

The Impact of Redox Cycling on Nickel Cermet Anodes for Solid Oxide Fuel Cells

By: Bowen Song

Advisor I: Prof. Nigel P Brandon

Advisor II: Dr. Enrique Ruiz-Trejo

October 2018

'Man's dearest possession is life.

It is given to him but once, and he must live it so as to feel no torturing regrets for wasted years, never know the burning shame of a mean and petty past; so live that, dying, he might say: all my life, all my strength were given to the finest cause in all the world.'

-- How the Steel Was Tempered

Nikolai Ostrovsky

ABSTRACT

Fuel Cells comprise a broad range of technologies that offer more efficient ways of converting fuel into electricity. The solid oxide fuel cell (SOFC) is a promising energy conversion device, which offers a high operating efficiency alternative to combustion technology for electricity production. Nickel-Yttria-stabilized zirconia (Ni-YSZ) cermets are a commonly used anode material with relatively low cost and good performance.

In order to understand the interaction between microstructural, mechanical properties and electrochemical changes of Ni-YSZ electrodes after redox cycling, the impact of redox cycling on electrode degradation has been studied, including: conventional Ni-YSZ, Ni infiltrated YSZ scaffolds, and Ni infiltrated YSZ fibre scaffolds in Chapters 4, 5 and 6. It has been found that, due to the nickel volume change during redox cycling, the YSZ framework breaks down in conventional Ni-YSZ electrodes, inhibiting ionic transport and leading to significant electrochemical degradation; in order to enhance the YSZ framework stability, the sintering temperature impact on YSZ scaffold has been studied based on balancing the mechanical properties and porosity. Then the selected YSZ scaffold was infiltrated with nickel to test its redox cycling stability. It was found that the YSZ scaffold kept a stable structure, while the infiltrated nickel migrated out to the electrode top surface, leading to a significant nickel content loss within the electrode. This indicates that the nickel dewetting behavior plays an important role during anode degradation. A multi-porosity layered electrode, comprising a top fiber layer and scaffold base layer, was introduced to eliminate the triple phase boundary loss when the nickel moved to the electrode top surface. In this structure, the scaffold layer contributes to a high electrochemical performance at a lower temperature compared to

conventional analogues. The fiber layer improved electrochemical stability due to its highly porous and larger pore size compared to the YSZ scaffold layer.

In Chapter 7, Ni dewetting behavior was also studied utilizing a new methodology developed in this work, based on 2D Ni films on YSZ electrolytes. By in-situ observation, it was found that both electrochemical impedance spectroscopy measurement (EIS), electrode simulation, and experimental Environmental-SEM (E-SEM) images consistently identified a maximum in active triple phase boundary (aTPB) length before the start of Ni de-percolation. Results reveal that neither evaporation-condensation nor surface diffusion of Ni are the main mechanisms of dewetting over the temperature range 560-800 °C. Rather, the energy barrier for pore nucleation within the dense Ni film appears to be the most important factor. The proposed methodology allows the prediction of Ni dewetting behavior and its impact on the electrochemical degradation of SOFC anodes under a variety of conditions, unparalleled to current methods.

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere appreciation to my two supervisors, Prof. Nigel Brandon and Dr. Enrique Ruiz Trejo, who took me on as their student three years ago, for their valuable guidance, encouragement and excellent advice throughout my PhD studies in Imperial College London.

I would particularly thank Prof. Nigel Brandon for the wonderful opportunities he has made possible for me to present my work in a number of national and international workshops and conferences. My special gratitude also goes to Dr. Enrique Ruiz Trejo for his kind support and discussions throughout my PhD research. Dr. Antonio Bertei, Dr. Sam Cooper and Dr. Xin Wang are highly acknowledged for the helpful discussion and collaboration during later stage of my PhD.

The colleagues and staff of the Department of Earth Science and Engineering (particularly in the Electrochemical Science and Engineering Group) at Imperial College London are also acknowledged for their technical assistance: Dr. Zhangwei Chen for extensive help in nanoindentation. Special thanks are due to Dr. Vladimir Yufit, Dr. Farid Tariq, and Dr. Kristina Kareh for their help on FIB-SEM, 3D structure analysis and valuable discussions; Dr. Victoria Bemmer for AFM; Mr. Richard Sweeney for XRD. Mr. Gary Jones and Mr Graham Nash for help and discussions with lab work and equipment manufacturing issues. The help and training received from staff in materials characterisation laboratory for SEM, XRD, FIB and sample preparations are also appreciated.

Last but not least, my deepest gratitude goes to my dearest parents, wife, younger brother and my cutest cat Coco and Dodo, without whose love, encouragement, support and sharing this work would not have been possible.

My gratitude also goes to some of my friends who are currently or were previously studying or working together, for their constant spiritual encouragement. The Chinese Scholarship Council and Bank of Parents are gratefully acknowledged for financial support of my life and studies here.

DECLARATION OF ORIGINALITY

I herewith declare that the work in this thesis is my own, and that all else has been appropriately referenced.

Bowen Song

DECLARATION OF COPYRIGHT

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Bowen Song

CONTENT

Abstract.....	3
Acknowledgements.....	5
Declaration of Originality.....	7
Declaration of Copyright.....	8
Content	9
List of Figures	15
List of Tables	27
List of Abbreviations	29
Chapter 1 Introduction.....	30
1.1 Global background	30
1.2 Fuel cell Technology and Application.....	31
1.3 Solid Oxide Fuel Cells	33
1.4 Research Focus.....	33
1.5 Research Objectives	35
1.6 Thesis Outline	36

Chapter 2 Literature Review	38
2.1 Operating Principles of SOFCs	38
2.2 Fundamentals OF SOFCs	40
2.2.1 Anode	41
2.2.2 Electrolyte	43
2.2.3 Cathode	45
2.2.4 Cell Configuration of SOFCs	46
2.2.5 Triple Phase Boundaries	50
2.3 Ni-YSZ Material Operating Issues	52
2.3.1 Nickel dewetting	53
2.3.2 Redox Cycling Issues	56
2.4 Ni-YSZ Material Characterisation	58
2.4.1 Mechanical Properties of Ni-YSZ.....	58
2.4.2 Microstructure of Ni-YSZ.....	60
Chapter 3 Experimental Methods	63
3.1 Cell Manufacturing.....	63
3.1.1 Ink Preparation	63

3.1.2	Electrode Manufacturing	64
3.1.3	YSZ Scaffold and Conventional anode Sintering	70
3.2	Material Characterisations	73
3.2.1	Electrochemical Impedance Spectroscopy (EIS) Measurement and Analysis ...	73
3.2.2	Microstructure Characterisation	76
3.2.3	Mechanical Characterisation	82
3.2.4	Microstructure 3D Reconstruction	87
3.3	Chapter Summary.....	94
Chapter 4	Characterisation of Ni-YSZ Anode Degradation Upon Redox Cycling	95
4.1	Redox cycling procedure	95
4.2	Electrochemical Degradation During and After Redox Cycling.....	96
4.3	Microstructural Characterisation	100
4.4	Mechanical properties change upon redox cycling	105
4.5	Microstructure analysis based on SEM and Nano-indentation response	109
4.6	Chapter Summary.....	114
Chapter 5	Quantitative Study of Redox Cycling Impact on Mechanically Improved Ni Infiltrated YSZ Scaffolds	116

5.1	Sintering Temperature Study for YSZ Scaffold selection based Mechanical Properties and Porosity changes	116
5.2	Material degradation upon redox cycling	119
5.2.1	Electrochemical degradation	119
5.2.2	Microstructure changes	123
5.2.3	Mechanical properties change on redox cycling and comparison with the conventional Ni-YSZ anode.....	125
5.3	Chapter Summary.....	126
Chapter 6 Characterization of the Nickel Impregnated Yttria-stabilized Zirconia Fibre Scaffold Electrodes		
		128
6.1	Microstructure characterization	129
6.1.1	As-prepared NiO-YSZ Fibre Scaffold	129
6.2.2	As-reduced Ni-YSZ Fibre Scaffold	130
6.2.3	Aged Ni-YSZ Fibre Scaffold	132
6.2.4	Redox cycled Ni-YSZ Fibre Scaffold	134
6.2	Electrochemical performance	135
6.3	Quantitative analysis	138
6.4	Mechanical properties characterisation	142

6.5	Microstructure explanation for material stability	143
6.6	Chapter Summary.....	144
Chapter 7 Study of Ni Dewetting and Pore Formation from the 2D Ni-YSZ Electrode.....		146
7.1	Background of Ni Dewetting	146
7.2	Pre-experiment	148
7.3	Surface morphology evolution.....	150
7.3.1	High magnification images: morphology of Ni dewetting.....	150
7.3.2	Low magnification images: General behaviour of the Ni layer migration.....	152
7.4	Active TPB Estimation	154
7.4.1	Lattice model for TPB estimation	155
7.4.2	Wire model for TPB estimation	157
7.4.3	Active TPB density obtained from Image analysis.....	158
7.5	Electrochemical performance	160
7.6	Microstructure simulation	161
7.6.1	Nickel Wetting Angle and Dihedral Angle.....	161
7.6.2	Nickel Dewetting Simulation.....	163
7.7	Active TPB Comparison	167

7.8	Chapter Summary.....	169
Chapter 8 Conclusions and Future Work		172
8.1	Conclusions.....	172
8.2	Future Work	175
List of Publications		177
References		179

LIST OF FIGURES

Figure 1-1 World primary energy supply by source ¹	31
Figure 2-1 Schematic of H ₂ -O ₂ SOFC. The ceramic electrolyte is solid state. A nickel-YSZ cermet anode and a mixed conducting ceramic cathode provide the required thermal, mechanical, and catalytic properties at high SOFC operating temperature. Water is produced at the anode ¹⁸	39
Figure 2-2 Solid oxide fuel cell – planar design ³⁹	47
Figure 2-3 Cross section of three ceramic layers of a tubular SOFC from Westinghouse design ^{39,43,44}	49
Figure 2-4 sketch of the TPB in a Ni-YSZ material for SOFC application.....	50
Figure 2-5 TPBs presented in different types of structure. a) the TPBs observed in FIB-SEM cross-sectional images; b) TPB in 2D Ni-YSZ structure; c) the TPB observed from a conventional Ni-YSZ as-reduced sample; d) the TPB observed from a Ni infiltrated YSZ scaffold as-reduced sample. All images from this work.....	51
Figure2-6 Length scales of tomography techniques ¹¹⁴	61
Figure 3-1 A Schematic drawing shows the tape casting process used in laboratory for sample preparation; top view of the tape-cast electrode.	65
Figure 3-2 Presentation of a typical screen printing process, a) the principle of ink spreading process; b) the principle of the screen printing process.	67

Figure 3-3 Schematic illustration of the preparation of YSZ nanofiber films by electrospinning ¹²⁴ .	68
Figure 3-4 Impregnation of a porous scaffold. A metal nitrate solution is infiltrated into the scaffold. This is heated to decompose the nitrate to the oxide. The operation is then repeated several times. ⁶¹	69
Figure 3-5 Schematic presentation of nickel thin film sputtering.	70
Figure 3-6 2-stage process for sintering YSZ scaffold electrodes.	72
Figure 3-7 sintering temperature impact on the YSZ grain size, grain boundaries and porosity of the YSZ scaffolds. The initial YSZ inks are prepared with same YSZ particle size (<5 μm) and same amount of pore formers (10 wt%).	72
Figure 3-8 Schematic of the electrochemical test rig. The rig has a single fuel gas inlet and the arrows represent the fuel gas flow paths.	73
Figure 3-9 the nyquist plot of the impedance spectrum of a symmetrical Ni-YSZ electrode usually, shows one or more flattened semicircles, and the equivalent circuit model used for impedance analysis.	75
Figure 3-10 Schematic of SEM working principle; in the E-SEM, the sample holder functioned as the heating element.	77
Figure 3-11 Schematic of AFM working principle.	78
Figure 3-12 Schematic of FIB-SEM working principle and the illustration of sample milling steps.	79

Figure 3-13 Ni wetting angle measurement using FIB-SEM cross-sectional imaging.	81
Figure 3-14 Schematic of XRD working principle.....	82
Figure 3-15 Schematic of nanoindentation experiment set-up and working principle.	83
Figure 3-16 various components of a nanoindentation test cycle, h is displacement, P is loading force.	85
Figure 3-17 Compliance loading-unloading curves. From a nanoindentation experiment with maximum load P_{max} and depth beneath the specimen free surface h_{max} . The depth of the contact circle h_c and slope of the elastic unloading dP/dh allow specimen modulus and hardness to be calculated. h_r is the depth of the residual impression, and h_e is the displacement associated with the elastic recovery during unloading.	87
Figure 3-18 image processing in YZ direction, the presentation of the raw image stack, after aligning and after shearing.	88
Figure 4-1 Representation of the redox cycling procedure. Impedance spectra were taken during each reduction process as a function of time.	95
Figure 4-2 Impedance spectra recorded, within the frequency range $10^6 - 10^{-1}$ Hz, after 0, 5, 10, 15, 20 redox cycles at 800 °C, 2h after the introduction of wet 5 vol % H_2 , AR represents as-reduced, R5 represents 5 redox cycles, R10 represents 10 redox cycles and so on. The inset shows the equivalent circuit used to fit the results. R_1 , R_2 , R_3 represent the high-frequency intercept resistance, intermediate frequency resistance and low-frequency resistance	

respectively; CPE₂, CPE₃ represent constant phase element for the corresponding frequency⁹⁶.
96

Figure 4-3 Resistances as a function of time during the reduction process of redox cycling as from EIS fitting. The solid green line is a guide to the degradation trend. The cross marks represent the time scale of the samples used for 3D tomography reconstruction. 98

Figure 4-4 Active TPB density vs time for different redox cycles as determined from 3D tomography (symbols) and EIS modelling (line). The error bars refer to the uncertainty in positioning the time scale of the reconstructed samples, due to the cooling time of the samples. Note that, differently from other samples, sample R20 refers to the end of the annealing time. 99

Figure 4-5 a) Top-surface SEM images of an as-reduced Ni-YSZ electrode showing the detachment between Ni and YSZ caused by Ni volume shrinkage after reduction, leading to a relatively large space in between; b) Top-surface SEM images of Ni-YSZ electrodes after 5 redox cycles showing the crack along the YSZ grain boundaries, with an approximate gap of 10nm, and the Ni nanoparticles; c) Top-surface SEM images of Ni-YSZ electrodes after 10 redox cycles showing YSZ grain detachment from its framework and Ni surface roughness, agglomerated nickel particles. 101

Figure 4-6 representation of the 3D reconstructed microstructure of the as-reduced Ni-YSZ, with Ni in transparent green, YSZ in transparent red and where the green line indicates the active TPBs. 102

Figure 4-7 Left: SEM images of five redox cycled samples. Middle: FIB-milled cross-sectional micrographs of Ni-YSZ anodes after different redox cycles. Light grey: Ni, dark grey: YSZ, and black: pore. Right: the segmented images corresponding to the left side. Blue: Ni, green: YSZ, grey: pore.....	104
Figure 4-8 a) Load- depth curves for Ni-YSZ anodes after different numbers of redox cycles as obtained from nanoindentation, the inset shows the area been indented on the as-reduced sample ; b) Hardness vs. numbers of redox cycles for the tested Ni-YSZ anodes; c) and Elastic modulus vs. numbers of redox cycles for the tested Ni-YSZ anodes. The standard deviations are obtained statistically from over 200 measurements per sample.	107
Figure 4-9 Elastic modulus vs porosity of reduced samples. The results of fitting using exponential and free linear model are represented as blue and black lines, respectively, while the red line corresponds to the exponential fit with a different porosity.	109
Figure 4-10 SEM top images of conventional Ni-YSZ anode after 10 redox cycles. a) The red circles highlight the YSZ cracking after redox cycling, resulting in a loss in ionic conductivity; b) and c) the high magnification images showing nickel expansion resulting in the YSZ framework break down.	110
Figure 4-11 images of nanoindentation on the Ni-YSZ samples after 10 redox cycles. a) shows the local region of the original sample from SEM image; b) shows local material deformation after indentation.....	111

Figure 4-12 images of nanoindentation on the as-reduced Ni-YSZ. a) shows the indentations from the SEM image; b & c) show the local material deformation before and after the indentation respectively.	112
Figure 4-13 Hypothesis establishing a relationship between the Ni-YSZ fracture and the loading curve during nanoindentation.	113
Figure 5-1 SEM images of YSZ scaffolds after 2 hours of sintering at different temperatures.	117
Figure 5-2 YSZ thickness (measured by SEM), porosity (based on the weight gain calculation), elastic modulus and hardness of the YSZ scaffold as a function of sintering temperature, the red points represented the measurement results of tape-cast conventional Ni-YSZ sintered in 1200 °C.	118
Figure 5-3 Ohmic resistance, Electrochemical reaction polarisation resistance and Diffusion resistance as a function of time during the reduction process (wet 5 vol % H ₂) of redox cycling from EIS fitting for the Ni-YSZ scaffold, 550 °C; Comparison of stabilized electrochemical reaction polarisation resistance between conventional Ni-YSZ and Ni-YSZ scaffold, showing that the scaffold material has a good ability to work at lower temperatures with higher performance than Ni-YSZ prepared by powder mixing and sintering (conventional).	121
Figure 5-4 visual model of the loss of aTPB by YSZ framework break down. After several redox cycles, the Ni agglomeration accompanied by its volume expansion during oxidation could damage the YSZ structure in conventional Ni-YSZ cermets, but because the YSZ scaffold was stronger, it offers more resistance to mechanical damage from Ni redox volume change..	122

Figure 5-5 Top view of YSZ scaffold after Ni infiltration: a) As- prepared scaffold NiO-YSZ; b) As-reduced scaffold Ni-YSZ; c) the Scaffold Ni-YSZ after 5 redox cycles; d) Scaffold Ni-YSZ after 15 redox cycles.....123

Figure 5-6 Cross-sectional view of YSZ scaffold after Ni infiltration, near the YSZ substrate: a) As- received scaffold NiO-YSZ; b) As-reduced scaffold Ni-YSZ; c) the Scaffold Ni-YSZ after 5 redox cycles; d) Scaffold Ni-YSZ after 15 redox cycles; e) FIB-SEM images shows the Ni movement after 15 redox cycles, the brighter colour indicates Ni, grey is YSZ, black is pore. 124

Figure 5-7 Mechanical properties of Ni-YSZ anodes. The redox cycling degradation trend was compared between conventional Ni-YSZ and Ni-YSZ scaffold. 125

Figure 6-1 the microstructural images for as-received NiO-YSZ Fibre Scaffold, after 12 infiltrations and decomposition from $\text{Ni}(\text{NO}_3)_2$. a) FIB-SEM tomography image and 3D reconstructed structure, blue is NiO and yellow YSZ; b) 3D reconstructed images show transparent NiO covering YSZ structure. C) SEM images of NiO-YSZ fibre scaffold top view, shows NiO nanoparticles covering the YSZ fibre and filling the pores.....130

Figure 6-2 the microstructure for the as-reduced Ni-YSZ fibre scaffold: a) the electrode top surface with a single fibre, where the light blue represents nickel particles and yellow represents the YSZ structure. b) Bulk analysis for Ni particle size, presented with a colour code, and the active triple phase boundaries are highlighted with a green line, and YSZ in transparent yellow (due the image resolution limitation, particles below 50 nm could not be presented); c) SEM images for as-reduced Ni-YSZ fibre scaffold top view and cross-sectional view, with indication of the 3D-reconstruction region for all samples. 131

Figure 6-3 the microstructure of the aged Ni-YSZ fibre scaffold, 3000 min, 600 °C: a) the electrode top surface, the grey represents nickel particles and yellow represents YSZ structure. b) bulk analysis for Ni particle size are presented with colour code and the active triple phase boundaries are highlighted in blue, and the YSZ in transparent yellow c) SEM images for Ni-YSZ fibre scaffold top view. 133

Figure 6-4 the microstructure of the Ni-YSZ fibre scaffold after 20 redox cycles at 600 °C: a) bulk analysis for Ni particle size are presented with colour code and the active triple phase boundaries are highlighted in blue, and the YSZ in transparent yellow; b) FIB-SEM cross-sectional images of the samples, showing nickel agglomeration and internal pore after 20 redox cycles; c) SEM images of the sample top surface. 134

Figure 6-5 a) The specific area resistances for 20 redox cycles of the Ni-YSZ fibre scaffold symmetrical cell operated at 600 °C in diluted wet hydrogen (5% H₂, 95% N₂); b) the specific area resistances for in-situ isothermal annealing of the Ni-YSZ fibre scaffold symmetrical cell operated at 600 °C in diluted wet hydrogen (5% H₂, 95% N₂); c) Comparison of the stabilized electrochemical reaction polarisation resistance between conventional Ni-YSZ¹⁰² and Ni-YSZ scaffold¹⁴⁶ and Ni-YSZ Fibre-Scaffold, measured at 800 °C, 550 °C and 600 °C, respectively. 137

Figure 6-6 Microstructure comparison between as-reduced Ni-YSZ fibre scaffold and aged Ni-YSZ fibre scaffold. a) Ni particle size distribution, Ni neck size distribution and Ni particle distribution from the electrolyte to top surface. b) YSZ particle size distribution, YSZ neck size distribution. c) Pore size distribution, Ni neck size distribution and pore Ni particle distribution from the electrolyte to top surface. d) Active TPB distribution. 141

Figure 6-7 the mechanical properties of YSZ fibre layer from the electrode surface, 20 measurements were obtained for each condition. a) The nanoindentation measurement results based on a constant loading force. The elastic modulus and hardness have been compared with the conventional Ni-YSZ electrode and Ni-YSZ scaffold electrode; b) the nanoindentation measurement results based on the maximum loading depth.	142
Figure 6-8 sketches coupled with SEM images explaining the nickel control mechanism difference between the Ni-YSZ scaffold and Fibre-Scaffold.	143
Figure 7-1 a) the conventional Ni-YSZ observed before and after 10 redox cycling; b) The SEM image shows the grey region (from a)) in high magnification.	147
Figure 7-2 a) Map of the YSZ surface as measured by AFM before Ni deposition. b) Depth of the YSZ grain boundary measured along the line shown in a). A fictitious nickel layer of 40 nm is also illustrated in b).	148
Figure 7-3 XRD of as-prepared and aged 100 nm Ni thin film on YSZ substrate. The indicated peak is from Ni, all the rest are YSZ.	149
Figure 7-4 the images sequence of the change in charging effect observed from E-SEM during heating up, the bright colour indicates those nickel particles in an amorphous state, and the darker region indicates the nickel crystallization process is finished, where amorphous nickel nanoparticles become the thin layer.	150
Figure 7-5 experimental results of zirconia supported nickel film top surface morphology at 560 °C and 600 °C in the controlled gas mixture. Light blue represents the nickel particle	

boundaries at the initial time and the background SEM image is the real morphology at the ending time, as indicated under each image.....151

Figure 7-6 TPB density, Ni area coverage ratio and Ni percolation ratio data based on segmented images. a) Data obtained from HT-ESEM image series recorded at $T=560\text{ }^{\circ}\text{C}$. b) Data obtained from HT-ESEM image series recorded at $T=600^{\circ}\text{C}$. c) Superposition of data at $T=560\text{ }^{\circ}\text{C}$ (blue lines) and $T=600\text{ }^{\circ}\text{C}$ (red lines) after scaling the time of the data at $T=560\text{ }^{\circ}\text{C}$ according to the ratio of times corresponding to a coverage fraction of 0.63. The vertical dashed lines indicate the start of the agglomeration stage. 153

Figure 7-7 Lattice-based model. a) A random realisation of a square lattice, with clusters of percolated green pixels connected to the external boundaries and isolated red pixels. In this presented case: $d = 20$, $\phi = 0.5$, $a = 200/26 \approx 7.69$, $\gamma = 159/200 = 0.795$. b) Percolation fraction γ as a function of coverage fraction ϕ for different side lengths d . c) Normalised mean cluster area a/d^2 as a function of coverage fraction ϕ for different side lengths d 155

Figure 7-8 the image segmentation and wire based model used for aTPB statistics. The green line represents the wire current collector located at the different region with different width. The white area is the percolated nickel in contact with the current collector and the red line surrounding the white particle represents the corresponding active triple phase boundaries. 157

Figure 7-9 the aTPB estimation based on wire model and lattice model for the two samples recorded within wet 5 vol % H_2 at $T = 560\text{ }^{\circ}\text{C}$ (left) and $T = 600\text{ }^{\circ}\text{C}$ (right). The dark blue line

shows the total TPB, light blue line shows the calculated results from wire model and green line represent the calculation results from the lattice model.....159

Figure 7-10 a): the Ohmic resistance and electrochemical reaction polarisation resistance as a function of time as measured from impedance spectroscopy data at 600 °C; b): the active area ratio ω_{act} and active TPB density per unit of electrode area ρ_{aTPB} or active percolating area ρ_{aTPB}^{act} obtained according to Equations 12 and 13, respectively.....160

Figure 7-11 a) SEM images 2D Ni-YSZ after degradation at 600 °C, with dihedral angle measurements. Dihedral angle= $152^{\circ} \pm 7.2^{\circ}$; b) SEM images 2D Ni-YSZ after degradation at 500 °C, with dihedral angle measurements. Dihedral angle= $129^{\circ} \pm 10.2^{\circ}$ 162

Figure 7-12 FIB-SEM cross-sectional images for Ni wetting angle measurements. 163

Figure 7-13 Schematic representation of surface diffusion and fast diffusion models. a) Mass transport takes place along the nickel surface, step-by-step, until the matter voxel reaches the low energy vacant site; b) the high energy matter voxel can jump into the low energy vacant site in a single step; c) a grain boundary migration model presented that the higher energy voxels region (light grey and dark grey) change to lower energy voxels region (black) near the triple grain junction.....164

Figure 7-14 a) the initial microstructure of a representative area of nickel film b) the simulated microstructure evolved by using the surface diffusion model when nickel coverage is reduced to about 60%; c) a slightly larger area of nickel film than a), d) the simulated microstructure evolution from c) by employing a fast diffusion model, at this point the nickel coverage area is also reduced to about 60%.....165

Figure 7-15 Microstructural parameters (pore size, Ni size and TPB density) at the Ni percolation threshold obtained by different simulation models and evaluated in experimental E-SEM observations. In this graph, TPB values were calculated on a subset of the image area, thus they differ from those evaluated on the large dataset due to statistical variation. 167

Figure 7-16 the active TPB density obtained from 3D analysis and 2D image analysis on simulated microstructure evolution, compared with the experimental results (2D analysis).
.....168

LIST OF TABLES

Table 1-1 Comparison between different fuel cells and their most common attributes ^{11,12} .	32
Table 2-1 Advantages and disadvantages of some alternative materials considered for use in the fabrication of SOFC anodes.	43
Table 2-2 Values of ionic conductivity and activation energy of zirconia stabilized with different cations ³⁰	45
Table 2-3 Summary of single cell configurations for single cell ⁴⁰	48
Table 2-4 Properties of nickel and nickel oxide molar mass, specific mass and molar volume ⁸⁷ :	57
Table 3-1 Parameters and experimental conditions used during EIS measurements.	74
Table 3-2 Summary of the nanoindentation conditions used in this study.	84
Table 4-1 Calculated microstructure parameters from the reconstructed 3D tomographic datasets of anodes with different numbers of redox cycles.	102
Table 4-2 Linear and exponential correlations of elastic modulus vs porosity. E_0 is the elastic modulus of the fully dense material, b is a porosity constant and p is fractional porosity. b^* is the porosity constant fitted in this study, considering the microstructure damage caused by redox cycling.	108

Table 5-1 Calculated microstructure parameters from the reconstructed 3D tomographic datasets of Ni-YSZ scaffold with different numbers of redox cycles. The datasets of conventional Ni-YSZ were taken from a previous study ¹⁰²	120
--	-----

Table 6-1 Calculated microstructure parameters from the reconstructed 3D tomographic datasets of Ni-YSZ Fibre Scaffold before and after isothermal annealing.....	138
---	-----

LIST OF ABBREVIATIONS

2D	two dimensional
3D	three dimensional
YSZ	yttria-stabilised zirconia
FIB	focused ion beam
TPB	triple phase boundary
aTPB	active triple phase boundary
TPBL	TPB length
XRD	X-ray diffraction
SOFC	solid oxide fuel cell
IET	impulse excitation test
PEMFC	polymer electrolyte membrane fuel cell
RT	room temperature
SEM	scanning electron microscopy

CHAPTER 1 INTRODUCTION

This Chapter introduces the background and the motivation of the project, including: global environmental issues and the energy challenge, fuel cell (FC) technology and its applications, the actual issues this study will address, and the objectives of the research work.

