firing</td>
<td><img src="image1.jpg" alt="Picture 1" /></td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>extruded graphite</td>
<td>12 mm</td>
<td>Cracked during firing</td>
<td>Burning out the extruded graphite</td>
<td><img src="image2.jpg" alt="Picture 2" /></td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>Pencil lead (Kuhi Noor)</td>
<td>5.6 mm</td>
<td>Cracked cell</td>
<td>-</td>
<td><img src="image3.jpg" alt="Picture 3" /></td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>Pencil lead (Roma)</td>
<td>5.6 mm</td>
<td>Damaged and deformed cell</td>
<td>Melted residues</td>
<td><img src="image4.jpg" alt="Picture 4" /></td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>Pencil lead (Roma)</td>
<td>5.6 mm</td>
<td>The electrolyte peeled off</td>
<td>Thick electrolyte</td>
<td><img src="image5.jpg" alt="Picture 5" /></td>
</tr>
</tbody>
</table>
CHAPTER VII

POLYANILINE

7.1 Introduction

The importance of conducting polymers is highlighted by the awarding of the 2000 Nobel Prize in Chemistry to MacDiarmid, Shirakawa, and Heeger, “for the discovery and development of conducting polymers” [171]. Electronically conducting polymers can be divided into filled and intrinsically conducting polymers. Filled conducting polymers are composed of conducting components embedded in a nonconductive matrix [172]. Commonly used conducting components are metal or carbon powder while nonconducting matrix are polyethylene and polypropylene. Intrinsically conducting polymers possess conjugating (alternating) double and single bonds that provides a pathway for free-electron charge carriers [173]. Conducting polymers referred in this study is polyaniline (PANI), which is an intrinsically conducting polymer.

Conducting polymers are semiconductors with versatile properties and various applications. Many critical properties of conducting polymers including morphological structure may be tailored for a particular application. Conducting polymer nano-materials combine the advantages of conducting polymers with low-dimensional systems and therefore create interesting physicochemical properties and usages [174-176]. Some of the commercialized applications of PANI are listed in the literature: (i) antistatic layer
in computer disk (Hitachi-Maxell) [177]; (ii) 3V coin-shaped batteries [178]; (iii) solar cells [179]; (iv) gas sensors [180]; (v) anti-corrosion coating [181].

Polyaniline (PANI) has been identified as the most promising conductive polymer because of its ease of synthesis, low cost monomer, tunable properties, and good stability [182]. PANI is also unique among conducting polymers in that it has a very simple acid/base doping/dedoping chemistry. Depending upon the oxidation level, PANI has three basic structures, namely, (i) fully reduced leucoemeraldine base (LEB) where all repeating units have benzenoid structure (B), (ii) fully oxidized pernigraniline base (PNB) where all repeating units have quinoid structure (Q) and (iii) partially oxidized (~ 50%) form is known as emeraldine base (EB) having Q to B ratio ~ 1 [175].

A common method of producing doped PANI is acid-doping (or proton-doping). The presence of the acid (HA) results in the protonation of nitrogen atoms in PANI. The protonated polymer chain is positively charged, and has associated counter-anions. The imine sites are more readily protonated than the amine sites [183]. Neutral (or undoped) PANI exhibits conductivity on the order of $10^{-10}$ S/cm; as with doping can result in a significant increase in conductivity up to 10 S/cm (11 orders of magnitude) [184].

7.2 Literature review

Polyaniline membranes, the kinetics of aniline polymerization, the synthesis of PANI, and the deposition of PANI by in situ polymerization in the literature are reviewed.
7.2.1 Polyaniline membranes

PANI consists of chains of nitrogen containing groups. Therefore, the possibility of high CO$_2$ capture in PANI is predicted. Anderson et al. reported the potential application of free standing doped PANI for gas separations [185]. The process for tailoring gas selectivity of a PANI membrane involves improving the permeabilities of gases with small diameters [<3.5 Angstroms] by doping and de-doping the polymer film with counter ions of a proper size. High selectivities are then achieved by decreasing the permeabilities of larger gases (>3.5 Angstroms diameter) through controlled re-doping of the polymer.

Figure 7-1 shows a hypothetical cross section of a polymer membrane, and the effect of doping on the pore connectivity. The film-cast has some permeability of all gases that is size-dependent, leading to modest separation ratios. Heavy doping of the film reduces the permeability of all gases. De-doping the film increases the permeability of small gases compared to the film-cast. Moderate redoping blocks the permeability of the larger gases and leads to very high separation ratios. Figure 7-1 only depicts the effect of doping on diffusion rates, but solubility is also an important factor in obtaining high separation ratios [185].

Based on the variation in permeability coefficients with the doping, de-doping, and re-doping process the gases can be divided in two subgroups comprising H$_2$, O$_2$ and CO$_2$ (the smaller gases) and N$_2$ and CH$_4$ (the larger gases). After the doping, de-doping, and re-doping process the gas fluxes are increases by 15% for the smaller gases and are decreased by 45% for the larger gases. This can be interpreted by the partial-filling of large-sized free volume under moderate re-doping [186].
Kubawata and Martin discovered that doping level is the most important factor in modifying the gas separation performance; as doping level increased from 13 to 38%, the selectivities of O₂/N₂ and CO₂/CH₄ were improved by 43% and 20% [187]. Su et al. prepared free-standing thin films of polyaniline/polyimide blends from solution. The separation factors of the blends were higher than those for the polyimide homopolymer, but lower than or equivalent to those for base PANI. The selectivity of the blend membranes was higher than that for de-doped PANI, and was on the order of the selectivity for doped PANI [188].