1.1 GLOBAL BACKGROUND

The dichotomy between energy usage and development is an endless topic in human history. With the knowledge to use fire and ability to burn biomass (wood, animal dung, charcoal), humans had an important source of heat that accelerated civilization. In the late 1880s, the Industrial Revolution exploded energy consumption and changed human development in almost every way. The ability of mass production was based on a growing energy consumption rate¹. In recent decades, as shown in Figure 1-1 World primary energy supply by source¹, global primary energy demand increased rapidly with its associated impact on/from economic and population growth. Consequently, with increasing concerns over air pollution and fossil fuel supply and distribution, a global trend towards developing 'green' energy has been clearly felt for the past two decades².

It has been recognized that the development and implementation of alternative energy technologies plays a key role in reaching the targets of decarbonising power generation³. Driven by this incentive, most of the research efforts have been used to improve the efficiency of current and renewable energy devices. Compared with other energy conversion technologies, fuel cells stand out by offering very high-efficiency electrical power generation and the ability to use a variety of fuels with low levels of associated emissions^{2,4}.

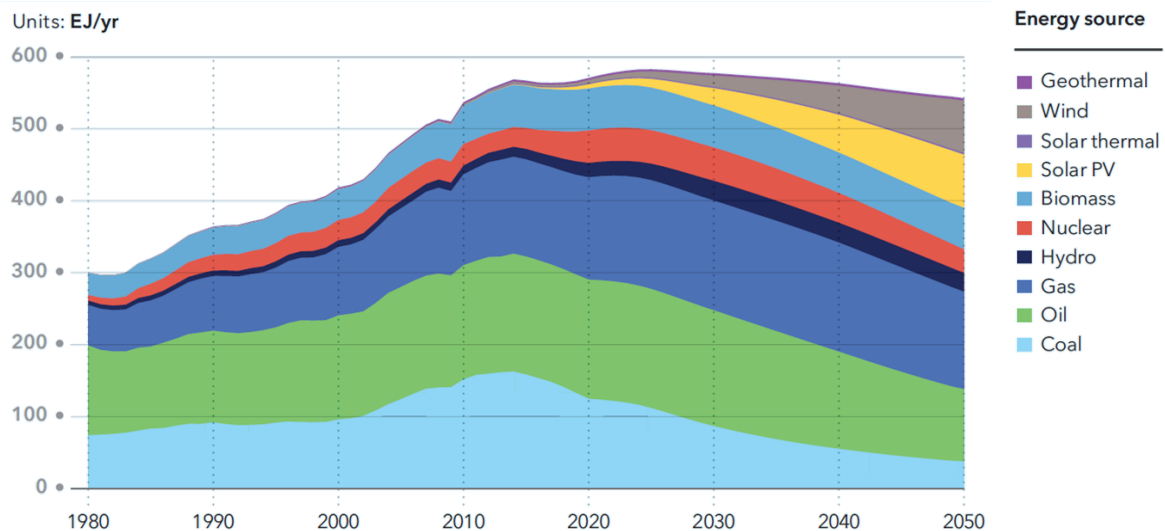


Figure 1-1 World primary energy supply by source¹.

1.2 FUEL CELL TECHNOLOGY AND APPLICATION

A fuel cell uses the chemical energy of hydrogen or another fuel to cleanly and efficiently produce electricity. If hydrogen is the fuel, electricity, water, and heat are the only products. Fuel cells are unique in terms of the scale of their potential applications; they can provide power for systems as large as a utility power station and as small as a laptop computer³.

Fuel cell technology has been developing since the early 20 century. In the late 1930s, Baur and Preis experimented with solid oxide electrolytes using materials such as zirconium, yttrium, cerium, lanthanum and tungsten oxide, at 1000 °C⁵. In the 1940s, in order to increase the electrolyte conductivity and mechanical strength, monazite sand was added to sodium carbonate, tungsten trioxide, and soda glass by Russian scientist Davtyan⁶. By the late 1950s, research on solid oxide fuel cell technology began to accelerate in the Netherlands, USA and some other developed countries. In 1962, researchers at Westinghouse experimented with a cell using zirconium oxide and calcium oxide⁷⁻⁹, which layed down the foundations for fuel

cell material development. Today, the main electrolyte types used in fuel cells are alkali, molten carbonate, phosphoric acid, proton exchange membrane, and solid oxide ceramics, as shown in the summary table presented in Table 1-1.

Table 1-1 Comparison between different fuel cells and their most common attributes^{11,12}.

	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Polymer (Fluorinated sulfonic acid polymer)	35-85% concentrated KOH in a matrix of asbestos	100% concentrated phosphoric acid	Molten alkali carbonates in a solid LiAlO_2 matrix	Solid and dense ceramic
Operating temperature	40-80 °C	50-220 °C	150-220 °C	600-700 °C	600-1000 °C
Catalyst	Pt	-Pt -Ni -Ag	Pt	Ni / NiO	Ni / Perovskite
Ion carried through the electrolyte	H^+	OH^-	H^+	$(\text{CO}_3)^{2-}$	O^{2-}
Maximum Efficiency (LHV)	60%	60%	55%	65%	65%
Start-up time	Minutes	Minutes	Minutes	Hours	Hours
Advantages	-High power density -Minimal corrosion problems	A wide range of catalysts	Less CO sensitive than PEMFC and AFC	No expensive catalysts	-High efficiency -Fuel-flexible, including CO
Problems	-Water balance -Sensitive to CO and S	If air is used CO_2 must be removed -CO sensitive	-Corrosive electrolyte -CO sensitive	-Corrosive and mobile electrolyte	Corrosion

More recently, climbing energy prices and advances in materials technology have reinvigorated work on fuel cells, and a recent report noted more than 100 companies working

on all kinds of fuel cells¹⁰. The global market for solid oxide fuel cells (SOFC) totalled \$303 million and \$622 million in 2008 and 2012, respectively. The market is expected to reach nearly \$1.2 billion by 2020 from \$662 million in 2015, increasing at a compound annual growth rate (CAGR) of 12.3% from 2015 to 2020¹⁰.

1.3 SOLID OXIDE FUEL CELLS

Solid oxide fuel cells (SOFCs), as one type of the most promising fuel cell variants, convert a diverse range of fuels to electricity with high efficiencies. High operating temperatures (600 °C -1000 °C) are required for oxygen anion diffusion from cathodes to anodes. State-of-the-art SOFCs commonly use dense yttria-stabilized zirconia (YSZ) as the oxygen anion conducting electrolyte and Ni-cermets as the anode. A variety of materials are used as the cathode, including doped manganite^{13,14}, cobaltites^{8,15} and ferrites¹¹. Ni is usually chosen as the metallic component of the anode because of its high electronic conductivity and stability under reducing conditions. It also serves as an excellent hydrocarbons reforming catalyst and electrocatalyst for electrochemical oxidation of H₂. The performance of SOFC anodes is linked with the length of the triple phase boundary (TPB), where the electrochemical reactions occur. This region is dependent upon the optimization of anode microstructure and composition.

1.4 RESEARCH FOCUS

Redox instability refers to the chemo-mechanical instability of the solid oxide fuel cell anode during reduction and oxidation conditions. This issue was first reported in 1996 by Cassidy et

al. for Ni-YSZ anode supported cells¹⁶. It has been found that continuous conditions change upon reduction and reoxidation ('Redox cycle') of the anode support electrode was measured as well as the loss of the open circuit voltage (OCV) due to cracking of the thin electrolyte, which could also lead to gas leakage between anode and cathode. The existing redox cycling study of Ni-YSZ anode material will be introduced in detail in Chapter 2.3.2.

Due to the impact of redox cycling on Ni-YSZ anode supported cells, combining the influence of anode microstructure change and electrolyte cracking, it is essential to study the redox cycling impact on each term. This work is going to focus on the impact of redox cycling on electrolyte supported Ni-YSZ electrodes, specifically on anode microstructure and electrochemical degradation. During the development of this work, many other ideas arose around the redox cycling, and can be seen in the layout of the thesis, from a redox study of the conventional anode, to the study of scaffolds as well as to the development of a technique that can study degradation of electrodes in a variety of conditions. As the work progressed, more questions arose and these can be represented in the corresponding chapters and research objective outlined below.

1.5 RESEARCH OBJECTIVES

- a. to study the impact of redox cycling on conventional Ni-YSZ anodes, combining its electrochemical performance, mechanical properties degradation and microstructural changes;
- b. to study the impact of sinter temperatures on YSZ scaffold fabrication;
- c. to study the impact of redox cycling on Ni infiltrated YSZ scaffold anodes, including its electrochemical performance and mechanical properties degradation;
- d. to analyses and quantify the 3D microstructure of Ni-YSZ anodes;
- e. to study the nickel dewetting behaviour of the 2D Ni-YSZ flat anodes and simulate anode degradation in controlled atmospheres.
- f. to study the impact of redox cycling and isothermal ageing of a Ni infiltrated YSZ fibre scaffold electrode, including its electrochemical performance, mechanical properties degradation and microstructural changes.

1.6 THESIS OUTLINE

This thesis is organised into 8 chapters as follows:

Chapter 1 presents an introduction to the thesis including the background and motivation for the research, fuel cell technology in general as well as the research objectives.

Chapter 2 presents an overview of literature related to solid oxide fuel cells (SOFCs), including their principles, components and materials. Another large part of this chapter is focused on SOFC anode materials, especially nickel yttria-stabilized zirconia (Ni-YSZ). The main discussion includes fabrication methods, microstructures, mechanical properties and electrochemical performance. The current gaps in knowledge are identified.

Chapter 3 outlines the experimental methodology used in this study. The techniques involved in electrode manufacturing, electrochemical testing, electrode microstructure and mechanical properties characterization are introduced.

Chapter 4 presents the redox cycling impact on conventional Ni-YSZ electrodes. Characterization includes electrochemical performance degradation, microstructure and mechanical properties evolution. The relationship between these three parameters upon redox cycling is discussed.

Chapter 5 is based on the conclusions from previous chapters, and a mechanically robust YSZ structure is introduced. This YSZ scaffold structure is sintered at different temperatures in order to find a compromise between mechanical stability and porosity. The YSZ scaffold was then infiltrated with Ni and characterized after redox cycling.

Chapter 6 presents YSZ structure tailoring with a YSZ fibre membrane produced by electrospinning. A sandwich like Ni infiltrated YSZ fibre scaffold is examined under isothermal and redox cycling condition. The improvement in the electromechanical performance stability is discussed.

Chapter 7 focuses on solid-state dewetting behaviour of a Ni thin film on a flat YSZ substrate. The relationship between pore formation and electrochemical performance are discussed. Two conceptual models are developed to calculate the active TPB based on 2D images and used to compare with aTPB from electrochemical polarization resistance. A dewetting simulation is presented and matches the TPB observation from both Ni thin film images and electrochemical impedance.

Chapter 8 presents the conclusions of this study and the future outlook.

CHAPTER 2 LITERATURE REVIEW

2.1 OPERATING PRINCIPLES OF SOFCs

The SOFC is expected to be one of the potential solutions for a high efficiency, flexible and low carbon emission energy supply system. Compared to other conventional power supply systems, SOFCs have a significant advantage in energy efficiency. The SOFC generates electricity directly from the fuel oxidation process, enabling an electrical efficiency of > 50% by using natural gas or hydrogen. With high operating temperatures, in the range 600-800 °C, SOFCs can be combined with heat recovery technologies such as heat exchangers to create a total system efficiency of up to 85%¹⁷. In addition, SOFCs have no moving parts or corrosive liquid electrolytes. They are expected to lead to electricity generation systems with less noise, high reliability and low maintenance.

In an SOFC, a single cell is composed of an electrolyte, and two electrodes (anode and cathode). The electrolyte must be dense with good ionic conductivity and low electronic conductivity. The electrodes are porous, they exhibit electronic conductivity and preferably also ionic conductivity at the operating temperature. A schematic of an SOFC is provided in Figure 2-1. The anode and cathode materials in an SOFC are different. The anode material must be able to tolerate a highly reducing high-temperature environment, while the cathode must be able to withstand a highly oxidizing high-temperature environment. The most common material for the anode in the SOFC is a Ni-YSZ cermet. Nickel provides conductivity and catalytic activity. The YSZ adds ion conductivity, thermal expansion compatibility, and

mechanical stability and maintains the high porosity and surface area of the anode structure. Water is produced at the anode, rather than at the cathode, as in a polymer electrolyte membrane (PEM) fuel cells (PEMFC). The cathode electrode is usually a mixed ion-conducting and electronically conducting ceramic material. Typical cathode materials include LSM (strontium-doped lanthanum manganite), LSF (lanthanum- strontium ferrite), LSC (lanthanum- strontium cobaltite) and LSCF (lanthanum- strontium cobaltite ferrite). These materials show good oxidation resistance and high catalytic activity in the cathode environment.

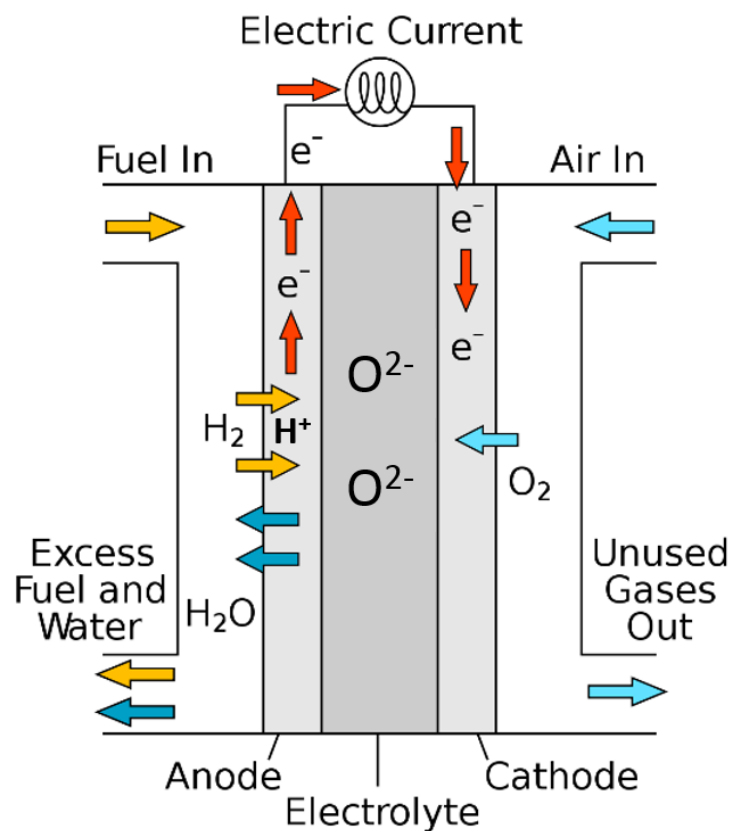
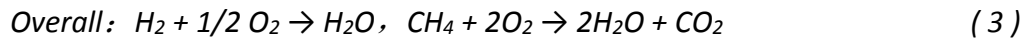


Figure 2-1 Schematic of H₂-O₂ SOFC. The ceramic electrolyte is solid state. A nickel-YSZ cermet anode and a mixed conducting ceramic cathode provide the required thermal, mechanical, and catalytic properties at high SOFC operating temperature. Water is produced at the anode¹⁸.

In oxide-ion conducting SOFCs, O^{2-} ions are transported from the cathode to the anode through the electrolyte and then react with H^+ ions at the anode and forming water. The SOFCs generate electricity by the flow of electrons from the anode to the cathode through the external circuit. The reactions continue as long as fuel is fed to the cells and the load is applied to the external circuits. The relevant reactions in an SOFC are as following:



By using Y-doped $BaZrO_3$ (BZY) electrolyte, the ion transport can be reversed¹⁹. In proton-conducting SOFCs, H^+ ions are transported from the anode to the cathode through the electrolyte, forming water at the cathode.

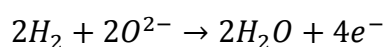
2.2 FUNDAMENTALS OF SOFCs

The selection of materials for use in SOFCs is a challenging process. Each component of the SOFC has to meet certain requirements, such as high catalytic activity, high conductivity, good temperature stability, and structural rigidity^{20,21}. Since the SOFC is operating at a relatively high temperature, ceramic materials with similar thermal expansion coefficient are used for both the electrodes and the electrolyte. Ceramics are selected based on functionality, compatibility, and cost.

In recent years, there are several papers on the development of SOFC anode materials^{8,7}. Tao and Irvine²² reviewed the development of alternative SOFC anodes with fluorite, rutile, tungsten bronze, pyrochlore, perovskite and spinel structures. Liu²³ introduced a fuel-flexible anode composed of a lanthanum chromite perovskite, CGO, and a small amount of Ni metal in what could be viewed as a composite anode.

2.2.1 Anode

The function of an SOFC anode is to electrochemically oxidize the fuel gas, with oxygen ions, conducted through the electrolyte from the cathode, and form water molecule formed during oxidation, water vapour is produced as the only by-product in the anode chamber when hydrogen is the fuel.



Recently, as the fuel requirements tend to focus on hydrocarbon fuels with lower steam ratios, the anode requirement has changed. Progressively, discussions regarding anode materials are requiring the direct oxidation of hydrocarbon fuels at the anode, for which the traditional nickel-based cermets are unsuitable due to carbon deposition, as discussed by Mogensen²⁴. Some other types of approaches are being adopted by developers, for example Kim²⁵ developed Cu-Ni alloys as anodes for the direct oxidation of methane in SOFC at 900 °C.

The anode is essential for good fuel cell performance, as it provides sites for the electrochemical reaction of the fuels. As the most commonly used anode material in SOFC, Ni-YSZ cermets achieve stability in reducing atmospheres at high temperatures⁸, lower cost

compared to other materials, and a similar thermal expansion coefficient to YSZ-electrolyte. More importantly, the intrinsic charge transfer resistance that is associated with the electrocatalytic activity at the Ni/YSZ boundary is low, which means the high catalytic activity of nickel could break the H-H bond easily. More than 30%, by volume of interconnected porosity in the anode is required to facilitate the transport of reactant and product gases. Nickel serves as an excellent reforming catalyst and electrocatalyst for electrochemical oxidation of hydrogen. It also provides electronic conductivity for the anode. The YSZ constitutes a framework for the dispersion of Ni particles and acts as an inhibitor for the coarsening of Ni powders during both consolidation and operation.

Recently, $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (CGO) based cermet anodes have emerged as attractive candidates⁹ for use in SOFCs. When compared to stabilized zirconia, doped ceria presents ionic conductivities approximately one order of magnitude greater, for lower temperature conditions^{20,26,27}. This is due to the larger ionic radius of Ce^{4+} (0.87 Å) as compared to Zr^{4+} (0.72 Å) producing a more open structure through which oxide ions can easily conduct⁷. Hibino et al.²⁸ have investigated Ni-CGO anodes infiltrated with some noble metals, which act as a catalyst to reform the fuel, and 3 wt% of Ru was determined as optimal noble metal loading. They have also developed a Ni-ceria Samaria anode ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$), doped with Pd as the catalyst, that has a very high performance at 550 °C with a power density of 640 mW cm^{-2} . However, under the high temperature reducing atmosphere, Ce^{4+} could be reduced to Ce^{3+} , which induces electronic conductivity within in electrolyte, decreasing the open circuit voltage and consequently increasing fuel consumption and reducing the cell performance²⁹. This is the reason why CGO/CSO are used at lower temperatures (<700 °C) to minimise electronic leakage through the electrolyte.

In this case, the Ni-YSZ cermet offers the best available performance and stability at the current commercial manufacturing capability. Based on material selection conditions, there are some other types of anode materials have been developed, as shown in Table 2-1, combining pros and cons.

Table 2-1 Advantages and disadvantages of some alternative materials considered for use in the fabrication of SOFC anodes.

Anode material	Advantage	Disadvantage
LSCM ($\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.50}\text{Mn}_{0.50}\text{O}_{3-\delta}$)	Stable for both anode and cathode	Poor electronic conductivity and catalytic activity at interim temperatures
STO (Strontium Titanate)	Good chemical and redox stability	Low electronic conductivity in reducing conditions
Gandolinium-titanate based pyrochlores	Mixed ionic and electronic conductor	Interfacial reactivity with YSZ, low redox stability and electronic conductivity
LST (La-doped SrTiO_3)	Higher conductivity than STO	Negligible catalytic activity for the oxidation of hydrogen

2.2.2 Electrolyte

The electrolyte works with a function of conducting ions between the anode and cathode and separating the fuel from the oxidant in the fuel cell. Currently, there are three types of ionic transport mechanism can be considered to select electrolytes, including: anionic, protonic or mixed ionic. However, oxygen anionic (O^{2-}) transport, from the cathode to the anode, is the most common ionic transport mechanism in solid oxide fuel cells.

An electrolyte is essential for good fuel cell performance. Normally, there are several selection criteria must be considered for choosing the material^{12,30,31}, including:

1. The ionic conductivity should be better than $10^{-2} \text{ S cm}^{-1}$ under the operational temperature;
2. Negligible electronic conductivity;
3. The electrolyte should be a dense layer to prevent gas flow between anode and cathodes;
4. A good thermodynamic stability between different temperatures and oxygen partial pressures;
5. Suitable mechanical properties, with fracture resistance greater than 400 MPa at room temperature;
6. Negligible chemical interaction with electrode materials under operation and fabrication conditions to avoid interface blocking;
7. Ability to be fabricated as thin layers (less than 30 μm);
8. Cost effective raw materials and fabrication.

Zirconia based ceramics are the most used and understood electrolytes for high-temperature fuel cells. Zirconia is in the monoclinic phase at room temperature. When the temperature rises to 1170 °C, the structure transfers to a tetragonal phase, which is accompanied by a volume change around 3–5%¹⁶. And then, zirconia will be changed into the cubic fluorite structure on reaching 2370 °C and this phase kept until the melting point at 2680 °C³¹. However, practically this cubic fluorite structure can be stabilized, from room temperature up to the melting point, by doping with different ions. The doping process increases the oxygen ion vacancy concentration and consequently improves the ionic conductivity³¹. CaO, MgO, Y₂O₃, Sc₂O₃, Sm₂O₃ and Yb₂O₃ are most common dopants used to achieve high solubility in the zirconia fluorite structure, as shown in Table 2-2.

Table 2-2 Values of ionic conductivity and activation energy of zirconia stabilized with different cations³⁰.

Dopant	Content (% mol)	σ_i at 1000 °C (Scm^{-1})	Activation energy (kJ.mol^{-1})*
Y_2O_3	8	10.0	96
Sm_2O_3	10	5.8	92
Yb_2O_3	10	11.0	82
Sc_2O_3	10	25.0	62

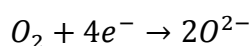
* $96.488 \text{ kJ.mol}^{-1} = 1 \text{ eV}$

Among different zirconia ceramics, Yttria-stabilized Zirconia is the most frequently used electrolyte. The ionic conductivity of Yttria-stabilized Zirconia is highly dependent on the Yttria dopant concentration. Several studies show that 8%mol Yttria-stabilized Zirconia ($(\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}$) provides the optimal ionic conductivity, rather than any other yttria concentration. For SOFCs, 8-YSZ is the most commonly used electrolyte due to its high ionic conductivity and chemical redox stability.

Scandia-stabilized zirconia (ScSZ) has also been widely used as electrolyte due to its high ionic conductivity. However, thermal ageing reduces its conductivity at high temperature, which is the main limitation of this material for SOFC³². Other factors such as purity, availability and cost limit scandium oxide being widely used as well³¹.

2.2.3 Cathode

The function of the cathode in SOFCs is to electrochemically reduce oxygen from O_2 to O^{2-} .



The oxygen ions are formed by reduction, then transported to the anode through the electrolyte, via oxygen vacancies. In order to function appropriately, SOFC cathode materials must be catalytically active to oxygen reduction, chemically and physically stable, compatible with the electrolyte, possess sufficient electronic conductivity and contain sufficient porosity.

Lanthanum strontium manganite (LSM) is a cathode material widely used for commercial application due to its compatibility with YSZ electrolytes. Mechanically, LSM has a similar thermal expansion ratio to YSZ and thus minimized expansion stress mismatch during heating and cooling. In addition to this, LSM has stable chemical reactivity with YSZ which extends the lifetime of the cell. However, due to the poor ionic conductivity of the LSM, the electrochemical reaction is limited to the cathode triple phase boundary (TPB). LSM works well as a cathode at high temperatures, but its performance quickly falls as the operating temperature is lowered below 800 °C. In order to increase the reaction zone beyond the TPB, the cathode material must be able to conduct both electrons and oxygen ions. Mixed ionic/electronic conducting (MIEC) ceramics, such as the perovskite LSCF, are also being studied for use at an intermediate temperature as they are more active and can make up for the increase in the activation energy of the reaction^{33–38}.

2.2.4 Cell Configuration of SOFCs

By using the different combination of material layer formats, an SOFC single cell can be designed in different configurations. Based on the specific requirements, such as considerations of sealing the anode and cathode compartments, manufacturing ability and ohmic resistance minimisation, there are two main different design configurations that have

been developed, with planar and tubular structures being the most commonly used designs. Each design combines advantages and disadvantages, and it is difficult to indicate the optimal solution, i.e., the planar design offers higher power densities and cheaper manufacturing cost, rather than other shapes; but by considering the long-term stability and demonstration, the tubular configuration offers better seal and thermal cycling resistance.

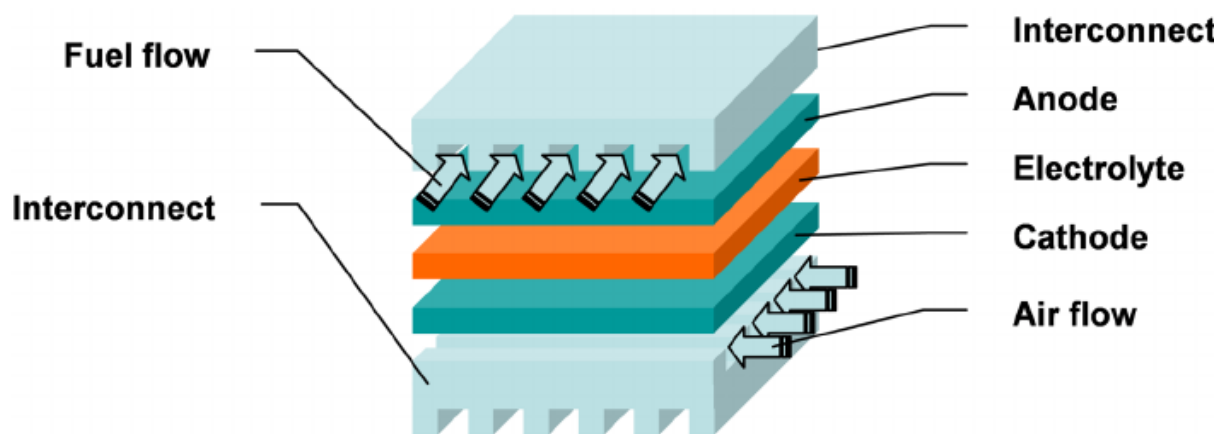
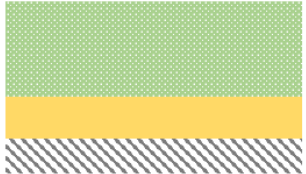
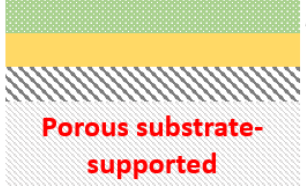


Figure 2-2 Solid oxide fuel cell – planar design³⁹.

The planar design is the most widely used cell configuration, and is formed by sintering flat and thin cermet plates, as shown in Figure 2-2. By using the combination of these electrode /electrolyte layers, the electrical resistance of the cell can be minimized, consequently achieve higher efficiency. The shape of the plate can be modified based on different design requirements, i.e., rectangular, square or circular. The planar SOFCs can also be categorized on the basis of the supporting component of the cathode/ electrolyte/anode structure, as summarized in Table 2-3. The operational temperature of the planar cells are normally at 800 °C or below. This advantage in lower operating temperature than the tubular SOFC enables less exotic materials of construction, thus cost saving.

Table 2-3 Summary of single cell configurations for single cell⁴⁰.

Cell configuration		Advantages	Disadvantages
Self-supporting	Electrolyte-supported 	- Relatively strong structural support from the dense electrolyte - Less susceptible to failure due to anode reoxidation (Ni/YSZ anode) and cathode reduction (LSM cathode)	- Higher resistance due to thick electrolyte - Higher operating temperatures required to minimize electrolyte ohmic losses
	Cathode-supported 	- No oxidation issues but potential cathode reduction due to electrolyte failure - Lower operating temperature via use of thin electrolyte	- Lower conductivity - Mass transport limitation due to thick cathodes
	Anode-supported 	- Highly conductive anode - Lower operating temperature via use of thin electrolytes	- Potential anode reoxidation due to electrolyte failure - Mass transport limitation due to thick anodes
External-supporting	Porous substrate 	- Thin cell components for lower operating temperature - Potential for use of non-cell material for support to improve properties	- Increased complexity due to the addition of new materials - Potential electrical shorts with porous metallic substrate
	Interconnect-supported 	- Thin cell components for lower operating temperature - Stronger structures from metallic interconnect	Flowfield design limitation due to cell support requirement

The SOFC tubular configuration has been developed since the late 1950s. As presented in Figure 2-3, a porous cathode base tube is made to allow rapid transport of the air; the electrolyte is applied to the cathode tubes by electrochemical vapour deposition (EVD); the anode layer can be added by using dip coating^{41,42}. And currently, there are other tubular designs based on anode supports being developed. The typical operating temperature is between 900-1000 °C. This tubular structure offers a simplified sealing mechanism, but at the same time, a relatively high electrical resistance reduced the cell efficiency. Some tubular designs also eliminate the need for seals and allow for thermal expansion.

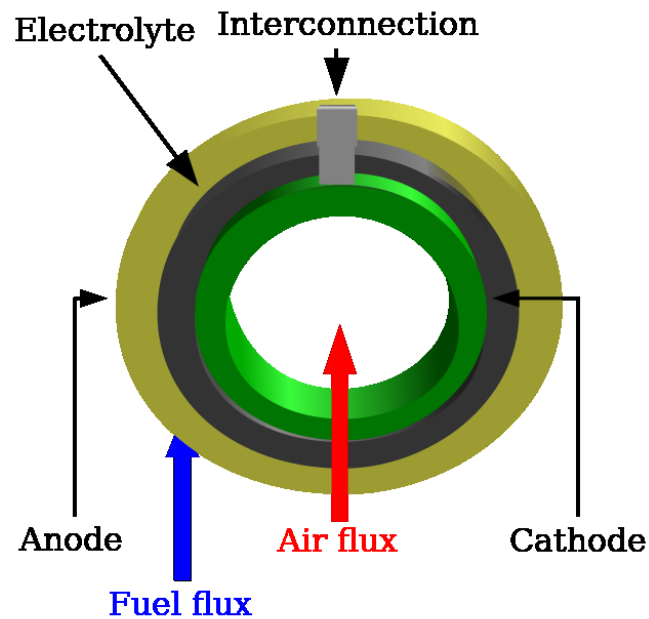


Figure 2-3 Cross section of three ceramic layers of a tubular SOFC from Westinghouse design^{39,43,44}.

2.2.5 Triple Phase Boundaries

The electrochemical reaction at the anode and electrolyte couples the charge transfer of oxygen ions in YSZ, electrons in Ni and the transport of fuels in the pores. It is commonly agreed and widely studied that the electrochemistry of hydrogen oxidation takes place at the active triple phase boundary (aTPB) of Ni, YSZ and pores. The active TPB is the theoretical contact perimeter between percolating Ni, YSZ and pore phase, where fuel oxidation and charge transfer occur^{45,46,47}. The rate of the electrochemical reaction is proportional to the TPB length, which is a function of particle size, distribution of the three phases and composition of the anode^{48,49}, as shown in Figure 2-4.

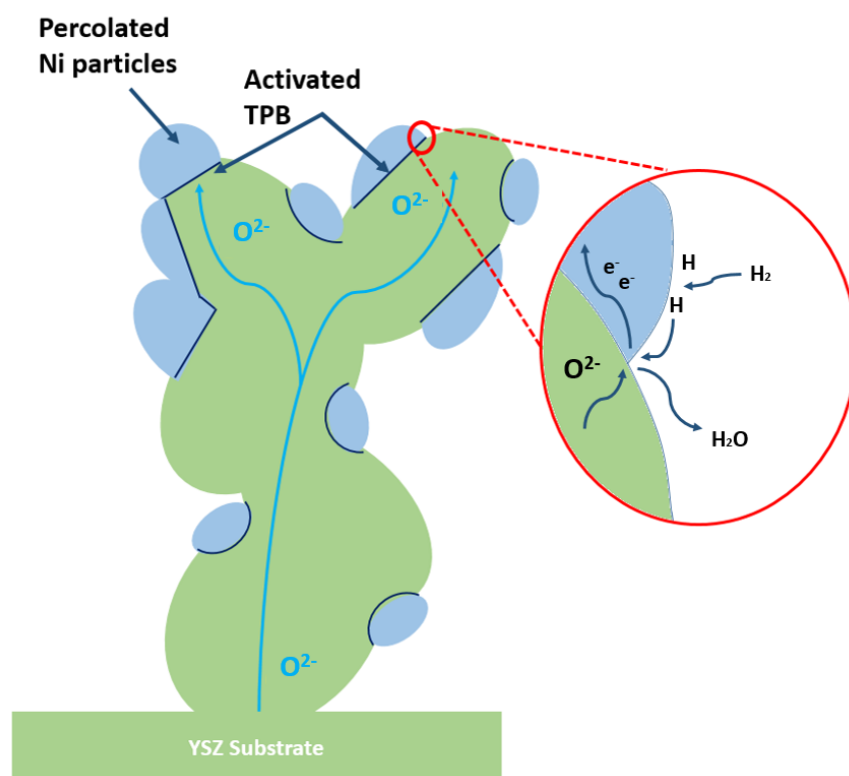


Figure 2-4 sketch of the TPB in a Ni-YSZ material for SOFC application.

Quantification of aTPBs is a valuable metric for the determination of the optimal structure and composition that yields maximum electrochemical performance, as well as for coupling the anode degradation in terms of aTPB loss with the reduction in electrochemical performance. The TPB can be identified by several means, as shown in Figure 2-5, the TPB observed from FIB-SEM cross-sectional views only shows the TPB as a point where all three phase are connected; in the novel flat Ni-YSZ electrode, presented in Chapter 7, the TPB can be physically measured by determining the length of nickel open pores; for the conventional Ni-YSZ and nickel infiltrated YSZ structure, the TPB is difficult to quantify as it appears as a 3D line where two materials are connected and exposed in the porous structure.

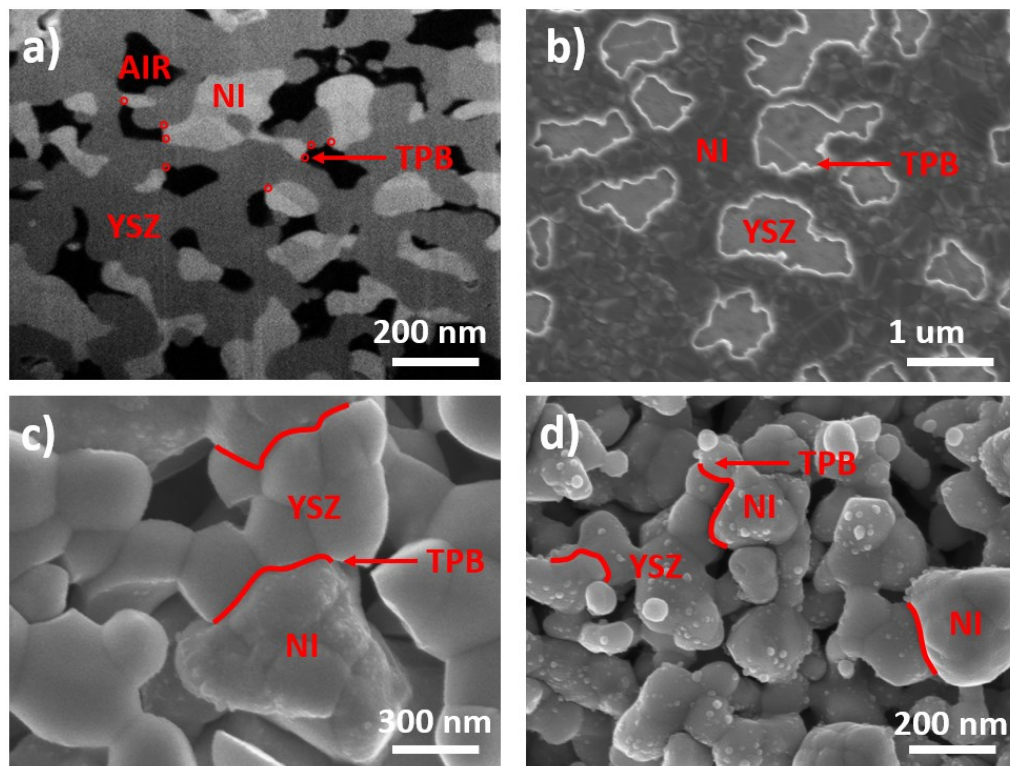


Figure 2-5 TPBs presented in different types of structure. a) the TPBs observed in FIB-SEM cross-sectional images; b) TPB in 2D Ni-YSZ structure; c) the TPB observed from a conventional Ni-YSZ as-reduced sample; d) the TPB observed from a Ni infiltrated YSZ scaffold as-reduced sample. All images from this work.

The active TPB can also be estimated from the cell electrochemical performance, the intermediate-frequency polarisation resistance, using a validated physically-based model⁵⁰.

$$R_2 = 2 \frac{t_{an}}{k_{eff}\sigma_{io}} \frac{\coth(\Gamma)}{\Gamma} \quad \text{Equation 1}$$

$$\Gamma = t_{an} \sqrt{\frac{F}{RT} \frac{i_0 L_{TPB}}{k_{eff}\sigma_{io}}} \quad \text{Equation 2}$$

where factor 2 represents the two electrodes for the symmetric cell, t_{an} is the anode thickness, F the Faraday constant, R the gas constant, T the operating temperature in K , k_{eff} is the effective conductivity factor of the YSZ phase, σ_{io} is the ionic conductivity of YSZ, i_0 is the exchange current density per unit of TPB length, L_{TPB} is the TPB density per unit of electrode volume. The parameters k_{eff} , i_0 , σ_{io} and YSZ volume fraction used in this simulation were assumed to be constant with time during reduction. It is assumed that polarisation degradation is caused solely by a decrease in TPB density⁵⁰. L_{TPB} can be evaluated by using Eqs. (1 & 2) from the polarisation resistance R_2 measured with EIS⁵⁰.

2.3 NI-YSZ MATERIAL OPERATING ISSUES

Thermal and mechanical strength are essential properties for SOFC devices, as they are formed by various layers of different materials that must demonstrate high-quality capability during manufacturing and operation. The operating temperature of the SOFC is currently between 600-1000 °C, the high temperature provides not only advantages but also challenges. The challenges include stack hardware, sealing, and cell interconnect issues. And it makes it

difficult to match the materials requirements, leading to mechanical issues and reliability concerns.

The Ni-YSZ material can degrade when subject to certain operating conditions, such as redox cycling during operation^{27,51–54}. Past work has often concentrated on Ni-YSZ microstructural evolution by annealing for long periods of time. It is commonly agreed that under these conditions the accompanying performance loss is caused by an increase in average Ni particle size and a decrease in TPB length per unit volume.

2.3.1 Nickel dewetting

Long-term durability is a key issue facing the commercial application of SOFCs as the elevated operating temperature can result in electrode degradation after long-term operation^{13,55,56}. The size changes of Ni particles were suggested to be due to the agglomeration of metallic nickel⁵⁷ and the formation of porosity upon reduction⁵⁸. These parameters also show a direct relationship with the change of the effective TPB length⁴⁶. The increase in Ni particle size could lead to a corresponding drop of TPB density and growth of polarisation resistance⁵⁹, moreover, due to the potential loss of Ni–Ni contact, the electrical conductivity can decrease as well.

A wide range of experimental evidence has proven that Ni dewetting can accelerate electrochemical performance degradation, by damaging the cermet microstructure and reducing the aTPB^{53,60,61} length. The investigation of Ni dewetting is also driven by the increasing interest in nanostructured infiltrated electrodes^{62–65}, whose initial performance before Ni dewetting makes this technology very promising for intermediate and low-temperature operation^{66–68}. Recently, Bertei et al.⁶⁹ pointed out that most of the

electrochemical degradation of nanostructured anodes stems from the evolution of Ni roughness at the nanometric scale. However, due to the large dimensional disparity between the thin layer of nickel and the large YSZ particles of the scaffold, the dewetting mechanism itself has proved challenging to investigate.

Dewetting describes the transformation of a thin film into an energetically favoured set of droplets or particles. Solid-state dewetting denominates this process to occur at temperatures well below the melting temperature of the bulk material⁷⁰. The driving force for dewetting is the minimization of the total energy of the free surface of the film and substrate, and of the film-substrate interface⁷¹. Metal film stability is a subject of immense technological and scientific interest⁷². In some cases dewetting needs be suppressed as the unstable electrode can limit the reliability of microsystems at elevated temperature⁷³. In other cases dewetting can be used to make nanoparticles for optical application⁷⁴, or as catalysts for the growth of carbon nanofibers⁷⁵ and nanotubes⁷⁶.

Dewetting of Ni films on YSZ substrates is a particularly interesting system which is relevant to Ni-YSZ cermet anodes. The partially dewetted Ni film itself is a workable anode for solid oxide fuel cells as it provides long triple phase boundary lines if the structure is fine enough. Meanwhile, the two-dimensional morphology and connectivity of nickel phase and pore phase as well as TPB lines can be directly observed and characterised. From a fundamental point of view the new information and understanding achieved by studying experimentally observed 2D phenomena can lead to better insight to 3D microstructure degradation of Ni-YSZ cermet. This is because the underlying mechanisms leading to dewetting of the thin film is the same as that causing 3D microstructure evolution in 3D Ni-YSZ. So far only limited work

has been done on nickel film dewetting. For example, Ye found that in solid-state dewetting of single-crystal nickel thin films, holes that form in the Ni films evolve to complex shapes that depend on the crystallographic orientation of the films and annealing ambient⁷⁷. In addition, hydrogen partial pressure has a drastic impact on the dewetting of very thin nickel films, possibly due to the formation of nickel metal hydride⁷⁶.

Some other works have also been focusing on the solid-state dewetting behaviour of other metal combining with YSZ substrate. Simrick⁷⁸ reported a thermal stability study of the silver thin films deposited, by evaporation, on the single crystal YSZ substrates under different annealing conditions (time and temperature), and it has been found that the rupturing first manifests itself as holes at three-grain junctions, as well as the average isolated particle diameter increases with higher anneal temperature after long-time annealing. In similar work, Toghan⁷⁹ investigated the solid-state dewetting of platinum thin films on YSZ substrates, prepared by sputtering, it has been observed that large voids developed resulting in a reduction in contact area, such structures also significantly reduced in mechanical strength of the films. Galinski⁸⁰ also studied the platinum thin films on dielectric substrates and reported the relationship between observable changes in the morphology of the thin film with the kinetics of the agglomeration process.

The solid-state dewetting of the thin film on YSZ is heavily depends on the film preparation method, thickness, operational atmosphere and annealing temperature^{70,71,76,79–81}. The sputtered films are initially quite compact but annealing transforms the films very strongly leading to dewetting and severe morphological changes.

2.3.2 Redox Cycling Issues

During SOFC operation , the anode layer of the SOFC is in a reduced state, but it is strongly sensitive to oxidizing atmospheres. Indeed, at operating temperatures, the Ni-YSZ oxidation process is significantly faster than in a nickel powder. So, the nickel in the anode can be transformed into NiO in a short time during an emergency system shut down. Therefore, repeated emergency starts and stops can lead to many cermet reductions and re-oxidation cycles. During these cycles, the composite has to accommodate the high dimensional changes of the nickel particles, discussed below. Due to this, the anode microstructure could be damaged, impacting negatively on electrochemical performance as well as the mechanical properties.

Ni-YSZ anodes are typically fabricated by mixing YSZ and NiO particles, which are subsequently reduced by H₂ during the fuel cell start-up, which increases porosity because of the NiO to Ni volume change. Reduction of the NiO–YSZ involves a quasi-reversible dimensional shrinkage of 41.6% by converting NiO to Ni, as shown in Table 2-4. During utilization, the metallic nickel phase re-organizes (agglomerates) due to high temperature, water vapor content and surface tension equilibrium^{82–84}.

However, Ni is strongly sensitive to oxidising atmospheres, such as those present during operation at high fuel conversion or during emergency shut-down, which can rapidly convert Ni into its oxidised state, involving a 71.2% volume expansion. These Ni volume changes result in irreversible microstructural damage, which includes bulk deformation of the microstructure, commonly leading to electrolyte cracking^{27,51,85}. It also has been found that

after redox cycling, polarisation resistance increased due to TPB length reduction and Ni surface area decrease^{5,9,19}.

Table 2-4 Properties of nickel and nickel oxide molar mass, specific mass and molar volume⁸⁷:

	NiO	Ni
M (g mol ⁻¹)	74.71	58.71
Density (g cm ⁻³)	6.6	8.9
V (cm ³ mol ⁻¹)	11.32	6.60

During reduction, the volume decrease described as:

$$\Delta V_{red} = \frac{V_{Ni} - V_{NiO}}{V_{NiO}} = -41.6\%$$

Equation 3

Upon re-oxidation, the volume increase could as high as 71.2%:

$$\Delta V_{ox} = \frac{V_{NiO} - V_{Ni}}{V_{Ni}}$$

Equation 4

Due to the impact of redox cycling on Ni-YSZ electrode combining the influence from nickel morphology change and electrolyte cracking, which directly leads to electrochemical and mechanical properties degradation, it is essential to study the redox cycling impact on each aspect, and then combine it with changes in the electrochemical and mechanical properties. Such a comprehensive study of conventional Ni-YSZ is not available in the literature and will be presented in Chapter 4 & 5

2.4 Ni-YSZ MATERIAL CHARACTERISATION

2.4.1 Mechanical Properties of Ni-YSZ

The functional layers of SOFCs must tolerate certain mechanical stresses during fabrication and operation in order to achieve long-standing stability and reliable performance. Knowledge of the mechanical properties of Ni-YSZ is essential for SOFC design. Therefore, appropriate mechanical properties are selected to prevent structural failures such as cracks, delamination and fractures^{88,89}. Such failures not only result in microstructure damage, but also lead to electrochemical performance degradation. Therefore, it is important to understand the mechanical stability of these materials in the form of the resistance to thermal expansion or redox cycling. The key mechanical properties that are the subject of this study are the elastic modulus and hardness. Past relevant studies have concentrated on the bulk structural damage and failure mechanism in a variety of operating environments for conventional electrolyte and electrode materials, such as YSZ^{88–90} and CGO⁹¹(electrolyte), LSM (cathode)⁹² and Ni-YSZ (anode)^{93,94}, respectively.

2.4.1.1 *Studies of Ni-YSZ Mechanical Properties*

The mechanical properties of conventional Ni-YSZ cermets have been widely studied with a various range of techniques. The Impulse Excitation Technique (IET) has been used to determine mechanical parameters in thick Ni-YSZ electrodes, 300 μm or above, determining the elastic modulus as a function of porosity, Ni content and sinter temperature^{27,95–97}. Empirical relationships between the porosity and elastic modulus of conventional Ni-YSZ has been reported and validated in several studies^{97,98}. A comparison of different mechanical

properties determined by these experimental techniques has been undertaken⁹⁹. The nanoindentation technique has been developed and is used to study the material indentation response and mechanical properties at the nanometric scale^{100,101}. Recent work has been focused on using nanoindentation to determine degradation of the mechanical properties of conventional Ni-YSZ thin films during redox cycling. The elastic modulus and hardness degradation during redox cycling were caused by the YSZ framework breaking down, which also significantly reduced the aTPB¹⁰².

Many studies have focused on the impact of redox cycling on conventional Ni-YSZ anodes, the main degradation mechanisms include: Ni-NiO volume changes, Ni agglomeration, and YSZ framework break down^{27,51–54,102}. The use of Ni infiltrated YSZ scaffolds minimises the degradation impact from Ni volume expansion during redox cycling⁶¹. The mechanical and initial electrochemical performance enhancement is the key advantage of this material compared to the conventional Ni-YSZ prepared from mixtures of NiO and YSZ powders. However, only limited work has focused on the impact of redox cycling on these scaffold structures.

2.4.1.2 *Nanoindentation for Porous/thin Material Studies*

The nanoindentation technique was first developed in the 1970s and used to measure the hardness of small volumes of material^{103–106}. Oliver and Pharr¹⁰⁷ developed an enhanced analysis method (the Oliver-Pharr method) for estimating elastic modulus and hardness from indentation load-depth curves. This technique uses a micro-level indenter to control the load and displacement, while recording the real-time load-displacement data. These enable

mechanical tests over a small region of the material, as the testing area can be controlled over a few micrometres or even nanometres scales. For this reason, the method is used extensively to measure the mechanical properties of thin films with microstructural feature size at the micron level. In addition to this, the nanoindentation technique has also been developed and used to study the response of the material at smaller length scales^{108,109}. Nanoindentation is thus an ideal technique to investigate the mechanical properties of Ni-YSZ films. The methodology of nanoindentation will be explained in detail in Chapter 3.

2.4.2 Microstructure of Ni-YSZ

It is widely known that the anode microstructure has a significant influence on fuel cell performance and cell stability^{110–112}. Traditional methods of visualising the material microstructures rely on the simplification of 3D microstructures into 2D planar representation using optical microscopy and SEM. A number of studies have been carried out on the 2D microstructural characterisation of SOFC electrodes in order to correlate microstructures with electrochemical performance. However, Ni-YSZ electrodes are formed of 3D microstructural features, which generates critical links to materials mechanical properties and electrochemical performance and consequently affect the durability of the cell. The microstructure features such as three-phase boundary length, volume fraction (e.g. porosity), particles size, particle surface areas and interface areas are essential factors for electrode characterisation. A high-performance electrode needs to be optimized for balancing a range of requirements.

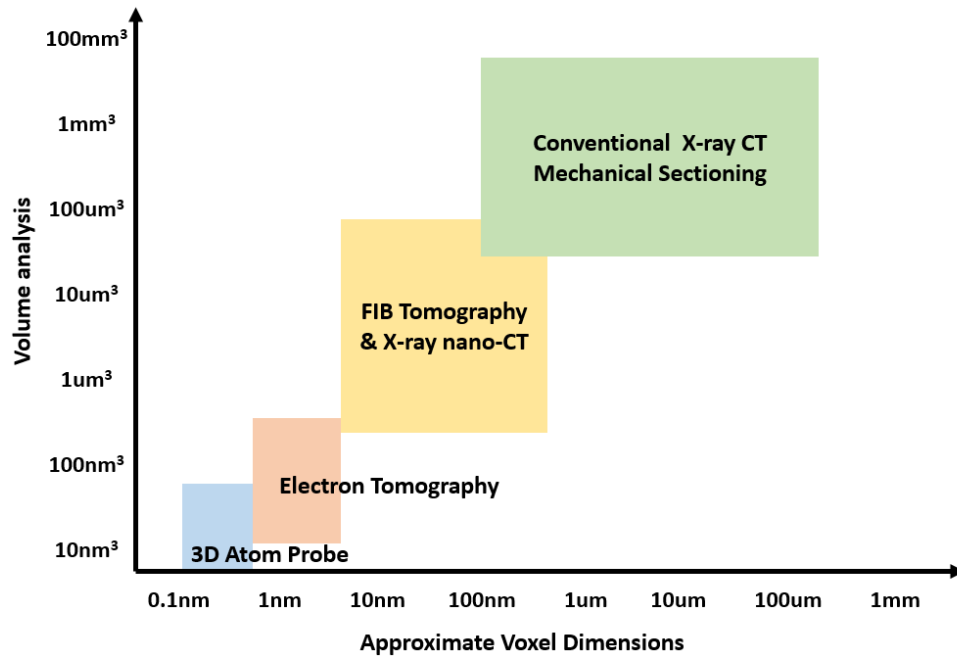


Figure2-6 Length scales of tomography techniques¹¹⁴.