![Image](image1.png)

Figure 7-1 (a) film-cast with no dopant ions; (b) after heavily doping in a strong acid solution; (c) after de-doping in basic medium; and (d) after re-doping in a mild acid solution [17].

Mishra and Ramaprabhu introduced polyaniline-graphene nanocomposite as a CO₂ capture candidate that demonstrates higher capture capacity compared to other solid sorbents reported under the same conditions. The increased capture capacity is directly attributed to the chemical interaction of CO₂ molecules with nitrogen containing functional groups along with molecular adsorption over the surface of the nanocomposite [189].

The polyaniline-polyvinylamine /Polysulfonate membranes have successfully displayed better CO₂ permeance and CO₂/N₂ selectivity compared with polyvinylamine
/Polysulfonate membrane. The higher CO\textsubscript{2} permeance and CO\textsubscript{2}/N\textsubscript{2} selectivity are attributed to the novel gas transport characteristic in polyaniline-polyvinylamine/Polysulfonate membranes. The N\textsubscript{2} barrier property of the PANI nano-particles and the interaction between CO\textsubscript{2} and PANI nano-particles enhanced the CO\textsubscript{2}/N\textsubscript{2} selectivity of the membranes. The increased free volume of PANI nanoparticles by a reaction of polyaniline nanoparticles with polyvinylamine was more conductive to CO\textsubscript{2} permeance in the polyaniline nanoparticles. The increased amorphous regions and free volume at the interface region in polyvinylamine adjacent to polyaniline nanoparticles due to disruption of polyvinylamine polymer chain packing in the presence of the polyaniline nanoparticles enhanced CO\textsubscript{2}/N\textsubscript{2} permeance and selectivity [190]. Zhao et al. constructed facilitated transport highways (FTH) through the combination of modified PANI nano-rods and polyvinylamine macromolecules. CO\textsubscript{2} molecules could diffuse rapidly into the membrane due to the reversible reaction with amino groups. Therefore, the nano-composite membrane exhibited outstanding permselectivity for CO\textsubscript{2} separation [191].

7.2.2 Kinetics of aniline Polymerization

Figure 7-2 shows the aniline polymerization with ammonium persulfate (APS) in HCl medium.

\[4n \text{NH}_2\text{HCl} + 5n (\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow \text{HN} \bigg[\begin{array}{c} Cl \\
\text{Cl} \end{array} \bigg]_n \]

\[+ 2n \text{HCl} + 5n \text{H}_2\text{SO}_4 + 5n (\text{NH}_4)_2\text{SO}_4\]

Figure 7-2 Aniline polymerization with ammonium persulfate (APS) in HCl medium.
Tzou and Gregory proposed a semi empirical kinetic model in which the consumption of aniline involves a slow, homogeneous reaction with the oxidant, and a much faster reaction with the precipitating polyaniline phase [192]. They proposed the following empirical rate equation:

\[
-d[AN]/dt = k_1[AN][APS] + k_2[AN][P] \quad (1)
\]

where [AN], [APS] and [P] are the concentrations of aniline, \((\text{NH}_4)_2\text{S}_2\text{O}_8\), and polyaniline respectively, and \(k_1\) and \(k_2\) are constants. \(k_2\) is a composite quantity containing a contribution from the specific surface area of the precipitating polymer. Since [AN], [APS] and [P] are functions of the reaction stoichiometry of the initial reagent concentrations, equation (1) can be integrated and fitted to experimental data, using \(k_1\) and \(k_2\) as variables.

It was claimed that this approach gives good fits and that \(k_1\) was primarily affected by the initial reactant concentrations and the presence of catalyst, whereas \(k_2\) depended on the acid concentration and the presence of added colloidal substrates. In general \(k_2\) was found to be two to three orders of magnitude larger than \(k_1\).

The oxidant concentration at any given time during the polymerization is given by

\[
[APS] = [APS]_0 - 1.25([AN]-[AN]_0) \quad (2)
\]

where the factor of 1.25 arises because one mole of aniline is consumed by 1.25 moles of APS (a two electron oxidant). Substitution from equation (2) allowed equation (1) to be integrated in terms of two variables, \(\beta_1\), and \(\beta_2\), which were defined by

\[
\beta_1 = 1.25k_1-k_2 \quad \text{and} \quad \beta_2 = k_1 [APS]_0 - \beta_1[AN]_0 \quad (3)
\]

The integrated rate equation is given by

\[
[AN] / [AN]_0 = \beta_2 / (\beta_1[AN]_0 \exp(\beta_2t) - 1) + \beta_2 \exp(\beta_2t) \quad (4)
\]
Table 7-1 summarizes the best feet values of the two rate constants, $k_1$ and $k_2$.

Table 7-1 Summary of kinetic data for aniline polymerization [193].