The development of advanced 3D tomographic techniques have made it possible to analyse the microstructures of SOFC electrodes by getting access to a variety of valuable microstructural information based on 3D reconstruction, which can also be used to correlate with previous research for a better understanding of SOFC electrode performance so that better designs of electrodes can be developed. For example, effects of morphology change and dependence on starting materials and fabrication methods have been reported^{53,112}. Figure2-6 shows the application of tomography techniques based on the sample volume that can be analysed, and the spatial resolution achievable, where FIB-SEM and X-ray tomography (XCT)¹¹³ appear to be appropriate for SOFC microstructure studies. Yokokawa et al. have also identified FIB-SEM as the ‘most important tool’ for microstructure characterisation and recognised the importance of FIB-SEM in studies of material degradation mechanisms¹¹⁴.

Recently, direct measurements of 3D SOFC electrode microstructures have been performed by focused ion beam scanning electron microscopy (FIB-SEM)^{110,111,115–117}. FIB-SEM tomography^{118,119} allows the Ni-YSZ electrodes microstructure to be quantified through ex-situ analysis, due to the good phase contrast between Ni and YSZ, and the relatively high resolution of the technique. From the 3D tomography reconstructed microstructure, parameters such as volume fractions, interfacial areas, TPB length can be quantified^{85,55,120–123}.

CHAPTER 3 EXPERIMENTAL METHODS

This Chapter introduce the main techniques involved in sample preparation, property characterisation, measurements and analysis of the practical part in this work, including the basic principles of equipment and the processing of data.

3.1 CELL MANUFACTURING

3.1.1 Ink Preparation

In this study two types of inks were prepared:

- i. Ink#1: the ink contained a mixture of commercial NiO-YSZ powder and solvent;

Ni-YSZ symmetrical cells were prepared with a NiO-YSZ slurry made from NiO-YSZ powder (Nexceris, USA, 60 wt% NiO, $2.45 \text{ m}^2 \text{ g}^{-1}$ surface area) mixed with terpineol, binder (Hercules ECN-7) and dispersant (Hypermer KD15).

- ii. Ink#2: the ink contained a mixture of commercial YSZ powder, carbon black and solvent.

The YSZ scaffolds were prepared by depositing and sintering a YSZ-carbon black slurry on top of a YSZ substrate. YSZ powder (Nexceris, USA, $11.0 \text{ m}^2 \text{ g}^{-1}$ surface area) and 10 wt% carbon black powder (Alfa Aesar, USA, $75.0 \text{ m}^2 \text{ g}^{-1}$ surface area, $80\text{--}120 \text{ g L}^{-1}$ bulk density) were pre-mixed with 2-propanol (EMSURE® ACS) for 24 h in a roll mill. This pre-mixed powder was dried

at room temperature and then mixed with terpineol, binder (Hercules ECN-7) and dispersant (Hypermer KD15).

3.1.1.1 *Conventional Ni-YSZ Ink*

The NiO-YSZ slurry was made from NiO and YSZ powder mixed with terpineol, binder and dispersant. The suspension was stirred for 48 hours to avoid particle agglomeration. A ceramic triple-roll mill (EXAKT, 80E, Germany) was used to homogenise the slurry for 20 min and eliminate agglomerates above 5 μm .

3.1.1.2 *YSZ Ink for Scaffolds*

Carbon black was used as a sacrificial pore former to obtain the desired porosity and scaffold structure. This pore former was then burned out during the firing step, leaving pores⁶¹.

The YSZ powder and 10 wt% carbon black powder were pre-mixed with 2-propanol for 24 hours in a roll mill. This pre-mixed powder was dried at room temperature then mixed with terpineol, binder and dispersant. The suspensions were stirred for 48 hours to avoid particle agglomeration. A ceramic triple-roll mill (EXAKT, 80E, Germany) was used to homogenise the slurry for 20 min and eliminate agglomerates above 5 μm in size.

3.1.2 Electrode Manufacturing

After the ink preparation, there were several approaches used for manufacturing electrodes for this study, including: tape casting and screen printing for producing conventional electrodes. In addition, some other novel approaches have been also developed for tailoring

electrode microstructure, ie. Ni sputtering was used for producing 2D cells, and an electrospinning fibre membrane was used to modify YSZ electrode structure.

3.1.2.1 *Tape casting*

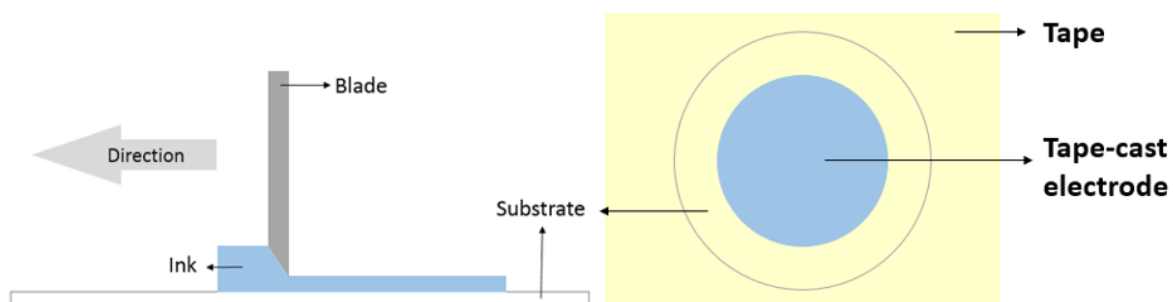


Figure 3-1 A Schematic drawing shows the tape casting process used in laboratory for sample preparation; top view of the tape-cast electrode.

Tape casting is a process used to manufacture relatively thick (30-80 μm after drying) and flat cermet from a slurry. The principle of tape casting is shown in Figure 3-1. In this study, tape casting consists of a blade moved in one direction, and a tape with a hole in the centre used to control the shape and thickness of the cermet slurry. The thickness of the cermet slurry can be controlled by adjusting a series of parameters such as the blade speed, the tape thickness and slurry viscosity. In typical tape casting equipment, the tape thickness varies from 30 μm to 100 μm . This could result in an electrode thickness of 15 μm to 50 μm after sintering. Due to this relatively thick electrode, the cells manufactured from tape-casting were used for nanoindentation to measure its mechanical properties, which will be explained in detail in section 3.2.3 of this chapter.

3.1.2.2 *Screen Printing*

Screen printing is widely used in many industrial areas. In this study, screen printing was used to produce thin electrodes of approx. 10 μm thickness or less after sintering. The basic parts of screen printing are shown in Figure 3-2, including a substrate, doctor blade, squeegee, paste material for deposition and a stencil with shaped mesh. The screen mesh can be made from polyester, stainless steel or nylon. The mesh is attached under tension onto a frame which is shown in grey. The frame is sufficiently strong to withstand the tension when the mesh is stretched as it approaches the substrate. The squeegee deflects the mesh and lets it contact the substrate. The process involves pouring the ink on one side of the screen and spreading this by doctor blade, then the squeegee is pressed firmly to the mesh and the mesh pressed onto the substrate. A steady and smooth pressure along the length of the squeegee and full contact between mesh and substrate over the whole area is essential. The material slurry fills the mesh and is deposited onto the substrate. The typical thickness of a screen printed electrode after sintering is around 5-10 μm . More passes can be applied to give a thicker deposit.

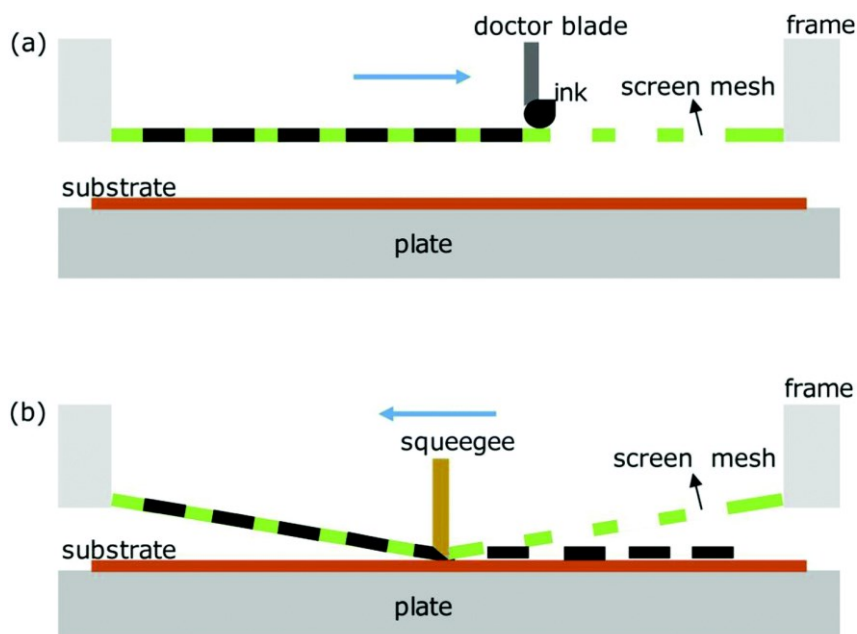


Figure 3-2 Presentation of a typical screen printing process, a) the principle of ink spreading process; b) the principle of the screen printing process.

3.1.2.3 *Electrospinning*

Electrospinning was used to produce YSZ fibres and form a highly porous YSZ membrane. The YSZ fibre was prepared by dissolving 85 wt% of 8YSZ powder and 15 wt% of PAN (Polyacrylonitrile) powder (Goodfellow Cambridge Limited Huntingdon, mean particle size 50 μm , mean molecular weight 230,000 g mol^{-1}) into dimethylformamide (DMF, VWR chemicals, 99.90%). The prepared YSZ suspension was filled into a syringe and ejected by a syringe pump. The metal syringe nozzle was held at 10 kV using a high voltage power supply (GenVolt 73,030) a distance of 17.5 cm from the aluminium electro spinner. The collected YSZ nanofibers were formed into a fibre membrane with an approximate thickness of 20 μm . Then a carbonization process was performed in order to obtain a stable nano-fibre structure. The YSZ fibre membrane was initially heated to 300 $^{\circ}\text{C}$ in air for 1 hour and then raised to 550 $^{\circ}\text{C}$ in pure

nitrogen for 1 hour. The obtained carbonized YSZ nano-fibre membrane was cut into shape for electrode preparation. The set-up is shown in Figure 3-3.

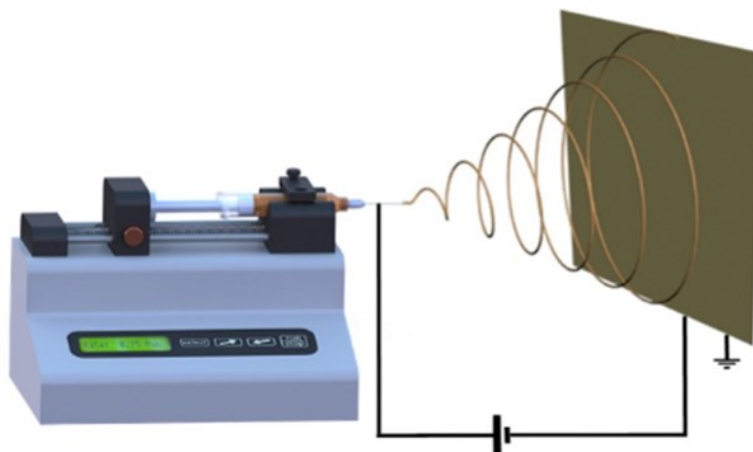


Figure 3-3 Schematic illustration of the preparation of YSZ nanofiber films by electrospinning¹²⁴.

3.1.2.4 Ni infiltration

Infiltration is a commonly used method to add in the metal phase into the scaffold structure⁶¹, as illustrated in Figure 3-4. For the SOFC anode, the pores of the YSZ scaffold are normally infiltrated with a metallic nitrate solution and then heated to obtain the metallic oxide by decomposition. Normally, multiple infiltration and heat treatment steps are required, due to the low loading of metal salts that can be achieved per impregnation step.

After heat treatment, it is relatively easy to obtain nickel nanoparticles into the electrodes. This is because the nickel phase does not experience high sintering temperatures during fabrication. In the infiltrated electrode, a significant increase in the triple phase boundary

density is obtained, due to the combination of scaffold high surface area and nickel nano particles⁶¹.

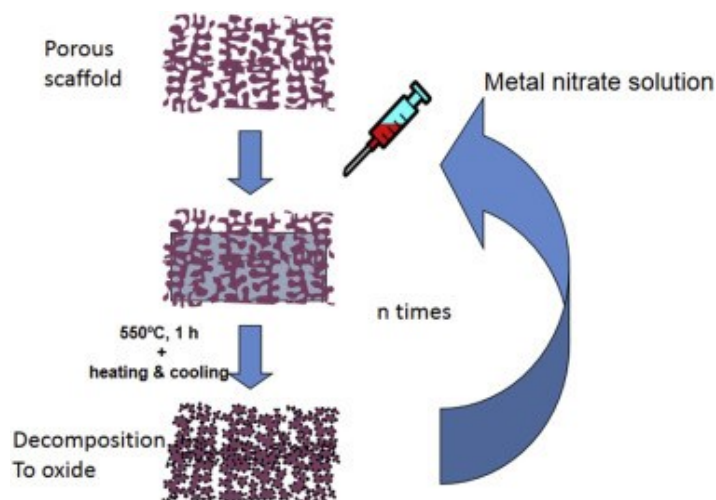


Figure 3-4 Impregnation of a porous scaffold. A metal nitrate solution is infiltrated into the scaffold. This is heated to decompose the nitrate to the oxide. The operation is then repeated several times.⁶¹

In this study, 2 μL of 2M nickel (II) nitrate ethanol solution was pipetted into the YSZ scaffold and the cell heated up to 550 $^{\circ}\text{C}$, with a 5 $^{\circ}\text{C}$ ramp rate, to decompose the nitrate into nickel oxide^{33,61,125–128}. The infiltration and decomposition process was repeated 15 times until the nickel content in the electrode was about 36 wt% with respect to the scaffold as measured by weight difference.

3.1.2.5 Ni sputtering

In this study, a novel concept of 2D symmetrical cell was designed to study the nickel dewetting behaviour. For cell preparation, sputtering was used to produce a well-controlled thin Ni electrode.

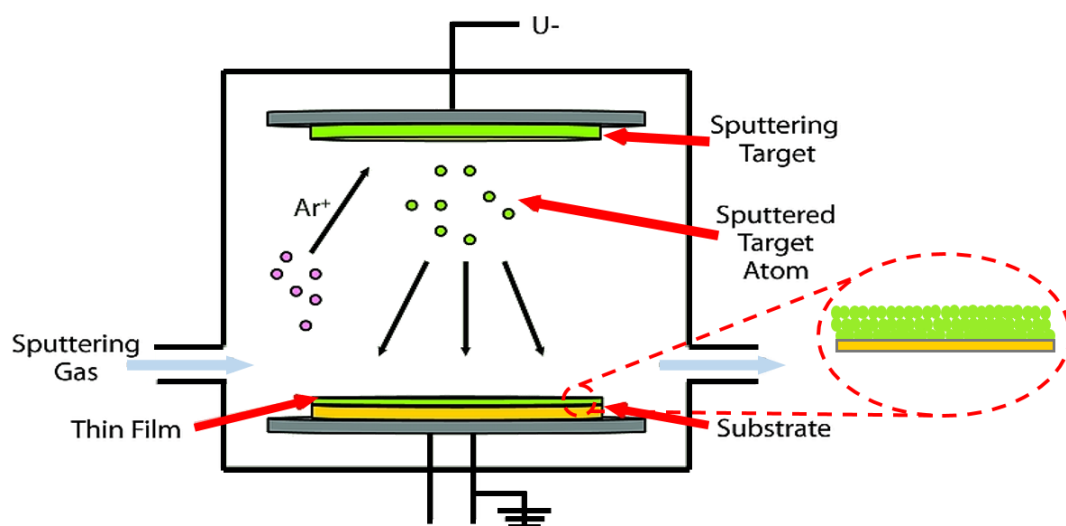


Figure 3-5 Schematic presentation of nickel thin film sputtering.

Sputtering is a process whereby particles are ejected from a solid target material due to bombardment of the target by energetic particles, particularly gas ions in a laboratory. In this work, a 99.99% purity nickel target was used. The nickel films were deposited on both sides of the 8YSZ substrates by magnetron sputtering (Ar pressure: 2.10^{-3} mbar, current: 100 mA, deposition rate: 20 nm min^{-1} , target-sample distance: 8 cm). The nickel thin film covered a 2 cm^2 surface area and had a thickness of 40 nm ($\pm 5 \text{ nm}$). After sputtering, the nickel film was nearly amorphous, formed by layers of nickel nanoparticles, observed by XRD and described in Chapter 6 in detail.

3.1.3 YSZ Scaffold and Conventional anode Sintering

Sintering is one of the most important steps in fabrication by generating a stable structure for conduction between particles. This is a process of transforming the deposited films it into a consolidated body at a relatively high temperature. The process temperature should be below

the melting point of the materials while allowing strong bonds to form between particles. During sintering, the diffusion of atoms takes place at higher temperature and grain growth occurs, while all the solvents, binders, dispersants, plasticizers, and pore formers are evaporated and/or burnt off.

The choice of temperature is crucial to obtain porous electrodes while maintaining the best possible scaffold structure. In this study, the sintering temperature impact on the YSZ grain structure has been studied. The YSZ scaffolds were prepared by depositing and sintering an YSZ-carbon black slurry on top of an YSZ substrate. The slurry was deposited by tape casting on an 8YSZ electrolyte and fired at 1000 °C, 1100 °C, 1200 °C, 1300 °C, 1400°C or 1500 °C respectively for 2 hours in air. A two-stage sintering process was used in this scaffold material study, as shown in Figure 3-6, avoiding the peeling off or delamination of the scaffold layer from the electrolyte. The final scaffolds had a thickness between 15-30 μm with a 2 cm^2 geometric area.

Figure 3-7 sintering temperature impact on the YSZ grain size, grain boundaries and porosity of the YSZ scaffolds. The initial YSZ inks are prepared with same YSZ particle size ($<5 \mu\text{m}$) and same amount of pore formers (10 wt%).

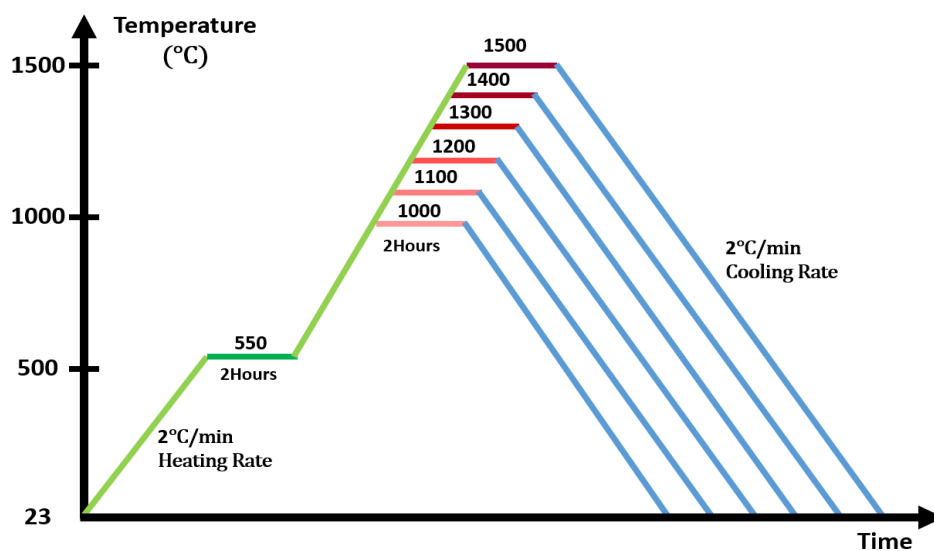


Figure 3-6 2-stage process for sintering YSZ scaffold electrodes.

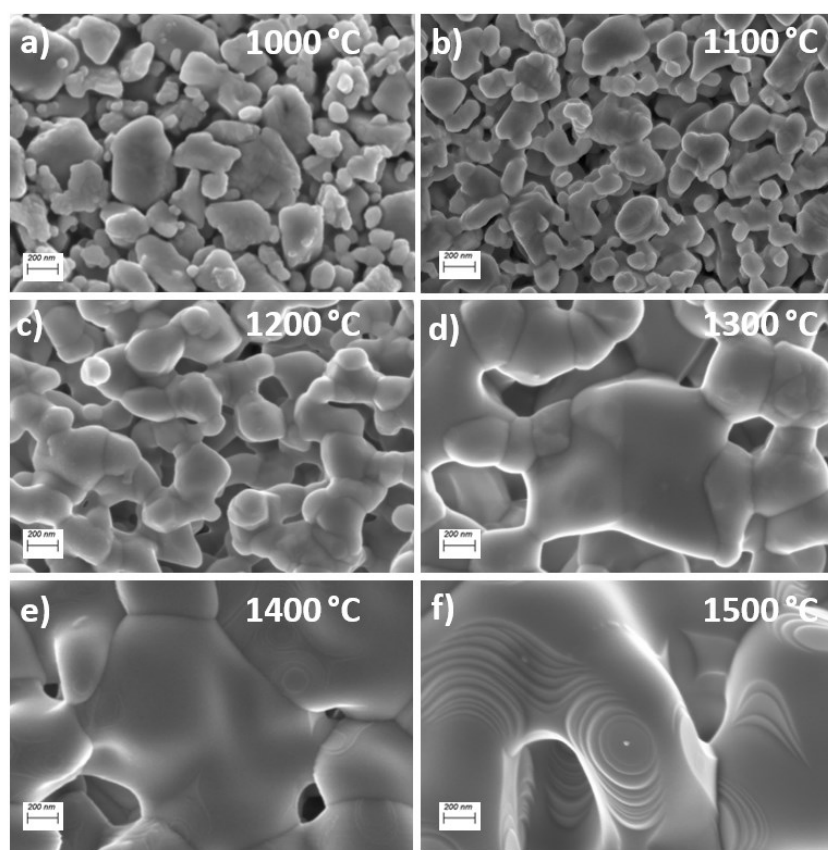


Figure 3-7 sintering temperature impact on the YSZ grain size, grain boundaries and porosity of the YSZ scaffolds. The initial YSZ inks are prepared with same YSZ particle size ($<5\ \mu\text{m}$) and same amount of pore formers (10 wt%).

3.2 MATERIAL CHARACTERISATIONS

3.2.1 Electrochemical Impedance Spectroscopy (EIS) Measurement and Analysis

Impedance spectroscopy is a widely used technique to study electrochemical characteristics of fuel cells, batteries, and capacitors. It consists of measuring the impedance of a system at different frequencies by superimposing a small AC voltage onto the voltage operating point. The underlying idea is that individual processes will appear in the impedance spectrum at different frequencies, according to their inherent rate. For example, a charge transfer process is likely to appear at higher frequencies than a slower diffusional process.

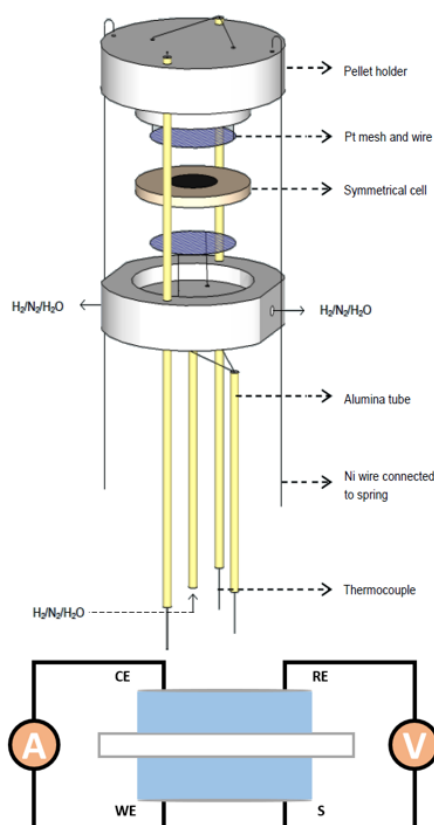


Figure 3-8 Schematic of the electrochemical test rig. The rig has a single fuel gas inlet and the arrows represent the fuel gas flow paths.

In this work, an in-house designed and built impedance test rig was used to conduct EIS measurements when redox cycling the symmetrical cell. Two Pt-meshes (>99.2% Pt) were used as a current-collector, which ensures a homogeneous current distribution over the electrode and low contact resistance at high temperature. No additional silver paint was used as current collector. All impedance measurements were obtained using a potentiostat (Autolab PGSTAT302N, Eco Chemie BV) coupled with a frequency response analyser (FRA). The EIS measurement was performed using a two-electrode configuration in a four-point set-up for both symmetrical at open circuit voltage (OCV). The measurement results were collected with a potentiostat Nova 10.1. The pellet holder was placed on ceramic tubes, which were also used to supply the fuel gas, as shown in Figure 3-8. The humidified fuel gas composition was regulated by mass flow controllers.

Table 3-1 Parameters and experimental conditions used during EIS measurements.

Parameters		Convention al-YSZ Cell	Ni-YSZ Scaffold Cell	Ni-YSZ Flat Cell	Ni-YSZ Fibre Scaffold Cell
Sinusoidal voltage amplitude (mV)		20	20	20	20
Frequency range (Hz)		$10^{-1} - 10^6$	$10^{-1} - 10^6$	$10^1 - 10^5$	$10^{-1} - 10^6$
Number of points per decade/Time		60/ 5 Min	50/ 4 Min	40/ 2 Min	50/ 4 Min
Experimental conditions	Temperature (°C)	800	500-600	400-650	600-700
	Gas mixture	Humidified 5 vol% hydrogen and 95 vol% nitrogen at a flow rate of 100 ml min^{-1}			

Typically, the impedance is presented in Nyquist plot, or the magnitude and phase shift as a function of the logarithm of the frequency (Bode plots). The Nyquist plot of the impedance spectrum of symmetrical Ni-YSZ electrodes usually shows one or more semicircles, due to the capacitive behaviour of the electrochemical processes involved, as shown in Figure 3-9. The relative position of these semicircles, their size, the apex frequencies, and the values of their intercepts with the real axis yield important information on the different processes within the cell. The table below shows the summarized EIS parameters and experimental conditions used in this study.

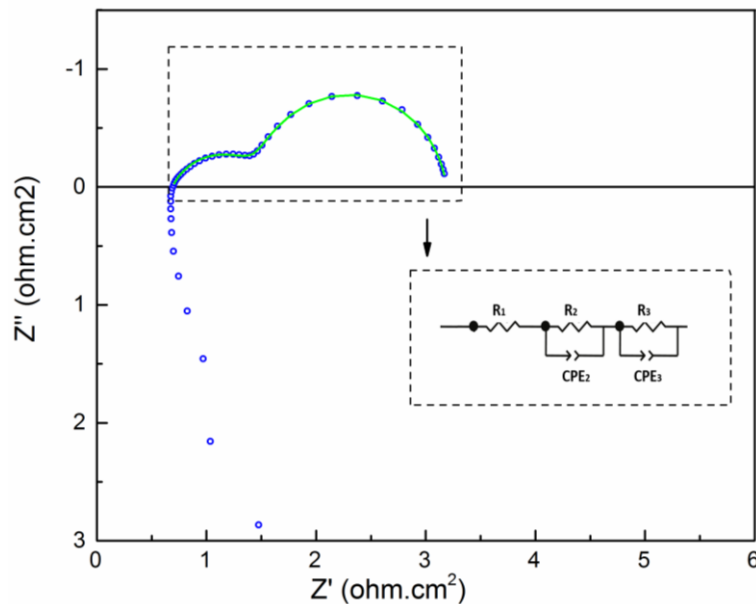


Figure 3-9 the nyquist plot of the impedance spectrum of a symmetrical Ni-YSZ electrode usually, shows one or more flattened semicircles, and the equivalent circuit model used for impedance analysis.

The obtained EIS data was analysed through Z-view (Scribner, USA) using an equivalent electrical circuit, as shown below, where R_1 is the overall ohmic resistance including: electrolyte resistance, electrode ohmic resistance, contact resistance at the Ni-YSZ/YSZ

interface and the contact resistance between the electrodes and current collector. To account for the depression of the electrode arc a constant phase element (CPE) was used in the circuit instead of a capacitor. The (R_2, CPE_2) and (R_3, CPE_3) correspond to the high-frequency and low-frequency arcs, which is electrochemical reaction polarization resistance and diffusion resistance, respectively. The values of R_1 , R_2 , R_3 and CPE_1 , CPE_2 can be obtained from fitting the impedance data with this proposed equivalent circuit.

The impedance of a CPE element is defined as:

$$Z_Q = Q_0^{-1}(i\omega)^{-n} \quad \text{Equation 6}$$

With Q_0 the admittance value at $\omega = 1 \text{ s}^{-1}$, i the imaginary unit, ω the angular frequency and n a number between -1 (ideal inductance) and 1 (ideal capacitance). In the fitting, Q_0 and n are usually used as fitting parameters. Throughout this work, only resistance values were discussed and referred to represents electrode electrochemical performance.

3.2.2 Microstructure Characterisation

In this study, the microstructure of the samples was evaluated by using a combination of various techniques. This combination of different tools enabled accurate characterisation of morphological, chemical and geometrical properties of materials. Here, the techniques involve scanning electron microscopy (SEM), environmental scanning electron microscopy (ESEM), atomic force microscopy (AFM), energy dispersive X-ray spectroscopy (EDS), X-Ray Diffraction (XRD) and focussed ion beam scanning electron microscopy (FIB-SEM).

3.2.2.1 Scanning Electron Microscopy (SEM) & Environmental-SEM

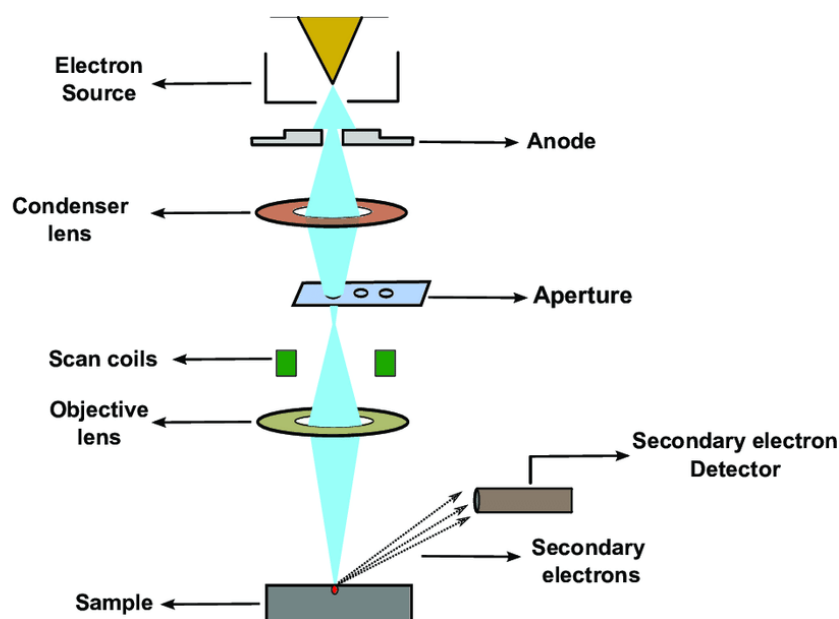


Figure 3-10 Schematic of SEM working principle; in the E-SEM, the sample holder functioned as the heating element.

The morphology changes of the electrode were observed by using SEM (LEO Gemini 1525 FEGSEM). Prior to imaging, the samples were coated with 15 nm of chromium to ensure sufficient electronic conductivity, preventing the accumulation of electrostatic charge at the surfaces, image drifting and improving the resolution. In this study, both high and low magnification imaging was performed using secondary electrons and Inlens detector. Samples were prepared from sample fractures to examine the morphology of the top surface and cross-section of the electrode. The Ni grain structure was detected by using SESI detector for the flat Ni-YSZ samples. The chromium coating was not applied to the flat Ni-YSZ samples.

The FEI Quanta 200 E-SEM apparatus with FEG (Field Effect Gun) was used for the in-situ dewetting progress, with help from Dr. Renaud Podor at Institut de Chimie Séparative de

Marcoule. The test atmosphere used was humidified (3%) forming gas (a mixture of 5 vol % H_2 and 95 vol % N_2) at 170 Pa chamber pressure. A dedicated in-situ heating stage accurately controlled the sample temperature at up to 600°C through a thermocouple in direct contact with the samples¹²⁹. Images with different magnifications were recorded throughout each experiment. The high magnification images (x10,000, 12.4 nm/pixel) were used to study local details of the nickel layer and to determine the local curvature; whereas, low magnification images (x5000, 24.8 nm/pixel) were used for statistical analysis on a larger field of view.

3.2.2.2 Atomic Force Microscope (AFM)

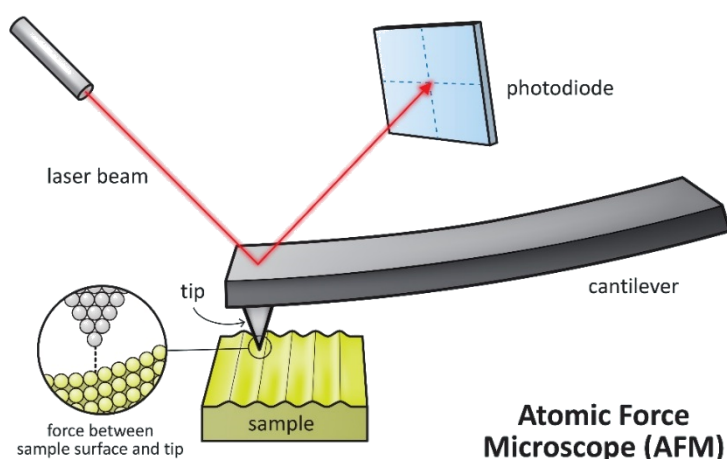


Figure 3-11 Schematic of AFM working principle.

Atomic force microscopy is a very-high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit, the principle of the AFM is shown in Figure 3-11. In this study, the depth of the grain boundaries of the YSZ substrate was mapped using AFM. The result was used for understanding the impact of YSZ grain boundaries on nickel thin film

dewetting. This work was supported by Dr Victoria Bemmer in Department of Materials, Imperial College London.

3.2.2.3 FIB-SEM Dual-beam Tomography

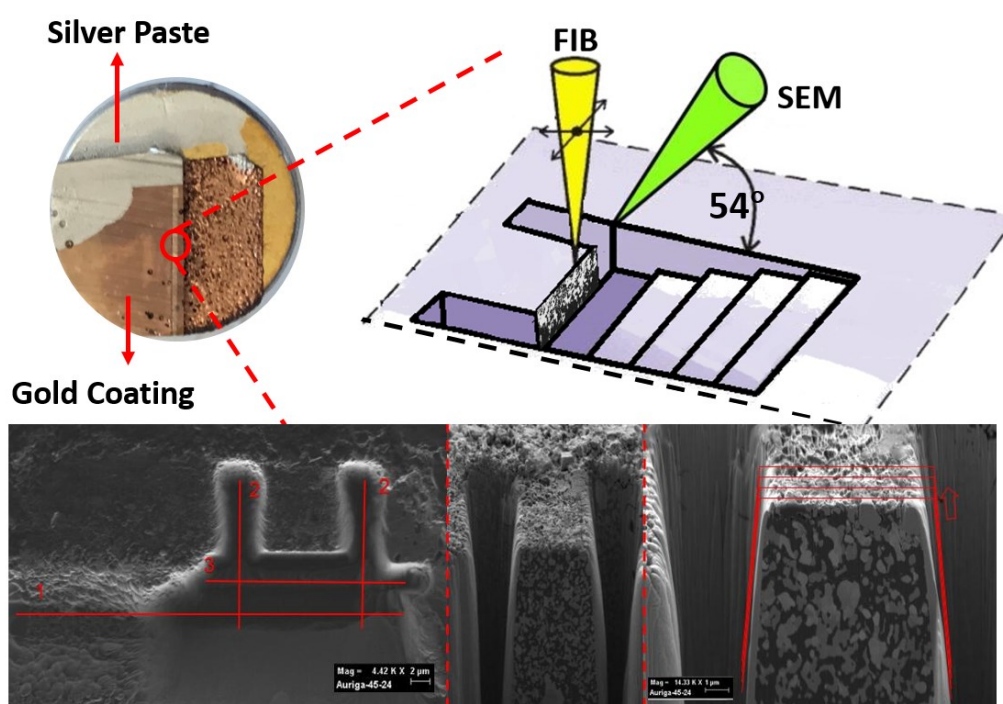


Figure 3-12 Schematic of FIB-SEM working principle and the illustration of sample milling steps.

Focused ion beam scanning electron microscopy (FIB-SEM, Auriga, Zeiss) was used to study the electrode microstructure in three-dimensions (3D). The electrode samples were prepared by impregnating a mixture of epoxy resin and hardener (Specifix 20, Struers) into the porous electrodes under vacuum (0.8 Bar) for 12 hours. This vacuum impregnation allows the resin

to fill the pores and distinguishes the open pores of the electrode during imaging. Then the sample was cut and polished into a thin cross-sectional layer using a diamond blade.

A 30 nm gold coating was deposited on the mounted electrode specimens by sputtering before FIB-SEM observation. This gold coating works as a conductive layer to prevent the charging effect, which would otherwise occur due to the accumulation of static electric fields. It also increases the amount of secondary electrons that can be detected from the surface of the specimen in the SEM and therefore increases the signal to noise ratio to improve the quality and brightness of the acquired images. For the FIB milling, the gold layer could also protect the sample from unintentional damage during milling.

Figure 3-12 shows the sample set-up and the working principle of the FIB-SEM. The FIB is used to mill the cross-section of the sample into slices of desired thickness, each of which is visualised by the SEM from an angle of 54° to the sample surface. Initially, the finely polished sample was coated with 30 nm gold, in order to protect the surface from unnecessary damage during the high energy FIB milling. A silver paste was also used to ensure the sample conductivity. The coated sample is placed onto the holder in the chamber and tilted to allow the sample surface to be normal to the FIB. The typical milling involves: 1. Finding and selecting the milling location; 2. Mill the trench; 3. Fine milling and imaging; 4. the images are combined in sequence and ready for 3D reconstruction.

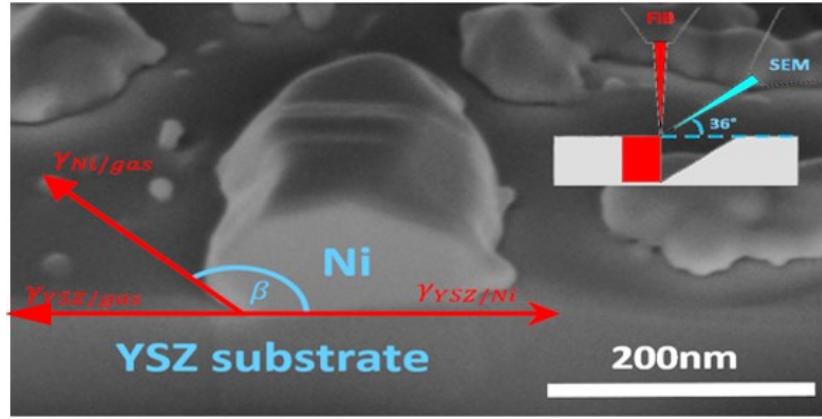


Figure 3-13 Ni wetting angle measurement using FIB-SEM cross-sectional imaging.

In this study, FIB-SEM is also used for measuring the Ni wetting angle, as shown in Figure 3-13. A wetting angle correction was considered due to the sample tilt of 54° for FIB milling. Here α is the real wetting angle, β is observed angle from SEM images. The contact point is a cross-section of a TPB (i.e., the intersection of gas/Ni/ YSZ).

$$\alpha = \arctan\left(\frac{\tan\beta}{\cos 36^\circ}\right) \quad \text{Equation 7}$$

3.2.2.4 X-Ray Diffraction (XRD)

In this study, a Philips PW 1729 diffractometer (operated at 40 kV and 40 mA) with a copper target producing Cu-K α radiation was used to obtain XRD data and to confirm phase purity and for structural analysis. All scans were performed between 20°-100° (with a step size of 0.02°/s and a dwell time of 10 seconds per step. The data analysis was performed using General Structure Analysis System and EXPGUI software based on Rietveld refinement which provided a method of analysing XRD patterns to obtain structural information, such as lattice

parameters and space group. This work was supported by Mr Richard Sweeney, Department of Materials, Imperial College London.

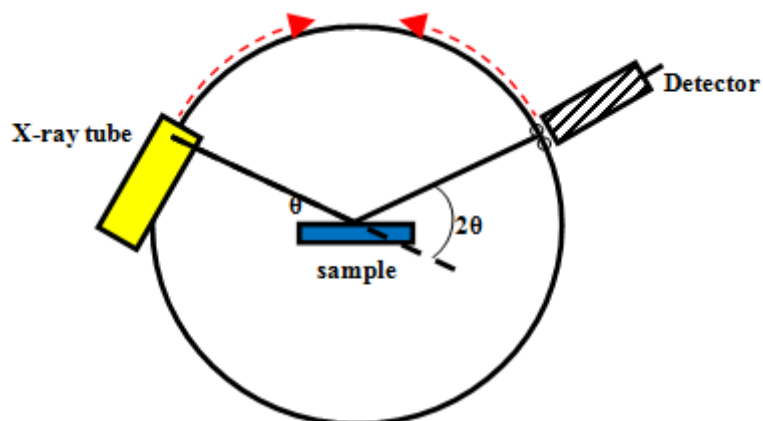


Figure 3-14 Schematic of XRD working principle.

3.2.3 Mechanical Characterisation

3.2.3.1 *Nanoindentation*

The indentation method is one of the most commonly used means of testing materials mechanical properties. In this study, the mechanical properties of Ni-YSZ thin films were measured by nanoindentation (NanoTest Platform, Micromaterial, UK) at room temperature. A sharp tip was indented into the material surface and the material response during the loading and unloading process was recorded, as shown in Figure 3-15.

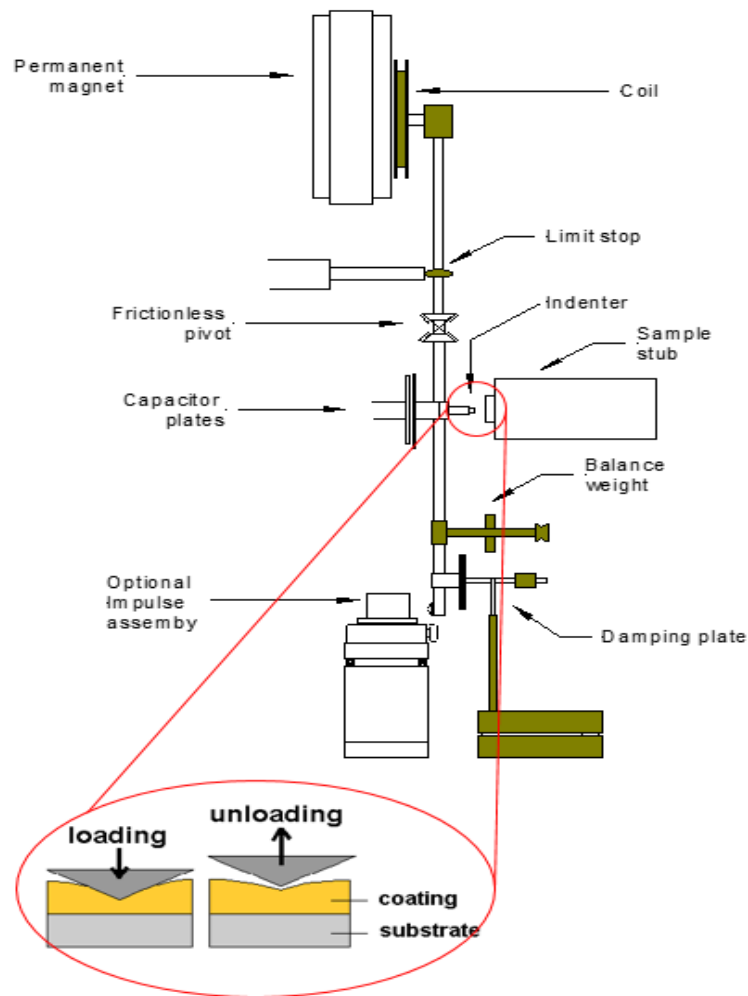


Figure 3-15 Schematic of nanoindentation experiment set-up and working principle.

Over 100 indentations per sample were carried out with a Vickers/ Flat Punch diamond tip with a 200 μm interval to obtain a statistically representative dataset and avoid outliers due to inhomogeneities. By considering the different thickness and microstructure of the samples, three different operational modes were used.

First condition mode: In this mode, the loading tip stops the load ramp when either of the maximum load or the maximum depth are reached; Load control mode: Setting the maximum and minimum loading force, the loading tip stops the load ramp when reach the maximum

force condition; Depth control mode: Setting the maximum and minimum loading depth, the loading tip stops the load ramp when reach the maximum depth condition

The table below shows the summarized nanoindentation parameters and experimental conditions used in this study.

Table 3-2 Summary of the nanoindentation conditions used in this study.

		Vickers diamond tip				Flat diamond tip	Punch diamond tip
Material		YSZ Pellet	Conventional Ni-YSZ	YSZ Scaffold	Ni-YSZ Scaffold	Ni-YSZ Scaffold	Fiber
Tip Parameters	Correction factor	1.055					
	Area(μm²)	$A = 4h_c^2 \tan^2 68^\circ = 24.504h_c^2$				A=3.14x202	
Operational Temperature		Normal Room Temperature 23 °C					
First condition Mode	Load (mN)		100-500				
	Depth (nm)		1000-3000				
Load Control Mode	Load (mN)	300-500	100-500	100-500	100-500	100-500	
	MAX Depth (nm)	10000	5000	5000	5000	3000	
Depth Control Mode	Depth (nm)		1000-5000	1000-5000	1000-5000	500-3000	
	MAX Load (mN)		300	300	300	200	

3.2.3.2 Mechanical Properties Data Analysis

The Nano-indentation machine measures the movement of a diamond probe in contact with the material surface. In order to make a measurement, an increasing load is applied and the probe indents the surface, as shown schematically below: Force, displacement and dwell time are recorded throughout the test.

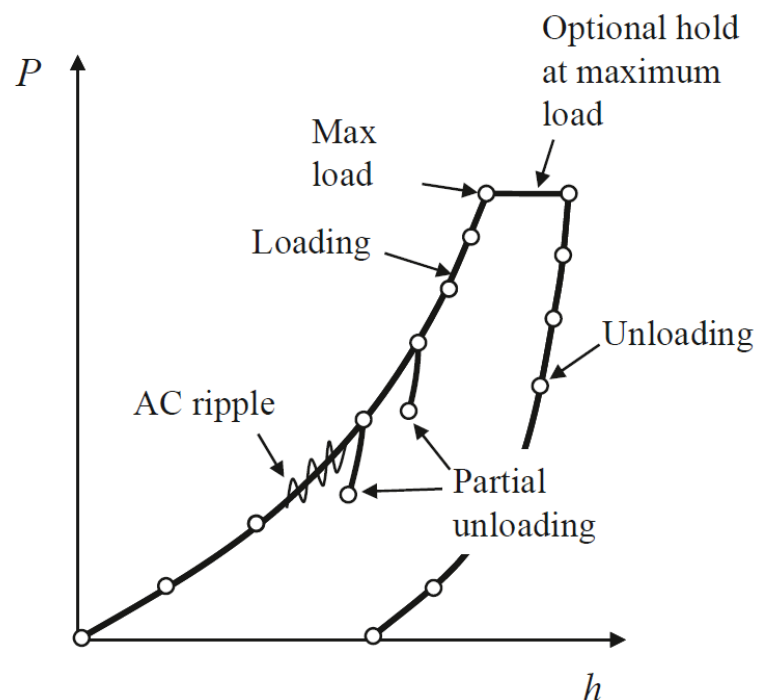


Figure 3-16 various components of a nanoindentation test cycle, h is displacement, P is loading force.

In an indentation, the elastic and plastic properties of the sample determine the shape of the unloading curve. It is customary for a nanoindentation instrument to allow for a dwell or hold period at each load increment and at maximum load. The dwell settings at each load increment allow the instrument and specimen to stabilize before depth and load readings are

taken. Hold period data at maximum load can be used to measure creep within the sample or thermal drift of the apparatus during a test. Figure 3-16 illustrates the loading, hold and unloading periods used in a typical test cycle.

The elastic modulus, E , and hardness, H , were calculated from the load–depth curves using Oliver–Pharr analysis¹³⁰:

$$E = \frac{1-\nu^2}{\frac{1}{M} - \frac{1-\nu_i^2}{E_i}} \quad \text{Equation 8}$$

$$M = \frac{\beta}{2} \left(\frac{dp}{dh} \sqrt{\frac{\pi}{A}} \right) \quad \text{Equation 9}$$

$$H = \frac{P_{max}}{A} \quad \text{Equation 10}$$

where ν is the Poisson's ratio of the specimen, which is 0.387 approximately¹³¹; E_i and ν_i are the elastic modulus=1220 GPa and Poisson's ratio= 0.07 of the diamond indenter, respectively; M is the indentation modulus, β is a geometrical correction factor, which is 1.055 for a Vickers diamond tip¹³²; P_{max} is the maximum load applied and A is the contact area between indenter and material, which is, $A = 4h_c^2 \tan^2 68^\circ = 24.504h_c^2$ for a Vickers indenter, where h_c is the indentation loading depth.

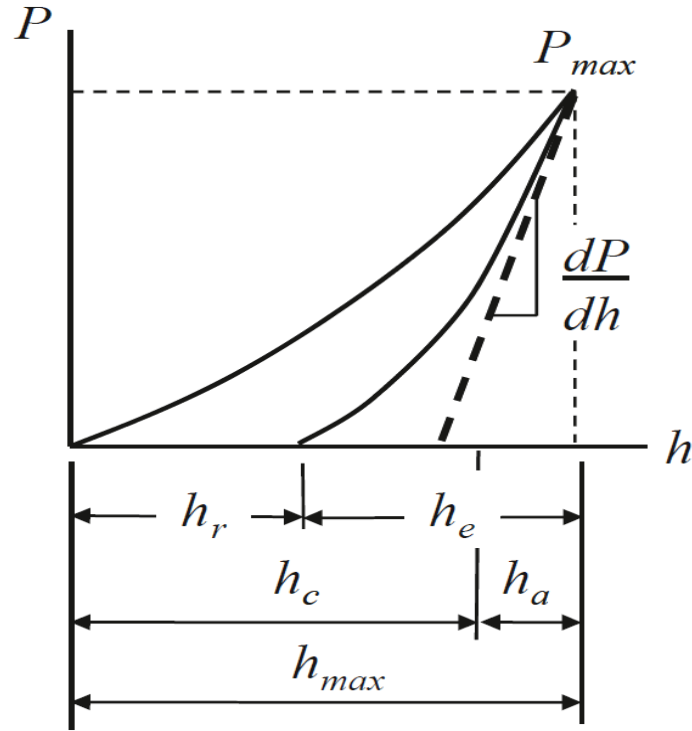


Figure 3-17 Compliance loading-unloading curves. From a nanoindentation experiment with maximum load P_{max} and depth beneath the specimen free surface h_{max} . The depth of the contact circle h_c and slope of the elastic unloading dP/dh allow specimen modulus and hardness to be calculated. h_r is the depth of the residual impression, and h_e is the displacement associated with the elastic recovery during unloading.

3.2.4 Microstructure 3D Reconstruction

3.2.4.1 Image processing

The Ni-YSZ material is composed of three components, i.e. air-filled pores impregnated with resin, solid Ni material and solid YSZ, which were normally represented by black, dark grey and light grey (or white) pixels in the FIB-milled SEM images obtained. In this study, all the

image processing and 3D reconstruction of the data were performed using the Avizo software package.

Normally, image processing and 3D reconstruction includes four steps, using Avizo:

- i. Alignment of the entire image stack to compensate for x-y plane shifting and z-direction drifting;

Due to the combination of charging and drifting problems throughout SEM imaging, image alignment is necessary to correct these distortions. This common image alignment involved drift correction and shear correction. Algorithm cross-correlation between two successive images in a stack ensured that all the images were aligned with the reference feature in the first image, and this was best achieved if the images were very similar from slice to slice, for example approximately the same intensity and brightness variations throughout the data stack, as shown in Figure 3-18.

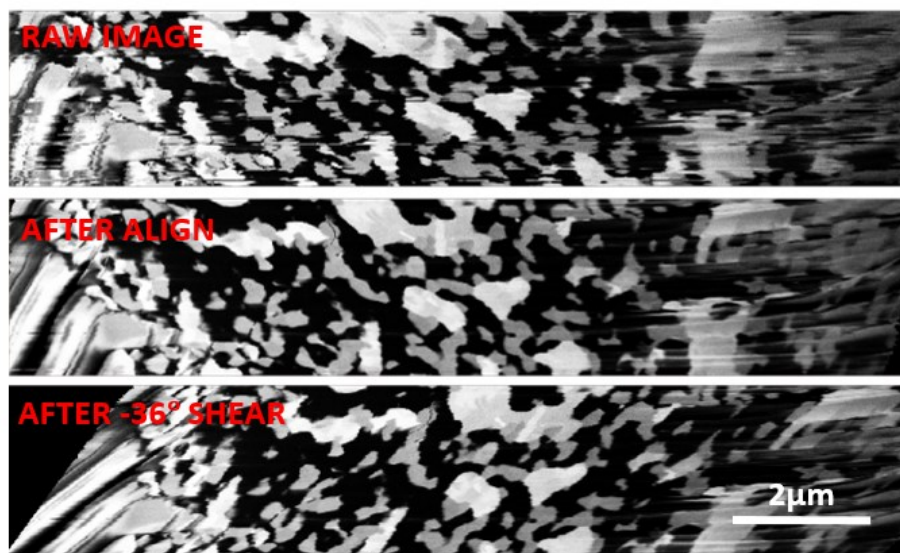


Figure 3-18 image processing in YZ direction, the presentation of the raw image stack, after aligning and after shearing.

- ii. choose and crop-out of a suitable sub-volume, as shown in Figure 3-19.