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_1$ (x 10$^3$ mol$^{-1}$ min$^{-1}$)</th>
<th>$k_2$ (mol$^{-1}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>5.2</td>
<td>3.1</td>
</tr>
<tr>
<td>298</td>
<td>47</td>
<td>6.8</td>
</tr>
</tbody>
</table>

7.2.3 Synthesis of PANI

Figure 7-3 shows the conventional method of PANI synthesis. The product of conventional PANI synthesis is PANI with irregular shapes. A small amount of nano-fibers can be observed among the irregularly shaped particulates in conventionally synthesized PANI [194]. The nano-fibrillar morphology significantly improves the processability of PANI and its performance in many applications. The nano-fiber formation is favored, while their overgrowth that would lead to irregularly shaped agglomerates needs to be suppressed [175, 194]. A simple approach to prevent the overgrowth of nano-fibers is to stop the polymerization after the formation of nano-fibers. This has been achieved by rapidly mixing the monomer and initiator solutions (Figure 7-4). When the reaction starts, the initiator molecules are consumed rapidly during polymerization and depleted after nanofiber formation. Thus, the overgrowth of PANI is suppressed due to lack of initiator molecules [194].
7.2.4 Deposition of PANI by in situ polymerization

The oxidation of aniline in an acidic aqueous medium produces aniline oligomers at first. These oligomers are more hydrophobic than the original anilinium cations. They have a tendency to be adsorbed at available surfaces in contact with aqueous reaction mixture as shown in Figure 7-5. The adsorbed oligomers have a higher reactivity toward initiating the growth of PANI chains, and the polymerization at the surfaces precedes the polymerization in the bulk of the reaction mixture. The first PANI chain anchored at the surface produces a nucleus of the future film. New oligomers are born and adsorbed
close to the nucleus, and stimulate the growth of new PANI chains. The PANI chains forming a film thus proliferate along the surface [195].

Figure 7-5 The model of film formation: (a) aniline oligomers (open circles) are adsorbed at the available interfaces and (b) they stimulate the growth of a PANI chain (thick curve). A nucleus is produced. (c) Other PANI chains grow due to the auto-acceleration mechanism close to the nucleus. The film spreads along the surface [195].

7.3 Experimental

Film deposition by in situ polymerization in liquid phase and in situ polymerization in gas phase, and dipping the substrate into the solution was performed:

7.3.1 In situ polymerization in liquid phase

25 mmol aniline was dissolved in 50 mL of 0.4 M HCl solution, then another 50 mL of 0.4 M HCl containing 8.3 mmol ammonium peroxidisulfate (APS) was added under vigorous stirring, followed by immersing a substrate (a piece of clean slide glass, or flexible polyethylene membrane) in the solution [179]. After being kept at 4 °C for 30 min, the substrate was taken out and rinsed with deionized water; then the PANI on the one side was removed. Polymerization at reduced temperature yields PANI with high molecular weight and enhanced degree of crystallinity [196]. Finally, the PANI/Substrate was redoped in 1 M HCl for 4 h, then rinsed and dried at 80 °C in vacuum for 30 min. This step removes any residual solvent, and is important for
reaching optimum electrical performance [197]. Polymerization of aniline achieved by rapidly mixing the monomer and initiator solutions is shown in Figure 7-6. Figure 7-7 shows the transparent PANI thin film deposited on the slide glass. Figure 7.8 shows the PE membrane before and after PANI deposition. Figure 7.9 shows the SEM micrograph of PE film before coating with PANI. Figure 7.10 SEM shows the SEM micrograph of PE membrane coated with PANI by liquid phase polymerization (polymerization time: 10 min, temperature: 4 °C). Figure 7-11 shows the XRD pattern of the PANI powder collected from the precipitates of the solution. Three peaks centered at 2θ= 15.5°, 20.5° and 25° are observed that are characteristic peaks of PANI, indicating the PANI is crystallized, and the strongest peak at 25° is ascribed to the face to face interchain stacking distance between phenyl rings [198, 199].

Figure 7-6 In-situ polymerization of aniline: the reaction times are (a) 0 s, (b) 60 s, (c) 90 s, (d) 120 s, and (e) 180 s.
Figure 7-7 Photograph of a slide glass coated with transparent PANI thin film compared to a bare slide glass. The green color indicates the emeraldine state.

Figure 7-8 (a) PE membrane before coating with PANI; (b) PE membrane coated with PANI by liquid phase polymerization (polymerization time: 10 min, temperature: 4 °C).

Figure 7-9 SEM micrograph of PE membrane before coating with PANI.
Figure 7-10 SEM micrograph of PE membrane coated with PANI by liquid phase polymerization (polymerization time: 30 min, temperature: 4 °C).

Figure 7-11 XRD pattern of the PANI powder collected from the aniline polymerization after 30 min.
7.3.2 In situ polymerization in vapor phase

In vapor-phase deposition, APS (0.3 M) was dissolved in 3 M HCl solution. PE membranes were soaked in aniline solution, and then held in a saturated oxidizer vapor atmosphere. APS vapors were generated by heating the oxidizer solution at about 70 °C in a closed vessel. Figure 7-12 shows PE membrane coated with PANI by vapor phase polymerization for 5 min and 15 min. Figure 7-13 shows the SEM micrograph of PE membrane coated with PANI by vapor phase polymerization for 5 min. Figure 7-14 shows the SEM micrograph of PE membrane coated with PANI by vapor phase polymerization for 15 min.

Figure 7-12 (a) PE membrane coated with PANI by vapor phase polymerization (polymerization time: 5 min, temperature: 75 °C); (b) PE membrane coated with PANI by vapor phase polymerization (polymerization time: 15 min, temperature: 75 °C)
Figure 7-13 SEM micrograph of PE membrane coated with PANI by vapor phase polymerization (polymerization time: 5 min, temperature: 75 °C).

Figure 7-14 SEM micrograph of PE membrane coated with PANI by vapor phase polymerization (polymerization time: 15 min, temperature: 75 °C).
7.3.3 Dipping

This method consists to dissolve polymer in an adequate solvent, the substrate is then dipped into the solution. The thickness of the deposited film depends on the solution viscosity, and duration. Polyemeraldine salt is insoluble in most ordinary solvents, and the general procedure is to use polyemeraldine base, totally soluble in N-methyl-2-pyrrolidinone (NMP). Dimethyl acetamide (DMAc) is another solvent that can be used to dissolve polyemeraldine base. 20 mg de-doped PANI was dissolved in 10 cc NMP. The PE film was dipped for 6 h and washed with DI water. Figure 7-15 shows the dipped PE membrane before and after doping with 1M HCl. Figure 7-16 shows the SEM micrograph of the PE membrane dipped in PANI dissolved in NMP.

Figure 7-15 (a) PE membrane dipped in PANI solution for 6 h; (b) Dipped PE membrane in PANI solution after doping by 1M HCl.
7.3.4 Conductivity

A home made four point probe was used to measure the electrical conductivity of PE membranes coated with PANI. Figure 7-17 shows a schematic configuration of four point probe. A constant electrical current of 1 mA was applied between outer electrodes (1 and 4) using a d.c. power supply and the voltage (E) was measured between inner electrodes (2 and 3). The electrical conductivity (S cm$^{-1}$) of the polymer films was calculated using following equation: $\sigma = IS / VDW$, where $V$ is voltage between the two inner electrodes recorded in volts, $D$ is width of the sample measured in cm, $W$ is the thickness of the sample measured in cm, $I$ is the applied current between two outer electrodes, $S$ is distance between the two points where the voltmeter wires make contact to the sample, measured in cm. Table 7-1 compares the conductivity of deposited PANI on polymeric substrates as reported in the literature.
Table 7-2 Results of the conductivity measurement for the polymeric substrate coated with PANI.

<table>
<thead>
<tr>
<th>Substrate Membrane</th>
<th>Deposited Polymer</th>
<th>Range (Scm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate filters</td>
<td>Polyaniline, Polypyrrole</td>
<td>14 – 50</td>
<td>[201]</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Polyaniline, Polypyrrole</td>
<td>0.1 – 6</td>
<td>[202]</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Polyaniline, Polypyrrole</td>
<td>1–10</td>
<td>[203]</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Polyaniline</td>
<td>10$^{-5}$–1</td>
<td>[204]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Polyaniline</td>
<td>10$^{-5}$–6x10$^{-3}$</td>
<td>[205]</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Polyaniline</td>
<td>10$^{-3}$–9</td>
<td>[206]</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Polyaniline</td>
<td>1–100</td>
<td>[207]</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Polyaniline</td>
<td>2x10$^{-4}$–6x10$^{-4}$</td>
<td>This study</td>
</tr>
</tbody>
</table>

7.3.5 In situ FTIR-ATR spectroscopic study

In situ Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopic study on the polymerization of aniline was performed [208]. The progress of polymerization was monitored in situ by FTIR spectroscopy using a home made reactor. The experimental setup is shown in Figure 7-18 (a). Figure 7-18 (b) shows the photograph of ZnSe crystal surface after the experiment. Figure 7-18(c) shows the optical micrograph of growth of polyaniline film on the ZnSe crystal surface after the experiment. Changes proceeding in the polymerization solution are reflected in the...
spectra. Figure 7-19 shows the absorbance (one over single beam) spectra of ATR background, after pouring the reaction mixture inside the reactor, and after polymerization for 45 min. Figure 7-20 shows the absorbance spectra of aniline and APS collected by in situ FTIR-ATR. Absorbance spectra (A) were obtained by $A = -\log(I/I_{ATR})$, in which $I_{ATR}$ is the single beam spectrum of the empty ATR cell and $I$ is the single beam spectra of the reaction mixture at the specified times.

Figure 7-18 (a) Experimental setup for the FTIR-ATR study of PANI; (b) photograph of ZnSe crystal after the experiment; (c) optical micrograph of the growth of polyaniline film on the ZnSe crystal surface.
Figure 7-19 Absorbance spectra of ATR before pouring the reaction mixture inside the reactor, after pouring the reaction mixture inside the reactor, and after polymerization for 45 min.

Figure 7-20 Absorbance spectra of aniline and APS collected by in situ FTIR-ATR. Absorbance spectra (A) were obtained by 
\[ A = - \log \left( \frac{I}{I_{\text{ATR}}} \right) \], in which \( I_{\text{ATR}} \) is the single beam spectrum of the empty ATR cell and \( I \) is the single beam spectra of the reaction mixture at the specified times.
In the absorbance spectra (Figure 7-20) the main peak at 1572 cm\(^{-1}\) corresponds to quinoid (Q) ring stretching deformations, and the main peak at 1481 cm\(^{-1}\) corresponds to benzenoid (B) ring stretching deformations [208]. The intense bands located at 1648 and 3378 cm\(^{-1}\) are associated to the scissors-bending (\(\delta\)) and O–H stretching (\(\nu\)) vibrational mode of water molecules. The strong broad IR absorption over 3000–3700 cm\(^{-1}\) region is associated with the hydrogen-bonding between the water molecules. The broad band at 1277 cm\(^{-1}\) and the sharp band at 1050 cm\(^{-1}\) are corresponded to the m(O–O) and m(S=O) of APS [209]. The absorption at 1141 cm\(^{-1}\) band is assigned to the vibration mode of the B–NH\(^+\)=Q in the protonated emeraldine base [210]. The broad band above 2000 cm\(^{-1}\) is the characteristic of the conducting form of PANI, decrease of this band may be attributed to the decrease in conductivity by de-doping [211, 212]. Peak at 1262 cm\(^{-1}\) is assigned to C–N vibration of primary aromatic amine (aniline), and peak at 3214 cm\(^{-1}\) is assigned to N–H vibration [213].