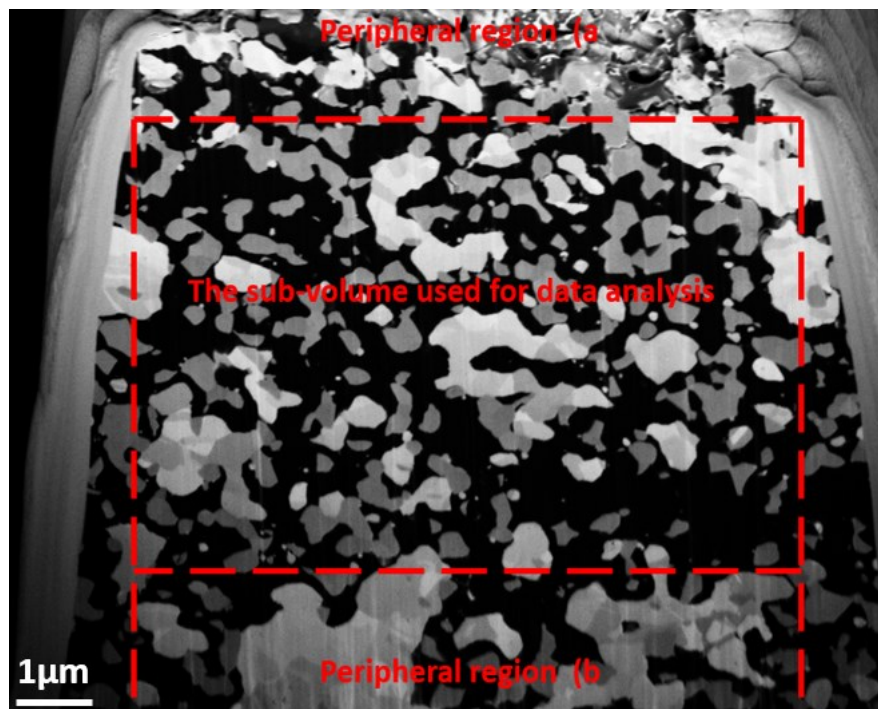


Figure 3-19 the suitable sub-volume is highlighted. Region (b) is excluded due to its over intensity grading, which could lead to imprecision in image segmentation.

- iii. image filtering:

A large numbers of filters are available in Avizo for smoothing, sharpening of objects and for noise removal in the grayscale images and the 3D volume. Cross-sectional image smoothing was based on a median filter algorithm to reduce noise before segmentation, as shown in Figure 3-20.

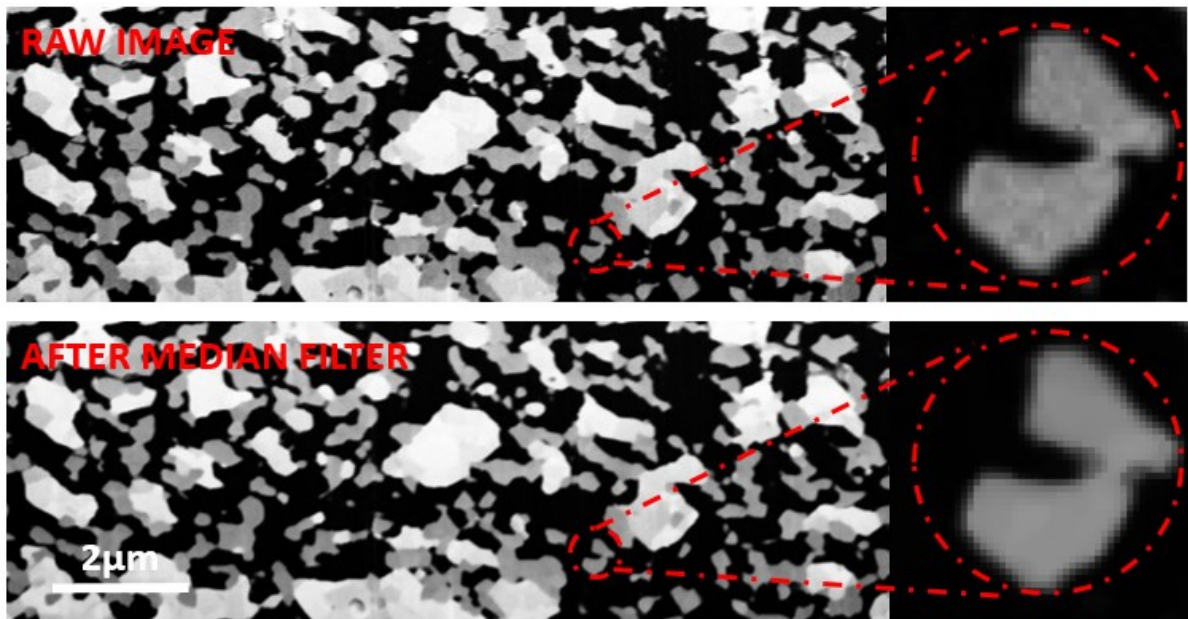


Figure 3-20 image processing in X-Y direction. The presentation of FIB-SEM raw images before and after Median Filter.

iv. Image Segmentation

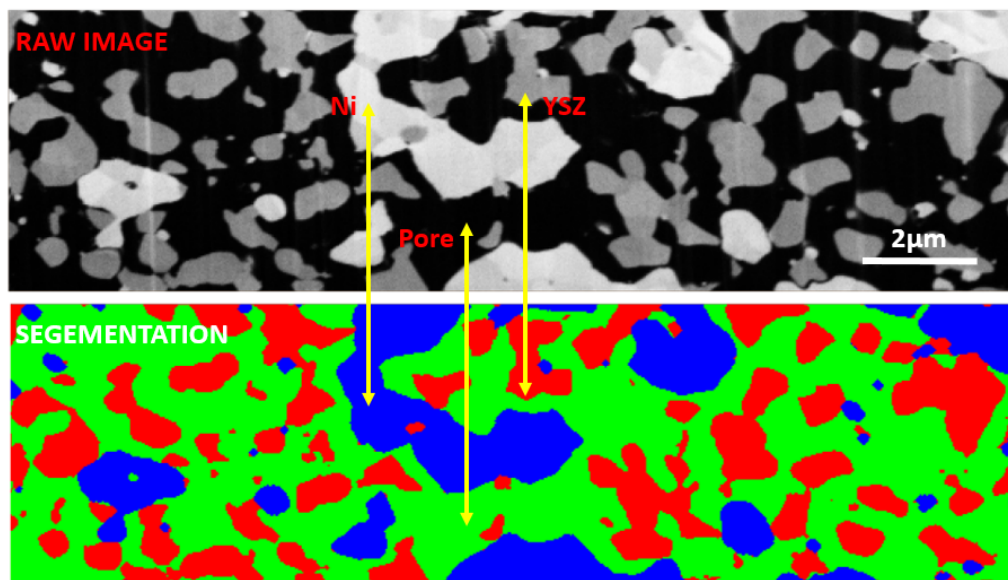


Figure 3-21 the cross-section raw images of FIB-SEM and its segmentation of a conventional Ni-YSZ sample.

Segmentation of the image stack by thresholding of the grayscale to accurately identify and partition the image into multiple segments which were assigned the same visual characteristics corresponding to relevant material components (or phases), as shown in Figure 3-21.

v. 3D visualisation and representation.

After the segmentation, each phase of the sample can be clearly identified for 3D reconstruction. Figure 3-22 shows the reconstruction results from the segmented image stack. This result is used for quantified analysis of the corresponding samples.

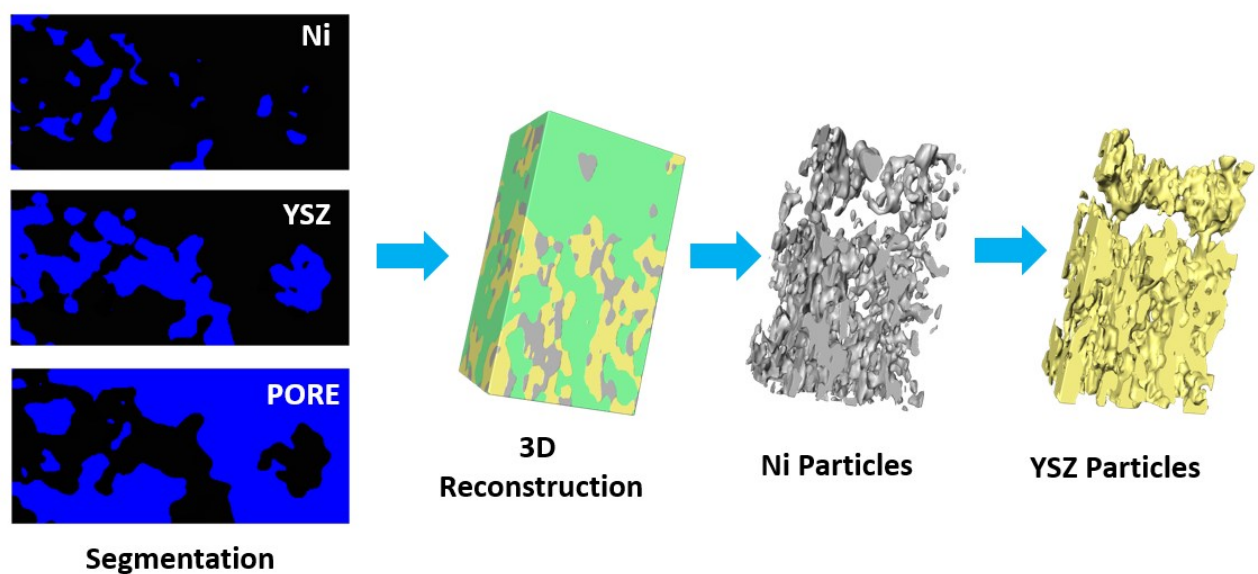


Figure 3-22 the presentation of FIB-SEM image segmentation (the selected phase is indicated in blue) and its 3D reconstruction. Each phase can be identified after 3D segmentation.

3.2.4.2 Particle Size and Distribution Measurement

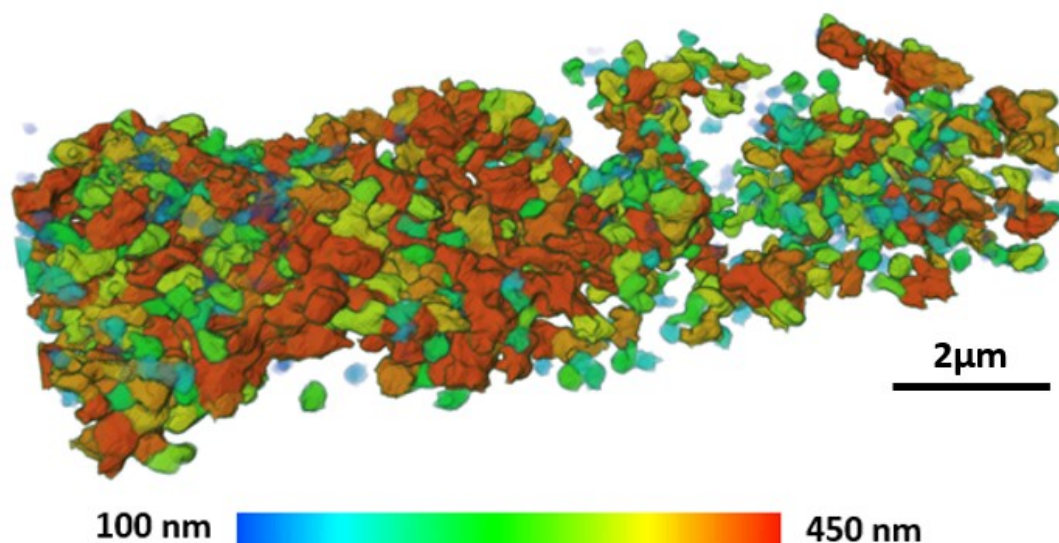


Figure 3-23 the 3D reconstructed microstructure for the Ni-YSZ, showing the Ni particles and their size distribution across the electrode.

Based on the 3D structure generated in the last process, the particle size and particle distribution of the electrode were quantified. This includes the Ni/YSZ/Pore size presented in a colour code and calculated based on the equivalent spherical diameter. This particles size analysis was supported by Dr. Vladimir Yufit and Dr. Farid Tariq using software developed by IQM Elements (London) ¹¹², only used in Chapter 6.

3.2.4.3 Porosity and Interfacial Area Measurement

Due to the very small volume of thin (15-30 μm) Ni-YSZ films, it was not possible to apply any physical method to measure their porosities and material interface area. Instead, they were measured using the quantification of Avizo 9.0.0 image processing software (VSG Co., USA) based on the actual 3D microstructural data of the films collected using the FIB-SEM

tomography technique. The porosity was quantified based on the volume percentage of pore phase to overall volume. The interface areas were quantified by calculating the contact area between each phase by using the statistic function provided by Avizo, i.e. Ni-YSZ, Ni-Pore and YSZ-Pore.

3.2.4.4 *Triple Phase Boundaries Measurement*

The triple phase boundaries (TPB) are the contact points of the nickel phase, YSZ phase and gas phase. From the 3D reconstructed microstructure, the TPBs can be identified and calculated. Normally, the total TPB can be simply calculated by measuring the three phase contacting length. The measurement of active TPB is more advanced, involving the percolation of each phase. In this work, the assumption when calculating active TPB length is that the TPB can be only be active when the corresponding YSZ phase is percolated from the electrolyte and the nickel and pore phases are percolating from the top surface.

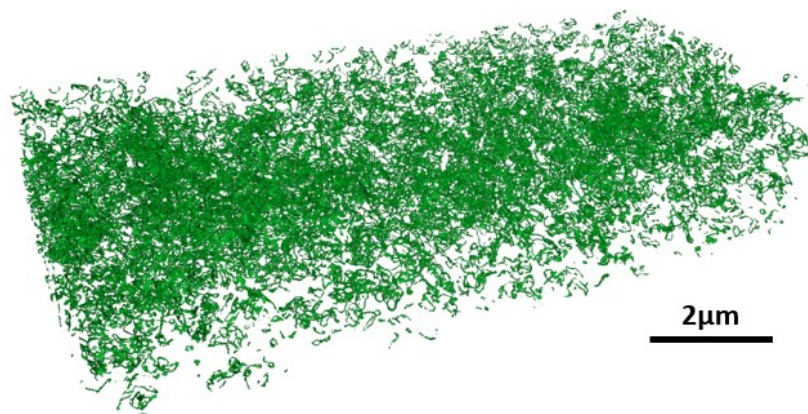


Figure 3-24 presentation of triple phase boundaries within a Ni-YSZ electrode from 3D reconstruction.

3.3 CHAPTER SUMMARY

In this chapter, all the details of sample preparation were introduced. These include conventional Ni-YSZ symmetrical cells, YSZ scaffold, Ni infiltrated YSZ scaffold symmetrical cells, Ni infiltrated YSZ fibre scaffold symmetrical cells and 2D thin film Ni on YSZ cells. The experimental conditions and operation procedures for material characterisation have also been explained. These include EIS, SEM, E-SEM, FIB-SEM, EDX and nanoindentation. In addition to these, the 3D reconstruction process has been introduced. These characterisation techniques were used for all the materials analysis presented in later chapters.

CHAPTER 4 CHARACTERISATION OF NI-YSZ ANODE DEGRADATION UPON REDOX CYCLING

4.1 REDOX CYCLING PROCEDURE

Redox cycling was carried out by sequentially exposing the cell to two different gas streams, air and diluted hydrogen (a mixture of 5 vol % H_2 and 95 vol % N_2), both humidified with 3% vol H_2O , with a flush of N_2 in between. The process was carried out at 800 °C within a quartz tube furnace. For each redox cycle, the samples were kept in air for 1 hour, flushed for 10 minutes in N_2 and then reduced in H_2 for approximately 5 hours, as schematically reproduced in Figure 4-1. This procedure, already adopted by Shimura et al.⁸⁵, rather than mimicking any specific accidental or emergency situation, represents a benchmark scenario for reproducible redox cycling measurements around the typical working condition of an SOFC.

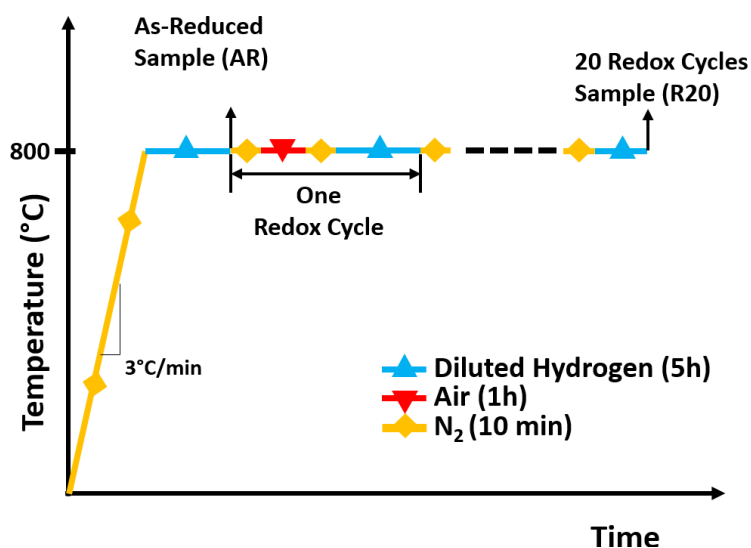


Figure 4-1 Representation of the redox cycling procedure. Impedance spectra were taken during each reduction process as a function of time.

4.2 ELECTROCHEMICAL DEGRADATION DURING AND AFTER REDOX CYCLING

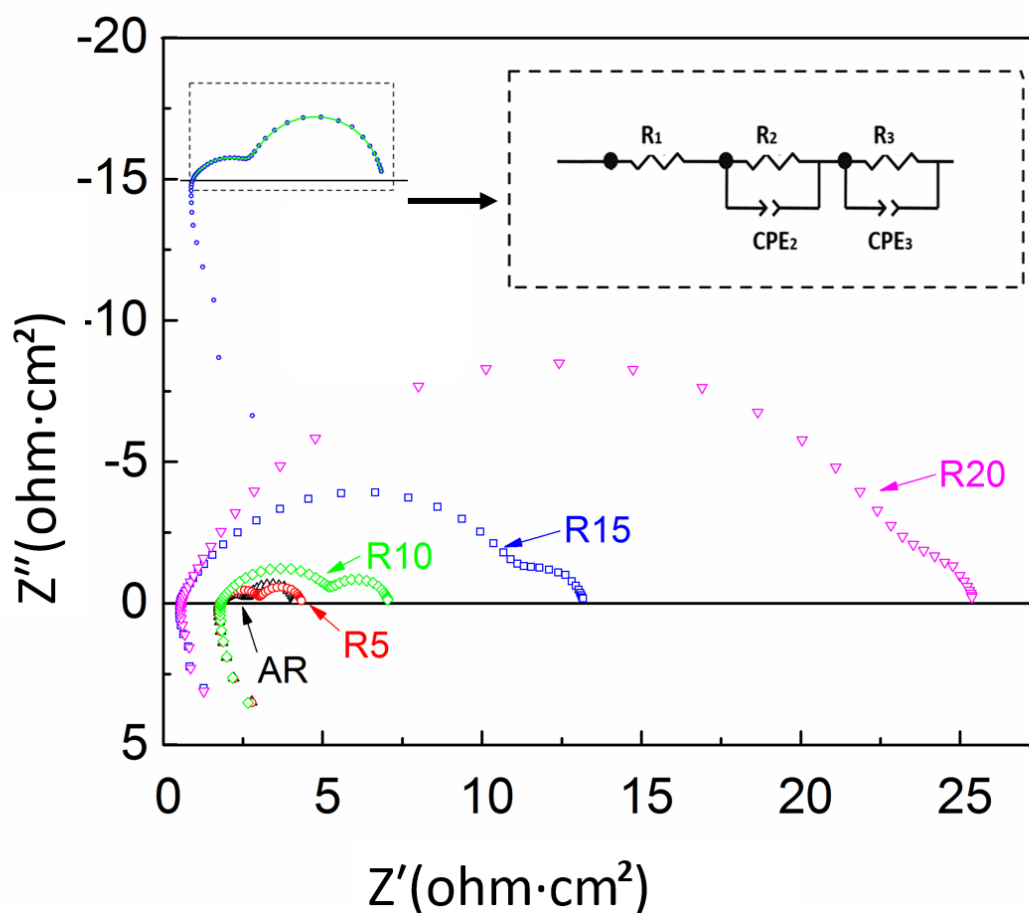


Figure 4-2 Impedance spectra recorded, within the frequency range $10^6 - 10^{-1}$ Hz, after 0, 5, 10, 15, 20 redox cycles at 800 °C, 2h after the introduction of wet 5 vol % H_2 , AR represents as-reduced, R5 represents 5 redox cycles, R10 represents 10 redox cycles and so on. The inset shows the equivalent circuit used to fit the results. R_1 , R_2 , R_3 represent the high-frequency intercept resistance, intermediate frequency resistance and low-frequency resistance respectively; CPE_2 , CPE_3 represent constant phase element for the corresponding frequency⁹⁶.

The electrochemical degradation of the cell was quantified by measuring the impedance upon introduction of hydrogen during the redox cycles. Five selected redox cycles are presented in

Figure 4-2: a minor change of ohmic resistance (R_1), a significant increase in electrochemical reaction polarisation resistance (R_2) and a relatively steady diffusion resistance (R_3) are observed. This is consistent with work performed by Laurencin et al.⁹⁶. The inset shows an example of fitting with the equivalent circuit, within frequency range of 10^6 – 10^{-1} Hz.

A physically-based model was used to estimate the active TPB density from the evolution of R_2 , under the assumption that the electrochemical performance changes are directly linked to the TPB density only⁵⁰. Figure 4-4 shows the TPB density estimated by the electrochemical model for the as-reduced sample and after 5, 10, 15 and 20 redox cycles. These data points are compared with the active TPB density evaluated from tomographic reconstruction at selected points. Within any redox cycle, the model predicts a fast decrease in TPB density within 2 hrs, followed by stabilisation. The Ni surface roughness and nanoparticles observed using SEM (see next section) may contribute significantly to the TPB evolution. Although not exhaustively proved yet, it could be proposed that, at an early stage, NiO-Ni deformation or asymmetrical reduction processes lead to a rough surface⁶⁹ and generate a large number of Ni nanoparticles¹³³. This surface roughness and the nanoparticles attached to the percolating Ni and YSZ frameworks can lead to a significant increase in TPB density. However, these features start to agglomerate with other Ni particles or form volatile Ni species¹³⁴, resulting in a subsequent rapid drop in TPB density. This rapid evolution of TPB density has also been reported in nano-infiltrated anodes^{69,135}. For the samples with more redox cycles, the initial degradation tends to be slower, as Ni particles are comparatively bigger (see next section). Overall, after stabilisation, the TPB density of samples shows a decreasing trend versus redox cycle number. This may be caused by Ni agglomeration during the overall redox cycling process.

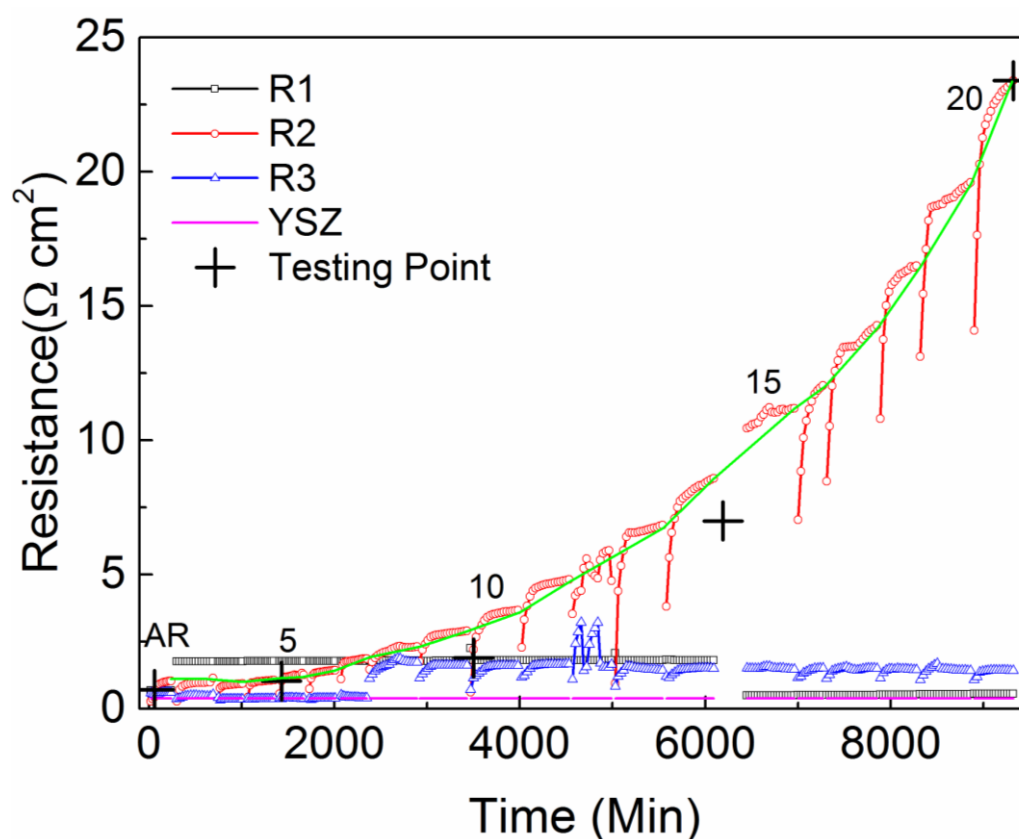


Figure 4-3 Resistances as a function of time during the reduction process of redox cycling as from EIS fitting. The solid green line is a guide to the degradation trend. The cross marks represent the time scale of the samples used for 3D tomography reconstruction.

The comparison of the active TPB density between FIB-SEM tomography and the model prediction shows a good consistency for the AR, R5 and R10 samples, see Figure 4-4. For the samples after 15 and 20 redox cycles, as the number of redox cycles increases, the difference between the 3D tomography data and the electrochemical model values increases. This is because the complex microstructural changes caused by redox cycling may not all be detected by 3D tomography since Ni nanoparticles, nano surface roughness and cracks may be beyond the resolution level, as shown in Figure 4-5 and extensively discussed by Bertei et al.⁶⁹. Moreover, the electrochemical model attributes all the degradation to the decrease in TPB

density, while cracks in the YSZ framework would reduce the effective ionic conductivity, which is considered constant in the model. Thus, the discrepancy of values for R15 and R20 suggests that the YSZ cracks, generated during redox cycling, led to a decrease in the effective ionic conductivity, not considered by the electrochemical model.