7.4 Conclusions

This study demonstrated that applying rapid mixing method for the in-situ polymerization of aniline is an effective method for the deposition of PANI film on PE membrane and glass. The PANI films prepared by liquid phase polymerization have a better uniformity than those prepared by vapor phase polymerization. SEM micrograph of the synthesized PANI showed that the reaction initiated with the molar ratio of 1/3 for [APS]/[AN] in 0.4M HCl produced PANI with granular microstructure.
CHAPTER VIII

CONCLUSIONS

8.1 Development of co-tape casting and co-firing

CHAPTER IV presents the development of co-tape casting, and co-firing techniques that allow the fabrication of multiple layers in one step can be regarded as a promising manufacturing technology with high reproducibility and low cost for mass production in industry. Development includes proper slip formulation to achieve a processable tape-cast without structural flaws, one cycle co-firing process, and the recycling of scraps. In addition, sinter plates fabricated by tape casting and lamination techniques for compressive sintering of green cells during the co-firing operation.

8.2 Compositional and structural study of the SOFCs

CHAPTER V presents the results of comprehensive compositional and structural study of the SOFC fabrication. For instance, the cathode sintering temperature optimized to prevent the formation of unfavorable LZO, and SZO compositions, and to achieve appropriate microstructure for cathode. The details of the fuel cells fabricated using co-tape casting, co-firing, and screen printing with optimized structure and composition are presented in Table 8-1.
Table 8-1 Specifications of the fuel cell with optimized composition and structure.

<table>
<thead>
<tr>
<th>Component</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode support</td>
<td>NiO/3YSZ : 65/35 wt.%, with 9 wt.% pore-former</td>
</tr>
<tr>
<td>Interlayer</td>
<td>NiO/ScCeSZ : 67/37 wt.% with 2 wt.% pore-former, 15µm thick</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>10SCZ, 10 µm thick</td>
</tr>
<tr>
<td>Cathode</td>
<td>Cathode interlayer: LSM/YSZ : 60/40 wt.% sintered at 1150 °C, with 2 wt.% pore-former. Cathode current collection layer: LSM, sintered at 1150 °C, with 5 wt.% pore-former</td>
</tr>
</tbody>
</table>

8.3 Development of the tubular SOFC fabrication

CHAPTER VI presents the development of tubular fuel cell fabrication. The tape-cast prepared to fabricate planar cells was rolled, and the rolled tubular cell was fabricated successfully, but due to rolling process the fabricated cell was not in a perfect cylindrical shape. Thus, multilayer dip coating and co-firing as economical techniques to fabricate the tubular SOFCs. A method developed for the fabrication of sacrificing core that is required for dip coating as a template developed. The fabrication of tubular half cells achieved in one co-firing cycle using cellulose core for the dip coating. The SEM micrographs of reduced tubular cell showed that the tubular cell fabricated by multilayer dip coating is comprised of three distinguishable layers including a porous anode support formed by burning out the pore-former, an anode interlayer with fine particle size, and a dense electrolyte. All of the components developed from this study for the planar cell could be used for developing tubular SOFC.
8.4 Polyaniline

CHAPTER VII presents the results of in situ polymerized polyaniline in liquid phase and and in situ polymerized polyaniline in gas phase. The uniform deposition of PANI on the polymeric substrate (PE membrane), and slide glass achieved by applying rapid mixing method for in situ polymerization in liquid phase. FTIR-ATR investigation of the PANI synthesis showed the capability of observing the IR-active species in an aqueous environment.

8.5 Future Studies

- To commercialize the applications of SOFC in various fields, it is essential to achieve high durability of stacks. The most technical feasible approach for scaling up the fuel cell is the use of tubular cell stack that could provide long term durability and high mechanical strength. Decreasing the operating temperature of the SOFC is necessary. Thus, fuel cell research should be focused on the development of intermediate-temperature (500–700 °C) SOFCs. In addition, modification of the anode by adding another metal or oxide to inhibit carbon formation and promote reforming/electrochemical oxidation reactions could help to develop highly durable fuel cell stacks.

- FTIR-ATR technique is capable of observing the IR-active species in an aqueous environment that is beneficial in determining the reaction pathways to synthesize different nanostructures of PANI. Moreover, in situ FTIR-ATR technique can be used to investigate other polymerization reactions in liquid phase, for instance, the in situ polymerized polypyrrole.
BIBLIOGRAPHY


95. Enhancing, S., Energy & Environmental Science.


98. Li, J., et al., **(La0.74Bi0.10Sr0.16)MnO3–δ–Ce0.8Gd0.2O2–δ cathodes fabricated by ion-impregnating method for intermediate-temperature solid oxide fuel cells.** Journal of Power Sources, 2009. 188(2): p. 453-457.


100. Jiang, S.P., et al., **Nanostructured palladium–La0.75Sr0.25Cr0.5Mn0.5O3/Y2O3–ZrO2 composite anodes for direct methane and ethanol solid oxide fuel cells.** Journal of Power Sources, 2008. 185(1): p. 179-182.