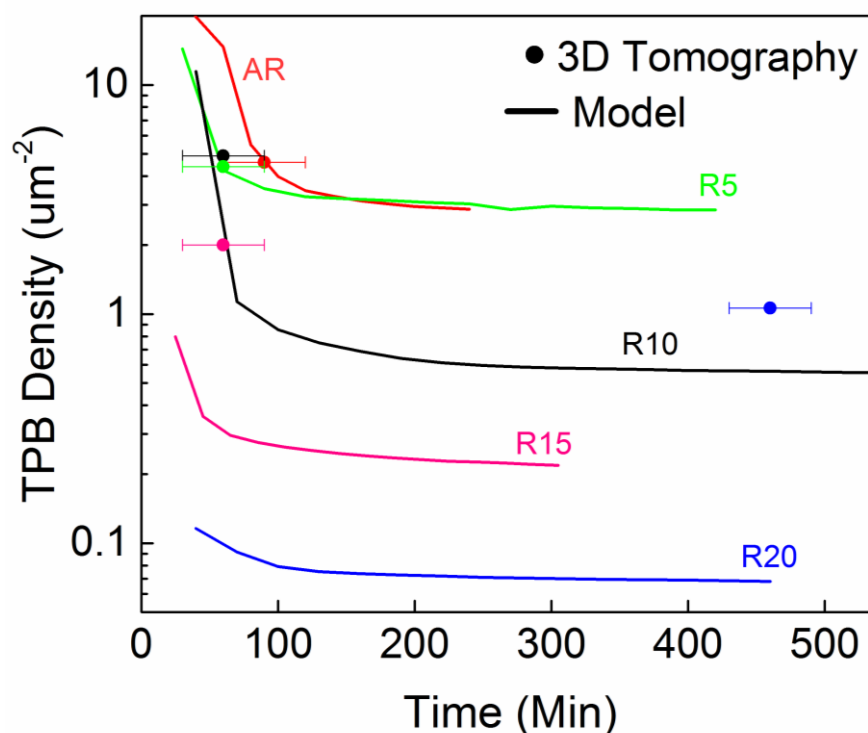


Figure 4-4 Active TPB density vs time for different redox cycles as determined from 3D tomography (symbols) and EIS modelling (line). The error bars refer to the uncertainty in positioning the time scale of the reconstructed samples, due to the cooling time of the samples. Note that, differently from other samples, sample R20 refers to the end of the annealing time.

4.3 MICROSTRUCTURAL CHARACTERISATION

The microstructural characterisation was carried out with both SEM image analysis and 3D tomography reconstruction. Five different samples, with various numbers of redox cycles, were tested. The approximate time scale of sample observation points is indicated in Figure 4-3 using black crosses. Figure 4-5 shows the SEM image of the Ni-YSZ electrode. In the as-reduced sample (a), detachment between Ni and YSZ particles is observed, as a consequence of Ni volume shrinkage after reduction. The bottom two images show the SEM top surfaces of redox cycled samples. Ni particle agglomeration is observed, that could result in the increase of pore size. More interestingly, a growing number of Ni nanoparticles appeared on the Ni surface and at the boundary between Ni and YSZ. This is consistent with the Ni microstructure change reported by Hanasaki et al.⁵². The Ni nanoparticles located at the boundary between Ni and YSZ can significantly extend the TPB length, which is consistent with the increase in TPB density seen in the early stage of each reduction process as estimated by the model from the analysis of EIS data (Figure 4-3 and Figure 4-4). In addition to this, cracks are found between YSZ grain boundaries, especially after a large number of redox cycles (>10). This could be due to the mechanical damage caused by Ni volume expansion during reoxidation, since this type of crack does not appear in the as-reduced samples. By constantly breaking the YSZ grain boundaries around Ni particles, the YSZ framework within the electrode results in smaller isolated regions, thus losing its ionic transport path and supporting function. This contributes to the steady increase in electrochemical reaction polarisation resistance as well as to the decrease in the material hardness and elastic modulus as discussed in the next section.

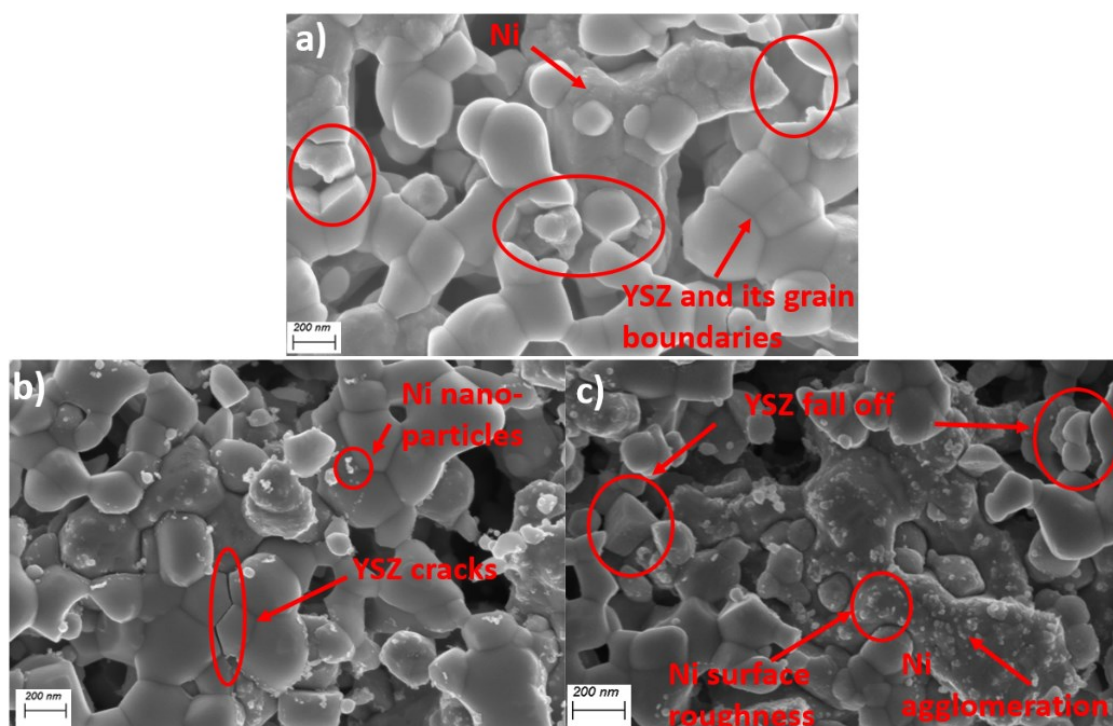


Figure 4-5 a) Top-surface SEM images of an as-reduced Ni-YSZ electrode showing the detachment between Ni and YSZ caused by Ni volume shrinkage after reduction, leading to a relatively large space in between; b) Top-surface SEM images of Ni-YSZ electrodes after 5 redox cycles showing the crack along the YSZ grain boundaries, with an approximate gap of 10nm, and the Ni nanoparticles; c) Top-surface SEM images of Ni-YSZ electrodes after 10 redox cycles showing YSZ grain detachment from its framework and Ni surface roughness, agglomerated nickel particles.

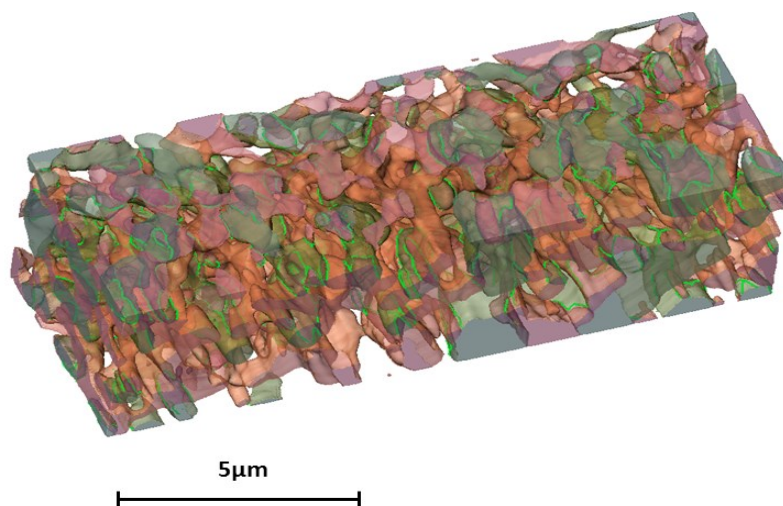


Figure 4-6 representation of the 3D reconstructed microstructure of the as-reduced Ni-YSZ, with Ni in transparent green, YSZ in transparent red and where the green line indicates the active TPBs.

The microstructural characterization is complemented by 3D tomographic reconstruction. The middle column of Figure 4-7 shows the cross-sectional images from FIB-SEM. The Ni particle (light grey) agglomeration is confirmed here, as well as the trend of the YSZ structure to be broken into smaller pieces, as discussed above. However, due to the limitation of FIB-SEM image resolution, the Ni nanoparticles cannot be detected. This is because the average voxel size of these FIB-SEM images is around 20 to 25 nm, which is about 2 to 5 times the diameter of the Ni nanoparticles observed with SEM⁶⁹. The presence of small nanoparticles around the TPB may also cause errors in the microstructural tomographic quantification because the colour of each pixel around the TPB is highly affected by the surrounding Ni nanoparticles, which makes image segmentation harder in redox-cycled samples.

Table 4-1 Calculated microstructure parameters from the reconstructed 3D tomographic datasets of anodes with different numbers of redox cycles.

		AR	R5	R10	R15	R20
Porosity		0.442	0.516	0.537	0.534	0.571
Active TPB Density (μm^{-2})		4.63	4.90	4.40	2.08	1.06
Surface Area Per Total Volume (μm^{-1})	Ni	7.90	7.05	5.97	6.42	5.08
	YSZ	3.65	4.22	3.00	3.82	3.04
	Pore	6.19	6.39	5.91	7.54	6.36
Interface Area Per Total Volume (μm^{-1})	Ni-YSZ	2.68	2.44	1.53	1.35	0.88
	Ni-Pore	5.22	4.61	4.44	5.07	4.20
	YSZ-Pore	0.97	1.78	1.47	2.47	2.16

A tomographic microstructural reconstruction was carried out for each sample^{112,136}. The original images were segmented into three different colours (Blue: Ni, green: YSZ, grey: pore phase), as shown at the right-hand side of Figure 4-7. Figure 4-6 shows a representation of the 3D reconstructed microstructure of the as-reduced Ni-YSZ, with Ni in transparent green, YSZ in transparent red and where the green line indicates the active TPBs. The calculated microstructural parameters are shown in Table 4-1. The anode porosity, initially similar to that of anode-supporting layers^{137,138}, increases with redox cycling, consistent with the previously-reported result from Holzer et al.¹³⁹. In addition, the TPB density decreased as redox cycles are repeated. The Ni surface area per volume decreased after the redox cycles, which corroborates the increase in Ni particle size observed from SEM and FIB-SEM images. The interfacial area between Ni and YSZ also decreased, suggesting that the detachment caused by Ni volume shrinkage during reduction can be one reason for the decrease in effective TPB density. Therefore, the quantitative 3D tomographic analysis confirms the

trends detected with SEM analysis regarding Ni agglomeration, loss in TPB density and cracking of the YSZ network upon redox cycling.

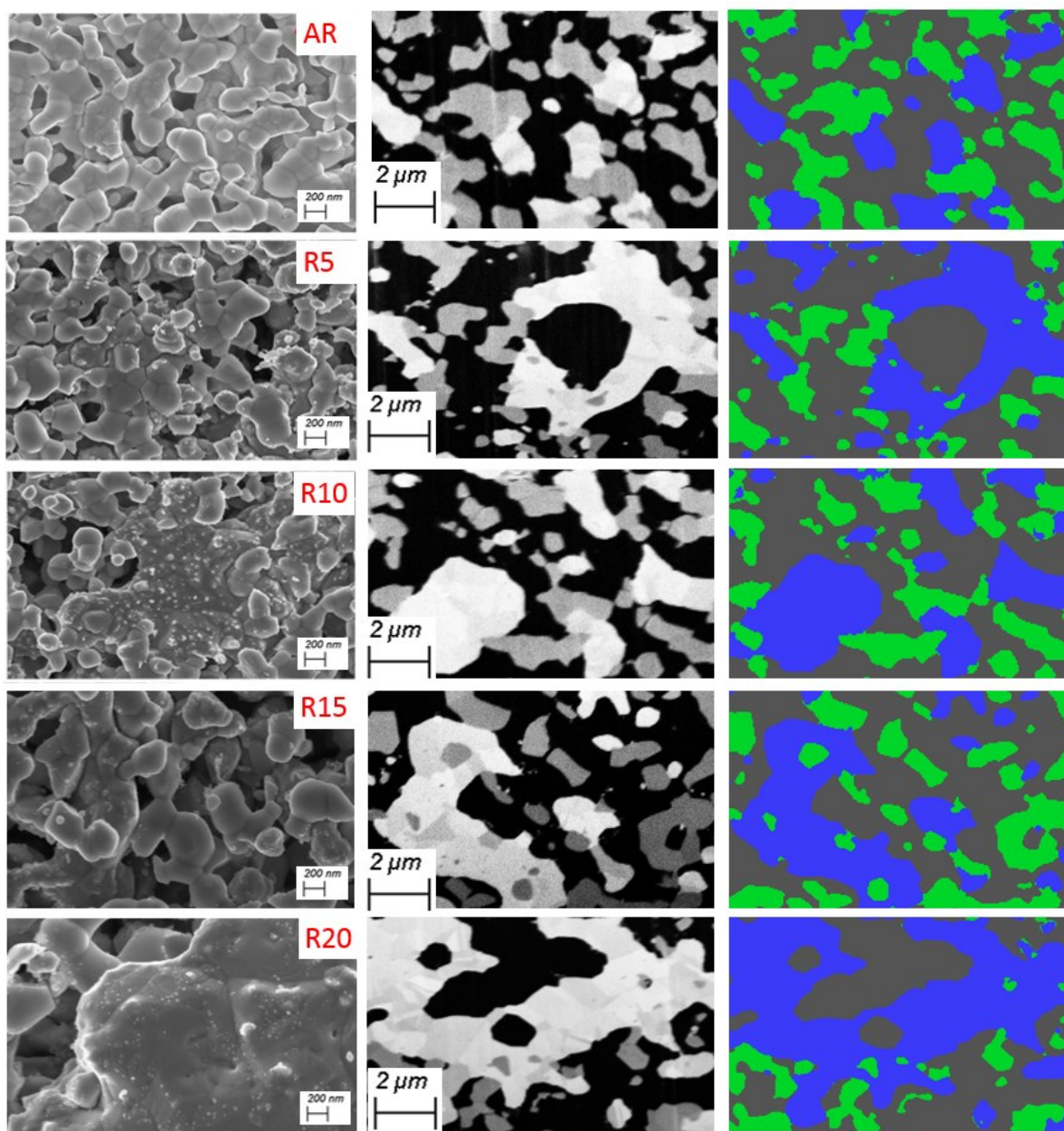


Figure 4-7 Left: SEM images of five redox cycled samples. Middle: FIB-milled cross-sectional micrographs of Ni-YSZ anodes after different redox cycles. Light grey: Ni, dark grey: YSZ, and black: pore. Right: the segmented images corresponding to the left side. Blue: Ni, green: YSZ, grey: pore.

4.4 MECHANICAL PROPERTIES CHANGE UPON REDOX CYCLING

The elastic modulus and hardness of each sample were measured using the nanoindentation technique. The load-depth curve of redox-cycled samples are plotted in Figure 4-8- a. In this experiment, the maximum indent load is 115 mN, producing a maximum indentation depth of between 3.5-5.0 μm . This indentation depth is kept to less than 20% of the electrode thickness (25-30 μm), so that the substrate effect on the measurement is negligible¹⁴⁰. Having used a symmetric setup rather than an anode-supported configuration makes the electrode constrained on one side by the stiffer YSZ substrate. Thus, the propagation of the mechanical stresses, internally generated within the anode by redox cycling, affects mainly the anode itself, without causing cracking of the YSZ electrolyte and subsequent stress relaxation. Therefore, the symmetric setup enables focus on the intrinsic mechanical behaviour of the porous anode alone, although the stiffness of the thick YSZ electrolyte may slightly amplify the internal anode cracking when compared to an anode-supported configuration.

The clear shift in the load curves indicates that the samples with more redox cycles display lower hardness, since the same loading force results in greater penetration depth. Since the nanoindentation has a strong sensitivity to individual dislocation interactions, oscillations in each loading curve were observed. This is caused by a complex combination of factors, such as mechanical instabilities, development of dislocation networks, and incipient plasticity¹²³. The variance of these oscillations shows that the sample with more redox cycles has a steadier loading curve. Probably, redox cycling promoted the fragmentation of the YSZ framework, which simplified the disorder interactions between the Ni-YSZ composite and indenter, as observed from both SEM and FIB-SEM. Figure 4-8-b & c show the nanoindentation results for

elastic modulus and hardness of the electrodes as a function of the number of redox cycles. The results show a clear decreasing trend in both the elastic modulus and hardness, accompanied by a different standard deviation which reflects the combined effects of surface roughness, densification and internal structure changes. With different indentation depths, the generally larger scatter in the data might be related to the greater roughness of the films when compared with the bulk samples. Nevertheless, for both the elastic modulus and the hardness, the standard deviation first increases until 10 cycles and then decreases, indicating that more reproducible data were collected after 20 redox cycles. The maximum in data scattering around 10 cycles can be explained by considering the progressive fragmentation of the microstructure in comparison with the indentation depth, which is 3-5 μm . In the as-reduced sample, the microstructure is macroscopically homogeneous, although Ni-dense and YSZ-dense regions are present at the μm scale as evident in Figure 4-5, causing a relatively narrow standard deviation. As the number of redox cycles increases to 5 and 10 cycles, cracks separate relatively big and stiff YSZ fragments from Ni regions (Figure 5), thus the microstructure becomes more locally heterogeneous, as revealed by a larger standard deviation in the mechanical properties. As the redox cycling proceeds (i.e., 15 and 20 cycles), the microstructure is fragmented into pieces smaller than the indentation depth (5 μm), so that the mechanical properties appear to be more spatially homogeneous, resulting overall in a lower standard deviation of mechanical properties (Figure 4-8).

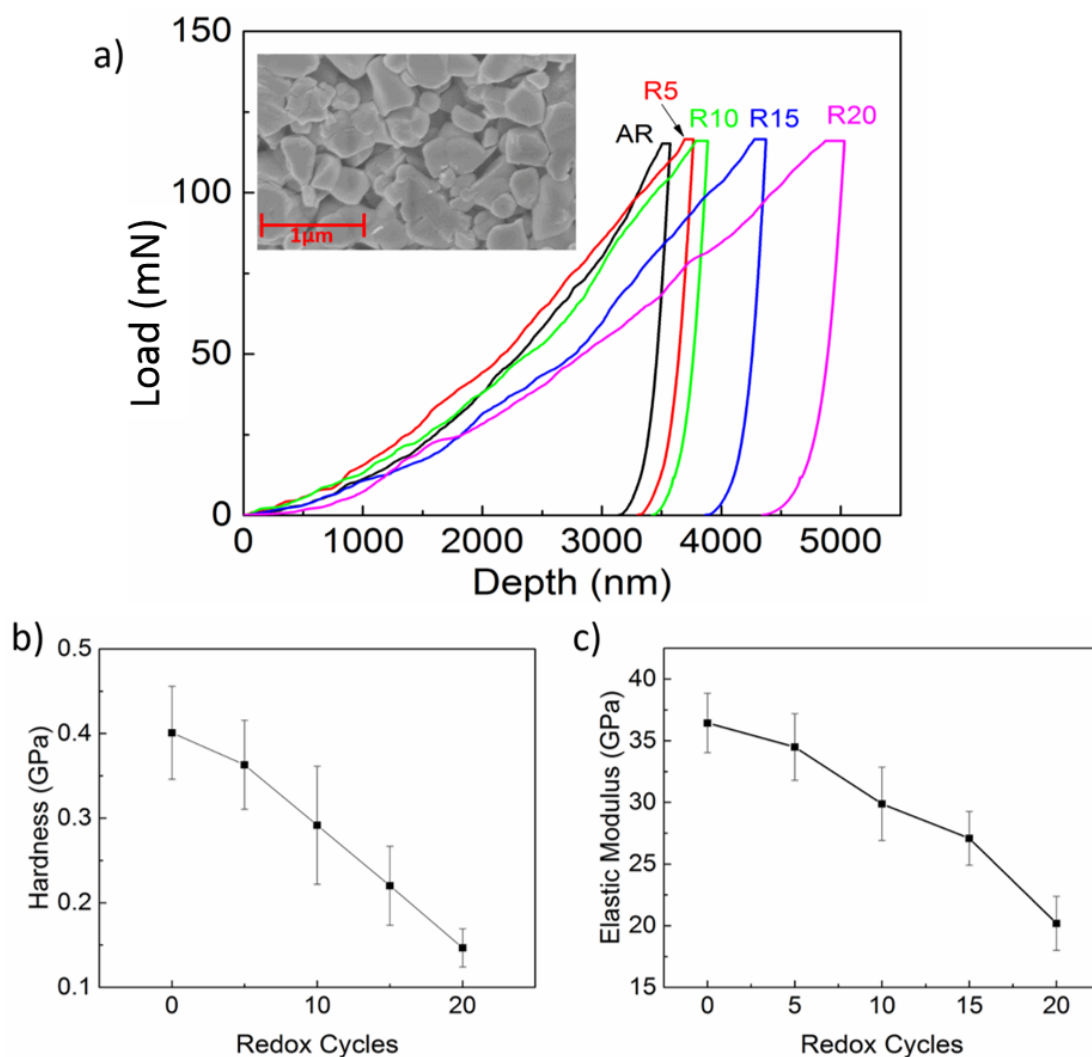


Figure 4-8 a) Load- depth curves for Ni-YSZ anodes after different numbers of redox cycles as obtained from nanoindentation, the inset shows the area been indented on the as-reduced sample ; b) Hardness vs. numbers of redox cycles for the tested Ni-YSZ anodes; c) and Elastic modulus vs. numbers of redox cycles for the tested Ni-YSZ anodes. The standard deviations are obtained statistically from over 200 measurements per sample.

Figure 4-9 shows the measured Ni-YSZ elastic modulus versus porosity compared with two empirical fitting formulas. The black dashed line represents a linear fitting of porous Ni-YSZ samples prepared by varying the porosity by changing the reduction temperature between 600 and 1000 °C as reported in the literature⁹⁷. The blue dashed line shows an exponential

fitting of a porous tape cast Ni-YSZ electrode, sintered at 1400°C in air for 2 h, as reported by Radovic et al.⁹⁵ The dense elastic modulus values E_0 and porosity constants b are listed in Table 4-2. While the data points obtained in this study (red symbols) cannot be fitted by a linear correlation, the exponential equation allows for a good fitting once the porosity constant is increased to $b^* = 3.813$ (see the red dashed line in Figure 8). This increase in porosity constant could be related to differences in the measuring techniques and input parameters as well as to the microstructural changes occurred during the redox cycling. In fact, redox cycling does not increase the porosity only, but it also leads to the internal YSZ framework break down, Ni agglomeration and change in pore shape, resulting in an elastic modulus smaller than that expected for non-redox cycled electrodes.

Table 4-2 Linear and exponential correlations of elastic modulus vs porosity. E_0 is the elastic modulus of the fully dense material, b is a porosity constant and p is fractional porosity. b^* is the porosity constant fitted in this study, considering the microstructure damage caused by redox cycling.

		$E_0(\text{GPa})$	b
Linear	$E = E_0(1 - bp)$	205.93 ⁹⁷	1.756
Exponential	$E = E_0 \exp(-bp)$	212.1 ⁹⁵	3.16
Exponential	$E = E_0 \exp(-bp)$	212.1	3.813*

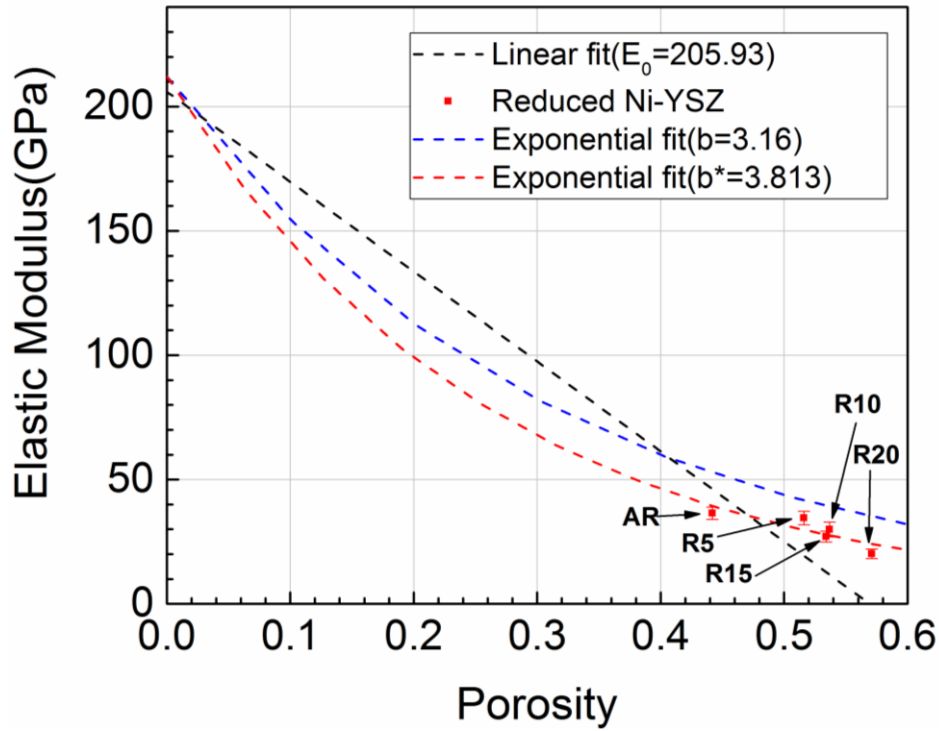


Figure 4-9 Elastic modulus vs porosity of reduced samples. The results of fitting using exponential and free linear model are represented as blue and black lines, respectively, while the red line corresponds to the exponential fit with a different porosity.

4.5 MICROSTRUCTURE ANALYSIS BASED ON SEM AND NANO-INDENTATION RESPONSE

Understanding the redox cycling impact of conventional Ni-YSZ material by combining microstructure evolution and mechanical response gives more insight into material degradation. Figure 4-10 shows the top view image obtained from the Ni-YSZ electrodes after 10 redox cycles. Figure 4-10 b & c) present the proposed mechanism for the YSZ crack generation process. Due to those nickel particles accommodated in the limited space between the YSZ frameworks, the volume expansion, during oxidation process, leads to the

cracks at YSZ grain boundaries. This YSZ framework cracking would be expected to result in a decrease in both ionic conductivity and mechanical stability.