167. Nguyen, T.L., et al., Fabrication and Characterization of Anode-Supported Tubular SOFCs with Zirconia-Based Electrolyte for Reduced Temperature


APPENDICES
APPENDIX A

SELECTIVE DEPOSITION OF CERIA

This study was conducted for the candidacy exam. Hypotheses and proposed study is as following:

A.1 Hypotheses

_Hypothesis 1:_ The Particle size of ceria would affect the electrochemical oxidation activity of Ni-YSZ solid oxide fuel cell anode.

_Basis:_ The electrochemical catalytic activity of ceria depends strongly on particle size that can be controlled by the synthesis methods [1]. The best performance is obtained when the added ceria is not sintered to high temperatures [2].

The hypothesis can be tested by conducting the following tasks:

Task 1: Impregnating the cells using cerium (III) acetylacetonate hydrate and cerium (III) nitrate hexahydrate solutions, firing the cells, and taking the XRD of impregnated cells.

Task 2: Taking the SEM micrograph of Ni-YSZ anode before and after impregnation.
Hypothesis 2: Selective deposition of ceria on YSZ would improve oxygen ion diffusion. Blocking the Nickel with acetate would allow the ceria selective deposition that improves the electrochemical oxidation activity.

Basis:

Acetic acid is a site blocking agent and was adsorbed at 30 °C on Nickel surface. Acetic acid decomposed to hydrogen and acetate, and the acetate blocked the Nickel surface [3, 4]. Thus, the ceria only deposits on YSZ surface. Figure 2 shows the adsorbed acetate anion on the nickel surface.

![Figure A-1 Adsorbed acetate anion on the nickel surface.](image)

The approach is covering the nickel surface using site blocking effect of acetate, selective deposition of ceria on YSZ, and then desorption of the acetate groups from nickel surface using a heat treatment process. The hypothesis can be tested by conducting the following tasks:

Task 3: Taking the SEM/EDS micrograph of the surface and cross section of impregnated Ni-YSZ anode to figure out the location of the impregnated species.

Task 4: Taking the XRF of impregnated anode to figure out the location of the impregnated species.
A.2 Experimental

A 0.1M solution including cerium III acetylacetonate (Aldrich chemicals, USA) in an acetic acid/water solvent was prepared. The cerium III acetylacetonate was mixed with acetic acid and deionized water with the ratio of 2/1, heated to 120 °C, and held under reflux conditions for 1 h, resulting in a yellow colored solution. Three drops of the solution was impregnated on the reduced anode support, followed by drying for 3 min at 100° C and pyrolysis for 3 min at 350° C. This procedure was repeated ten times. The sample sintered at 800 °C for 30 min. A 0.1M solution including cerium nitrate hexahydrate (Aldrich chemicals, USA) in deionized water was prepared, and impregnation on a reduced SOFC performed according to the mentioned procedure. A 0.1 M solution including cerium nitrate hexahydrate (Aldrich chemicals, USA) in Acetic acid and deionized water with the ratio of 2/1 was prepared. Samples sintered in a furnace to 600 °C for 1 hr in air.

A.3 Preliminary results for hypothesis 1

Figure A-2 shows the XRD pattern of the reduced SOFC before and after impregnation with cerium III acetylacetonate. The presence of CeO$_2$ particles in the impregnated sample was confirmed by the XRD method. Ni diffraction peaks weakened after the impregnation. Table A-1 lists the crystal size of different samples. Figure A-3 shows the impedance spectra of fuel cell before and after impregnation with CeAcAc (loading: 1.87 wt. %) operated at 750 °C in H$_2$/Ar (100 sccm, 50 vol% H$_2$).
Figure A-2 XRD patterns of Ni-YSZ anode and impregnated samples

Table A-1 Crystal size of different samples

<table>
<thead>
<tr>
<th>Crystal size</th>
<th>Reduced Cell</th>
<th>Imp. with Ce(NO$_3$)$_2$</th>
<th>Imp. with CeAcAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>-</td>
<td>13 nm</td>
<td>16 nm</td>
</tr>
<tr>
<td>YSZ</td>
<td>38 nm</td>
<td>36 nm</td>
<td>21 nm</td>
</tr>
<tr>
<td>Ni</td>
<td>38 nm</td>
<td>44 nm</td>
<td>29 nm</td>
</tr>
</tbody>
</table>

Figure A-3 (a) SEM of the CeAcAce impregnated cell; (b) SEM of the Ce(NO$_3$)$_2$ impregnated cell.
A.4 Preliminary results for hypothesis 2

EDX mapping of the impregnated surface (Figure A-4) exhibited that ceria has deposited on YSZ selectively. EDX mapping of the cross section (A-5) showed that most of the ceria is deposited on the surface, and a small amount of Ceria has diffused to the internal layers of anode support. EDX mapping of the deep cross section (Figure A-6) confirmed that the ceria deposition on the YSZ and Nickel in the internal layers of anode support is not selective. Figure A-7 shows the XRF mapping of the surface of impregnated cell with 0.1M cerium (iii) acetylacetonate solution. It can be seen in Figure A-7 that ceria has deposited on YSZ selectively.

Figure A-4 EDX mapping of the surface of impregnated anode with 0.1M cerium (iii) acetylacetonate impregnated solution.
Figure A-5 EDX mapping of the cross section of 0.1M cerium (iii) acetylacetonate impregnated anode.

Figure A-6 EDX mapping and SEM of deep cross section (40 µm) of anode.
Figure A-7 XRF mapping of the surface of impregnated cell with 0.1M cerium (iii) acetylacetonate solution.

A.5 Future studies

Task 5: Investigating the effects of molar concentration of solutions, firing temperature and dwelling time on the SOFCs electrochemical performance.

Task 6: Testing the long-term operation of impregnated cells in methane to investigate the effect of impregnation on durability of the cells.

Task 7: Investigating how the impregnated species affect their final location and performance.

Task 8: Investigating the long-term operation of impregnated cells in methane to investigate the effect of impregnation on durability of the cells.
A.6 References


APPENDIX B

COMPARATIVE STUDY OF SUCCESSFUL FABRICATION RATE OF SOFC

Cracking of the button cells during fabrication or firing has not been discussed in the literature. Cracking of the cells during testing has been sporadically reported. The results of comparative studies of the successful fabrication rate for fuel cell batches varying fabrication parameters are presented here:

B.1 Effect of the slip mixing time

The effect of the slip mixing time was studied on the survival rate of the produced cells. Two anode support slips prepared with 24 (AN1) and 10 hr (AN2) of mixing times. The specifications of fabricated cells from AN1 and AN2 are listed in Table B-1. Decreasing the mixing time from 24 to 10 hr decreased the overall survival rate of the cells from 60% to about 20%. Lower survival rate of the AN2 can be attributed less homogeneity of the tape and more cracked fuel cells.

Table B-1 Specification of fabricated fuel cells with 24 and 10 h mixing time of slips (green diameter: 22 mm).

<table>
<thead>
<tr>
<th>AN</th>
<th>#cut</th>
<th>Green Thk. (µm)</th>
<th>Di. (mm) after firing</th>
<th>Thk. (µm) after firing</th>
<th># good cells after firing</th>
<th>Shrinkage</th>
<th>Survival Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN1</td>
<td>20</td>
<td>986</td>
<td>18</td>
<td>874</td>
<td>12</td>
<td>18.2 %</td>
<td>60 %</td>
</tr>
<tr>
<td>AN2</td>
<td>12</td>
<td>934</td>
<td>19</td>
<td>852</td>
<td>5</td>
<td>13.6 %</td>
<td>42 %</td>
</tr>
</tbody>
</table>
B.2 Thermal compatibility of the layers

Thermal stress is a critical factor in the fabrication development of planar solid oxide fuel cells (SOFCs), which can be controlled by thermal compatibility of the fuel cell components. Table B-2 exhibits the successful fabrication rate, and testing results of batches with NiO/8YSZ interlayer and NiO/8YSZ+10SCZ Interlayer. Replacing 50% of the 8YSZ in the interlayer with 10SCZ improved the successful rate of fuel cell fabrication by increasing the thermal expansion compatibility between the cell components. Figure B-1 shows a large number of crack-free fuel cells fabricated with NiO/8YSZ+10SCZ Interlayer suggesting the feasibility of SOFC mass production by co-tape casting.

Figure B-1 Crack-free fuel cells fabricated with NiO/8YSZ+10SCZ Interlayer fabricated in one batch.
Table B-2 Average maximum current density of fuel cell batches prepared with different 8YSZ interlayer and composite interlayer (8YSZ+10SCZ).

<table>
<thead>
<tr>
<th>Batch</th>
<th>Interlayer (NiO/8YSZ/10SCZ)</th>
<th>Current density (mA/cm²)</th>
<th>OCV (mV)</th>
<th>#Tested Cells</th>
<th>Successful Fabrication Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Avg</td>
<td>Max</td>
<td>Min</td>
<td></td>
</tr>
<tr>
<td>8YSZ INT</td>
<td>63/37/0</td>
<td>675</td>
<td>835</td>
<td>380</td>
<td>967</td>
</tr>
<tr>
<td>Comp. INT</td>
<td>63/18.5/18.5</td>
<td>635</td>
<td>1200</td>
<td>295</td>
<td>945</td>
</tr>
</tbody>
</table>

B.3 Pore former content of the anode interlayer

Table B-3 presents the successful fabrication rate of fuel cell batches with 2, 4, and 6 wt.% pore-former in the interlayer. Increasing the amount of pore-former from 2 to 6 wt.% in the anode interlayer decreased the successful fabrication rate of fuel cells by 40%.

Table B-3 Specifications and successful fabrication rate of fuel cell batches (10SCZ electrolyte, 8 µm) prepared with different pore-former content of 10 µm anode interlayer (NiO/10SCZ : 63/37).

<table>
<thead>
<tr>
<th>Batch #</th>
<th>Interlayer (NiO/10SCZ)</th>
<th>Successful Fabrication Rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>130916</td>
<td>10SCZ / 8</td>
<td>82 (40 of 49)</td>
</tr>
<tr>
<td>131004A</td>
<td>10SCZ / 8</td>
<td>54 (22 of 41)</td>
</tr>
<tr>
<td>131006</td>
<td>10SCZ / 8</td>
<td>38 (13 of 34)</td>
</tr>
</tbody>
</table>

B.4 Ball milling the pore-former

Table B-4 presents the successful fabrication rate of batches with ball milled pore-former and non ball milled pore-former. Wet and dry ball milling of the pore-former with NiO-SCZ powder for 2, and 1 h decreased the fabrication survival rate by 25%.
Table B-4 Specifications and successful fabrication rate of fuel cell batches prepared with 4 wt% ball milled and 4 wt% non ball milled pore-former of 10 μm interlayer.

<table>
<thead>
<tr>
<th>Batch #</th>
<th>Interlayer PF wt.%</th>
<th>Successful Fabrication Rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>131004A</td>
<td>4 %, non ball milled</td>
<td>54 (22 of 41)</td>
</tr>
<tr>
<td>131004B</td>
<td>4 %, ball milled</td>
<td>28 (11 of 39)</td>
</tr>
</tbody>
</table>

B.5 Particle size of the pore-former

Table B-5 lists the successful fabrication rate of batches containing pore-formers with different particle sizes: PH-105 (particle size: 20 μm), and PH-301 (particle size: 50 μm). Comparison of the results shows that the particle size of the pore-former was not a governing factor for the successful fabrication rate.

Table B-5 Specifications and successful fabrication rate of fuel cell batches prepared with different particle size of former for the interlayer.

<table>
<thead>
<tr>
<th>Batch #</th>
<th>Interlayer PF wt. %</th>
<th>Successful Fabrication Rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>130802A</td>
<td>PH-105 (20 μm), 2 %</td>
<td>67 (16 of 21)</td>
</tr>
<tr>
<td>130825</td>
<td>PH-301 (50 μm), 2 %</td>
<td>77 (17 of 22)</td>
</tr>
</tbody>
</table>

B.6 Pore-former content of the anode support

Table B-6 presents the successful fabrication rate of fuel cell batches with 11, 15, and 20 wt.% pore-former in the anode support. Increasing the amount of pore-former in the anode support from 11 to 15 wt.% decreased the successful fabrication rate by about 25 wt.%. Increasing the pore-former content to 20% caused the cracking of all the fuel cells.
Table B-6 Specifications and successful fabrication rate of fuel cell batches prepared with different pore-former content of anode support.

<table>
<thead>
<tr>
<th>Batch #</th>
<th>Anode support PF, wt.%</th>
<th>Successful Fabrication Rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>130916</td>
<td>PH-301: 11</td>
<td>82 (40 of 49)</td>
</tr>
<tr>
<td>131012A</td>
<td>PH-301: 15</td>
<td>24 (16 of 56)</td>
</tr>
<tr>
<td>131012B</td>
<td>PH-301: 20</td>
<td>0 (0 of 15)</td>
</tr>
</tbody>
</table>

B.7 Thickness of the anode interlayer

Table B-7 shows the successful fabrication rate for the fuel cell batches with different anode interlayer thicknesses. Decreasing the 8YSZ anode interlayer thickness from 25 to 15 µm did not decrease the successful fabrication rate.

Table B-7 Specifications and successful fabrication rate of fuel cell batches with 8YSZ interlayer prepared with different interlayer thicknesses.

<table>
<thead>
<tr>
<th>Batch #</th>
<th>Interlayer</th>
<th>Successful Fabrication Rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>121218A</td>
<td>25</td>
<td>72 (22 of 27)</td>
</tr>
<tr>
<td>121218B</td>
<td>20</td>
<td>69 (27 of 24)</td>
</tr>
<tr>
<td>121218C</td>
<td>15</td>
<td>72 (16 of 21)</td>
</tr>
</tbody>
</table>

B.8 Thickness of the anode support

Table B-8 exhibits the successful fabrication rate of fuel cell batches with 740 and 900 µm anode support thicknesses. Decreasing the anode support thickness decreased the successful fabrication rate by 15%.

Table B-8 Specifications and successful fabrication rate of fuel cell batches prepared with different anode support thicknesses.

<table>
<thead>
<tr>
<th>Batch #</th>
<th>Anode support Thk.</th>
<th>Successful Fabrication Rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>130825</td>
<td>740 µm</td>
<td>68 (17 of 22)</td>
</tr>
<tr>
<td>130916</td>
<td>900 µm</td>
<td>82 (9 of 49)</td>
</tr>
<tr>
<td>Fabrication parameter</td>
<td>Effect</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Mixing time of the slip</td>
<td>Increasing the horizontal rotary ball milling time from 10 to 24 hr increased the successful fabrication rate by 18% through homogenizing the anode support slip.</td>
<td></td>
</tr>
<tr>
<td>Thermal compatibility of the layers</td>
<td>Thermal compatibility of the layers was increased by replacing the 8YSZ interlayer with 10SCZ-8YSZ interlayer resulting in 14% improvement of the successful fabrication rate.</td>
<td></td>
</tr>
<tr>
<td>Pore former content of the anode interlayer</td>
<td>Increasing the pore former content of interlayer from 2 to 6 wt % decreased the successful fabrication rate by 40 %.</td>
<td></td>
</tr>
<tr>
<td>Ball milling of the pore-former</td>
<td>Ball milling of the pore-former with NiO-SCZ powder led to about 25% decrease in the successful fabrication rate compared to the non ball milled pore-former.</td>
<td></td>
</tr>
<tr>
<td>Particle size of the pore-former</td>
<td>Increasing the pore-former particle size from 20 to 50 µm did not decrease the successful fabrication rate.</td>
<td></td>
</tr>
<tr>
<td>Pore former content of the anode support</td>
<td>Increasing the pore-former content of the anode support from 11 to 15 wt.% decreased the successful fabrication rate by about 25 wt.%. The pore-former content of 20% led to cracking of all the fuel cells.</td>
<td></td>
</tr>
<tr>
<td>Thickness of the anode interlayer</td>
<td>Decreasing the interlayer thickness down to 5 µm did not affect the successful fabrication rate.</td>
<td></td>
</tr>
<tr>
<td>Thickness of the anode support</td>
<td>Decreasing the anode support thickness decreased the successful fabrication rate by about 15%...........................................................................</td>
<td></td>
</tr>
</tbody>
</table>