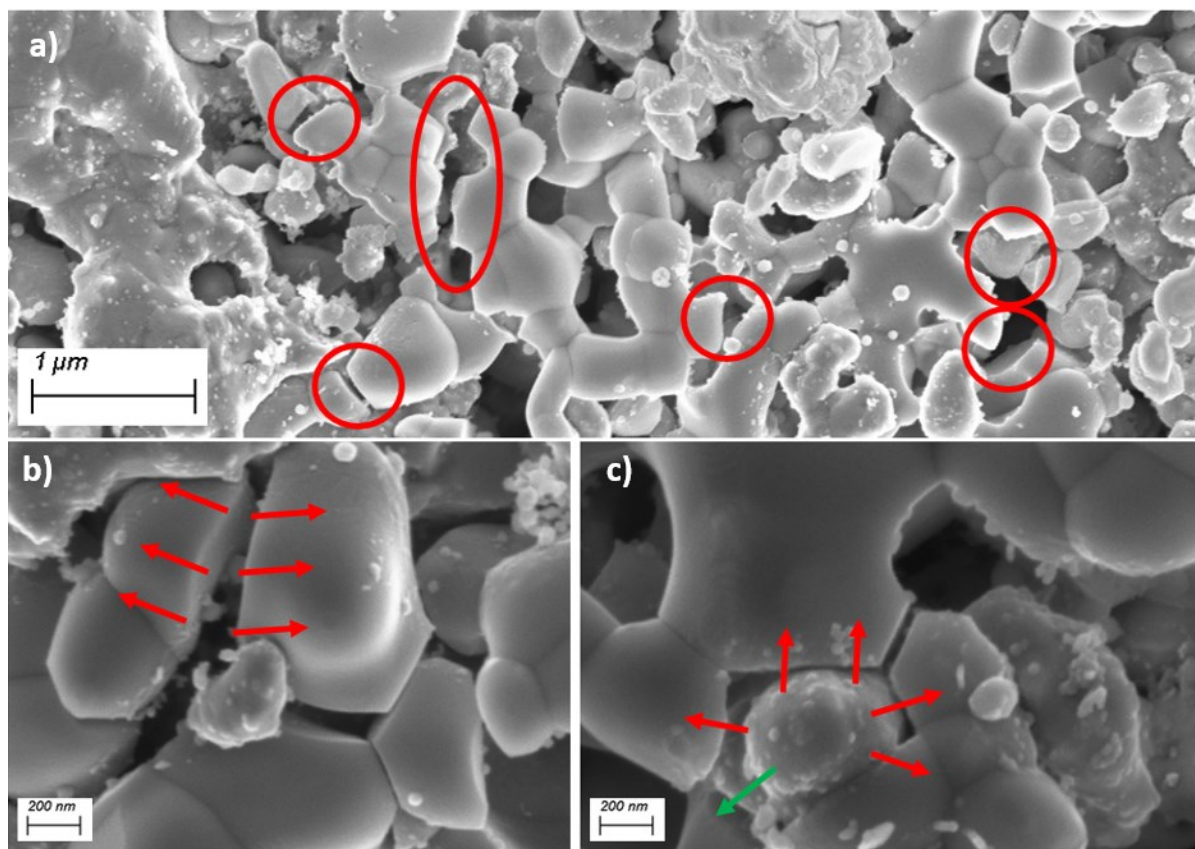


Figure 4-10 SEM top images of conventional Ni-YSZ anode after 10 redox cycles. a) The red circles highlight the YSZ cracking after redox cycling, resulting in a loss in ionic conductivity; b) and c) the high magnification images showing nickel expansion resulting in the YSZ framework break down.

Nanoindentation is a material damaging test, which could lead to material deformation after tests. Figure 4-12 shows the local material deformation of as-reduced Ni-YSZ before and after nanoindentation. The nickel and YSZ show different deformation: the nickel surface, in contact with the indenter, was pressed flat. However, the YSZ is a non-ductile material, which has less ability to deform into different shapes. In this case, by constantly applying the load

onto the electrode, the YSZ structure failed along the grain boundaries. This structure failure process can be accurately recorded during nanoindentation, and is reflected as a consecutive oscillation in the loading curve during measuring and the standard deviation of the bulk material measurements results, as shown Figure 4-8. The standard deviation of measured Ni-YSZ electrode mechanical properties presented in Figure 4-8 shows that the electrode, after more redox cycles, has lower elasticity and hardness, as well as displaying a smaller standard deviation in the measurements.

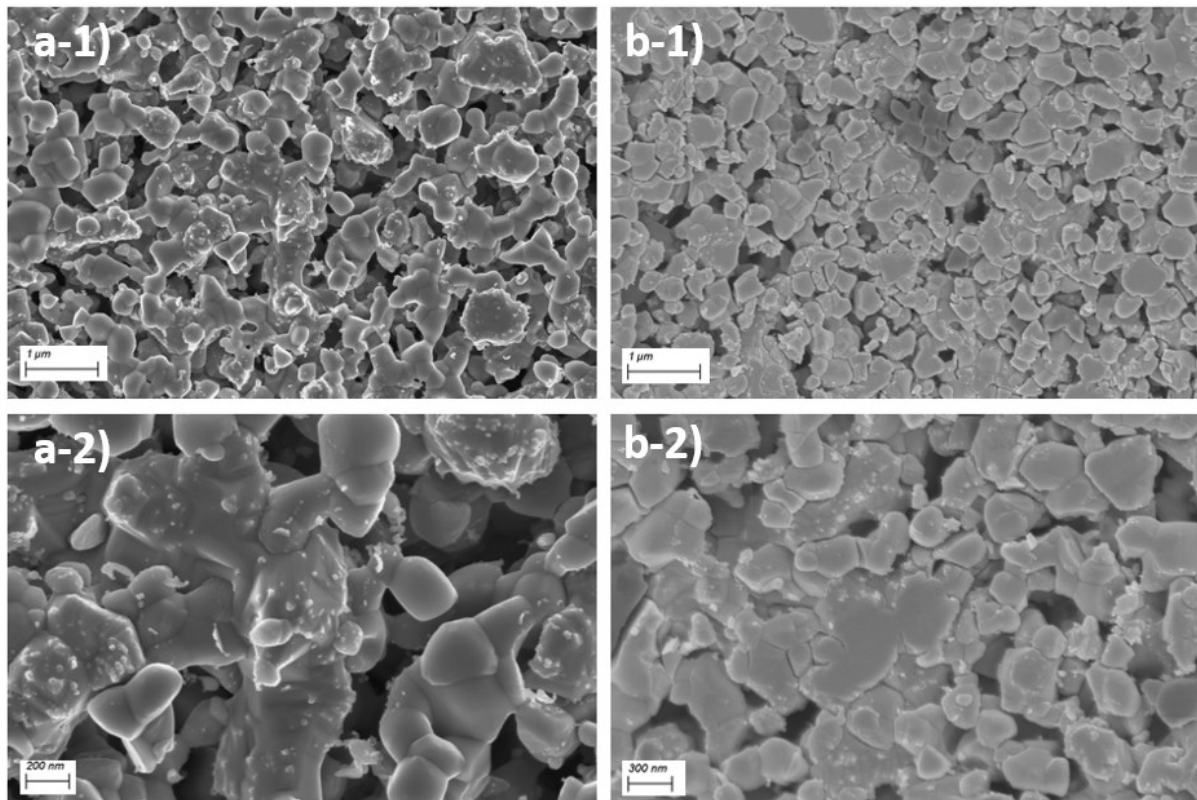


Figure 4-11 images of nanoindentation on the Ni-YSZ samples after 10 redox cycles. a) shows the local region of the original sample from SEM image; b) shows local material deformation after indentation.

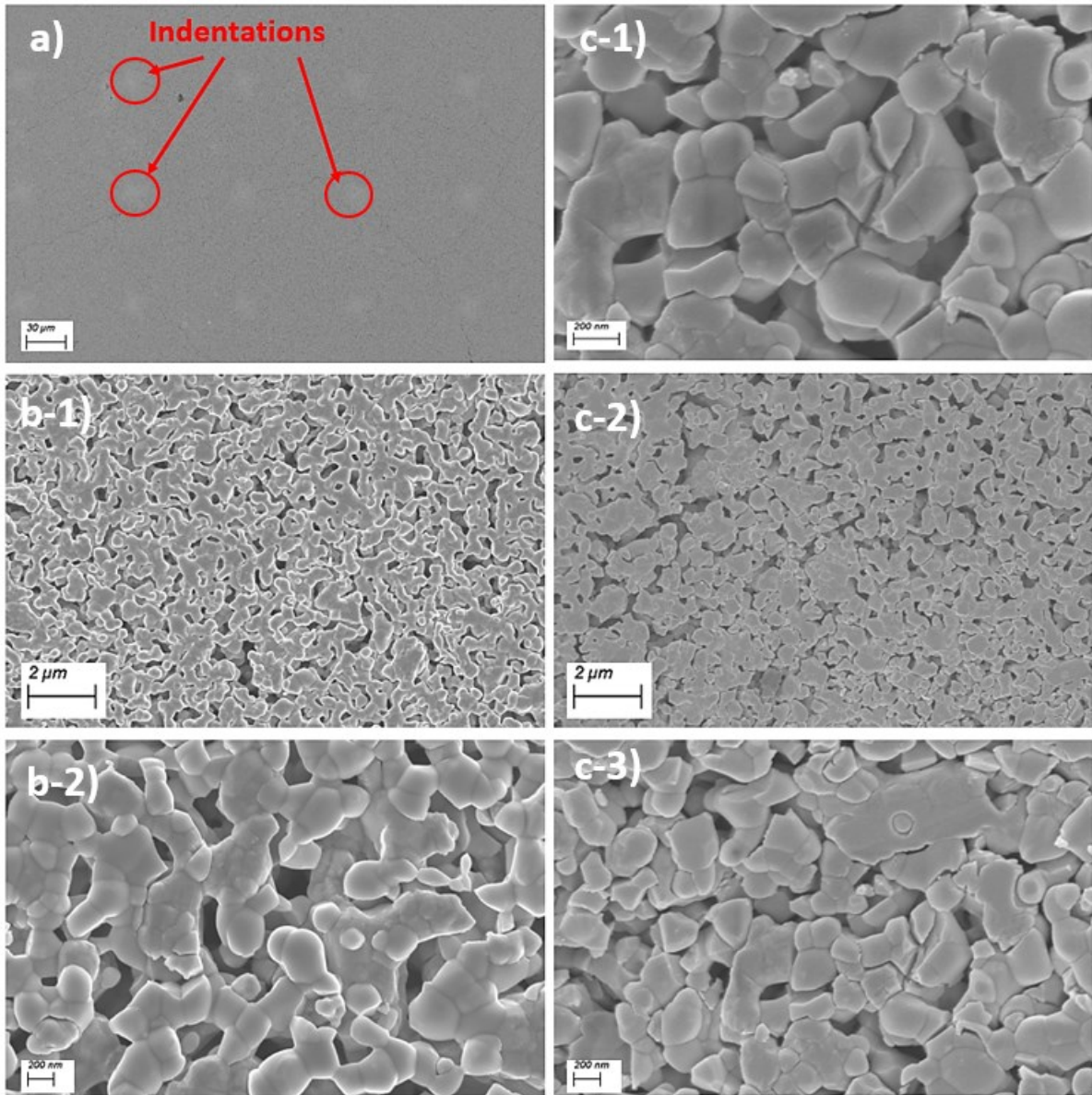


Figure 4-12 images of nanoindentation on the as-reduced Ni-YSZ. a) shows the indentations from the SEM image; b & c) show the local material deformation before and after the indentation respectively.

Figure 4-11 shows nanoindentation impact on the Ni-YSZ samples after 10 redox cycles. After redox cycling, the nickel agglomeration led to a higher porosity and larger pore size, which normally leads to lower material elastic modulus and hardness. At the same time, an increasing number of YSZ fractures was also observed in both SEM and FIB-SEM images. These

kinds of microstructure changes could lead to smaller oscillation of the nanoindentation loading curve as well as the measurement results. A picture hypothesis has been proposed as shown in Figure 4-13.

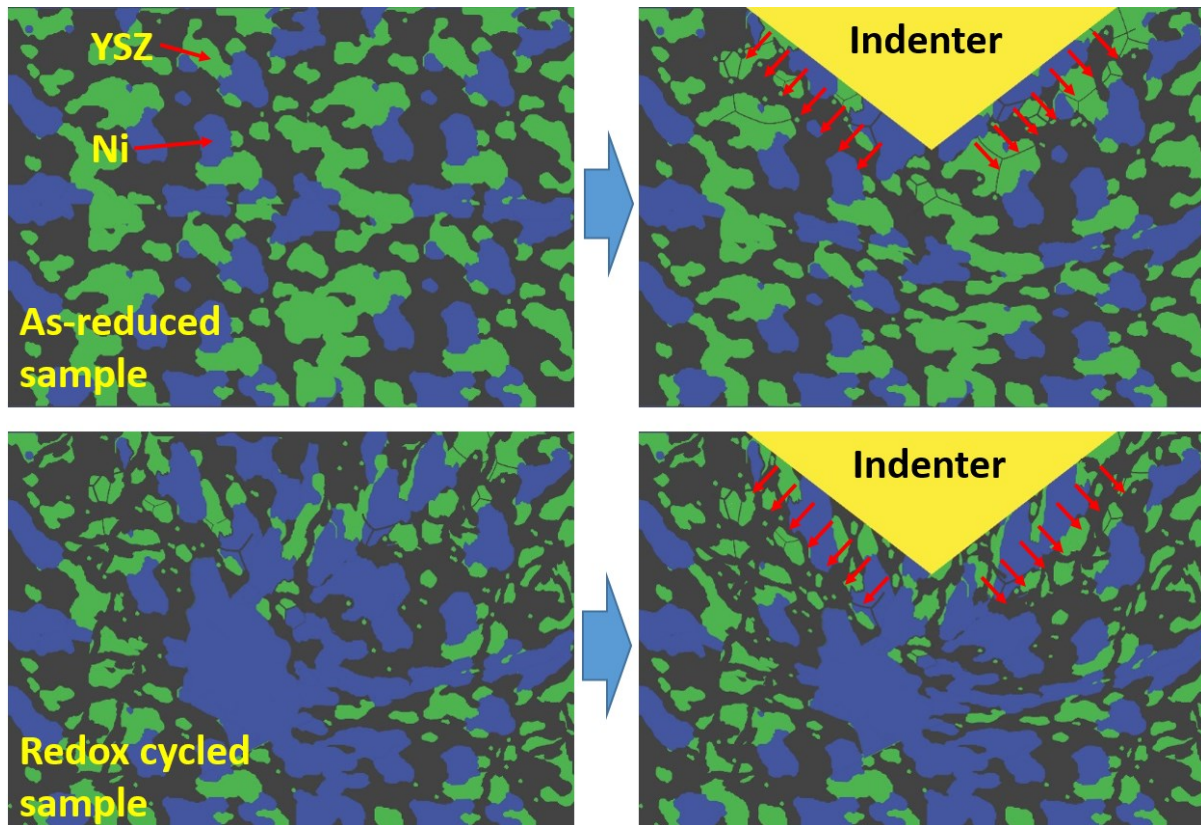


Figure 4-13 Hypothesis establishing a relationship between the Ni-YSZ fracture and the loading curve during nanoindentation.

With the aforementioned hypothesis, the redox cycling impact on the Ni-YSZ electrode performance can be linked with not only to the mechanical properties but also the standard deviation or material response during the measurement.

4.6 CHAPTER SUMMARY

The electrochemical and mechanical deterioration of Ni-YSZ anodes after up to 20 redox cycles was quantified by a combination of FIB-SEM tomography, impedance spectroscopy, nanoindentation and modelling.

Upon redox cycling the hardness decreases from 0.4 GPa to 0.15 GPa and the elastic modulus from 36.4 GPa to 20.2 GPa. This can be qualitatively associated to observations in the SEM: fractures at the YSZ grain boundaries, Ni-YSZ detachment, continuous nickel agglomeration and increasing porosity after each redox cycle, all of which seem to be irreversible. The effect of porosity in the mechanical properties can be understood using an empirical elastic modulus-porosity exponential relationship where only the porosity constant was re-fitted.

The electrochemical degradation was followed by impedance spectroscopy and a physically-based model was used to infer the active TPB length from the temporal evolution of the electrochemical reaction polarisation resistance, revealing a good match with TPB density obtained through FIB-SEM tomography. In particular, the model fits very well the initial, 5 redox and 10 redox samples, with a less satisfactory fit for higher redox cycles, attributed to the changes in the effective conductivity of the composite caused by YSZ fractures and nickel agglomeration. It is also observed that the electrochemical reaction polarisation resistance decreased temporarily by a factor ca. 2 upon each re-reduction, probably due to the transient generation of Ni nanoparticles around the TPB coming from the volume shrinkage from NiO to Ni. Although this causes a temporary decrease in electrochemical reaction polarisation resistance, after each redox cycle the degradation rate is even faster due to the promoted Ni

agglomeration. This results in an overall increase in electrochemical reaction polarisation resistance by about an order of magnitude as a consequence of a reduction in active TPB density (from $4.63 \mu\text{m}^{-2}$ to $1.06 \mu\text{m}^{-2}$) and fragmentation of the YSZ network along its grain boundaries due to Ni expansion upon oxidation.

This chapter shows that the microstructural changes during redox cycling are the primary cause of Ni-YSZ material degradation in both electrochemical performance and mechanical properties. The repeating Ni volume changes are the main cause of this degradation process, damaging the YSZ framework and reducing the TPB density as a consequence of accelerated Ni coarsening. The study further demonstrates that a comprehensive quantification of redox cycling can be achieved by coupling 3D tomography, real-time impedance spectroscopy and mechanical analysis.

.

CHAPTER 5 QUANTITATIVE STUDY OF REDOX CYCLING IMPACT ON MECHANICALLY IMPROVED Ni INFILTRATED YSZ SCAFFOLDS

5.1 SINTERING TEMPERATURE STUDY FOR YSZ SCAFFOLD SELECTION BASED MECHANICAL PROPERTIES AND POROSITY CHANGES

The YSZ-carbon black slurry tape casts were sintered at different temperatures for 2 hours. Figure 5-1 shows SEM images of the top surfaces of these YSZ scaffolds. As expected, with increasing sintering temperature, the YSZ grain size grew and the grain boundaries improved the connectivity with neighbouring particles. In addition to that, higher sintering temperatures also resulted in thinner films with less porosity. A higher porosity and proper pore size are necessary for the YSZ scaffold, in order to maintain volume for later Ni infiltration and gas diffusion^{141,142}.

The hardness and elastic modulus, Figure 5-2, show an increasing trend with higher sintering temperatures, potentially due to the stronger interconnection between YSZ grains and larger grain size, along with the accompanying decrease in porosity⁹⁷. Nevertheless, for the high sintering temperatures, the standard deviations of the measured YSZ scaffold mechanical properties were much higher, attributed to the much coarser surface features after sintering at higher temperature¹⁴³. By comparing with conventional Ni-YSZ thin films, the YSZ scaffolds with the same sintering temperature shows a slightly higher porosity, lower elastic modulus and greater hardness. This is because the YSZ scaffold, without Ni infiltration, has much higher porosity than the Ni-YSZ film, and the higher elasticity of conventional Ni-YSZ electrodes reflects their much larger Ni content.

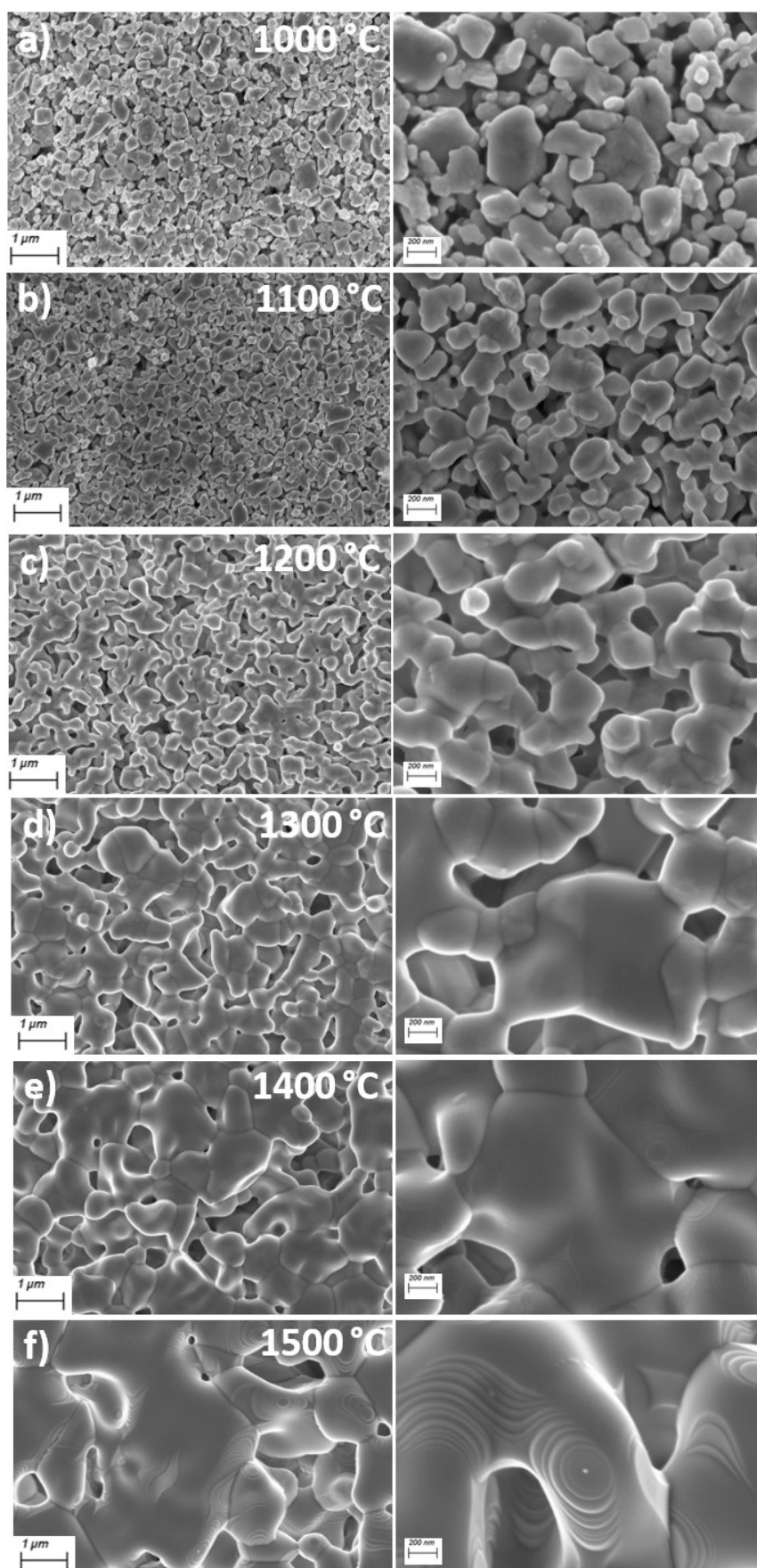


Figure 5-1 SEM images of YSZ scaffolds after 2 hours of sintering at different temperatures.

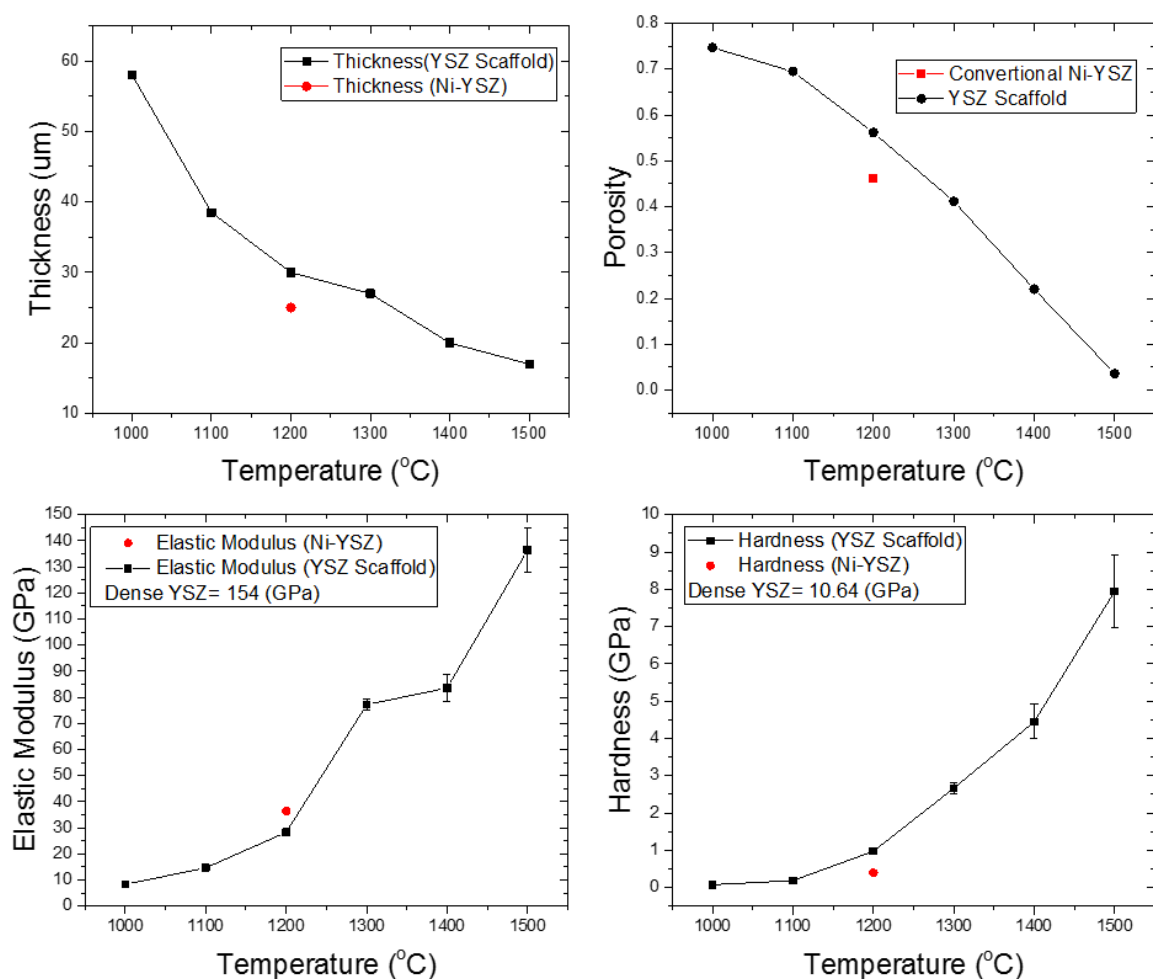


Figure 5-2 YSZ thickness (measured by SEM), porosity (based on the weight gain calculation), elastic modulus and hardness of the YSZ scaffold as a function of sintering temperature, the red points represented the measurement results of tape-cast conventional Ni-YSZ sintered in 1200 °C.

It was proposed that the YSZ scaffolds could improve electrode stability during redox cycling¹⁴². There are several requirements that the electrode microstructure needs to exhibit, including a mechanically strong YSZ framework that could prevent structural damage during redox cycles, a stable and sufficient ionic conductivity; sufficient porosity to ensure good gas diffusion, and a stable percolating Ni network for electronic transport and catalytic activity.

Figure 5-1 shows that the YSZ scaffolds sintered below 1200 °C exhibit poor contact between YSZ grains, resulting in a low ionic conductivity.

Considering the trade-off between the mechanical stability and porosity, the YSZ scaffolds sintered at 1200 °C were used for further study, as they showed a porosity over 55%, fine pore size below 400 nm and reasonable mechanical stability compared to the conventional Ni-YSZ anode.

5.2 MATERIAL DEGRADATION UPON REDOX CYCLING

Ex-situ microstructural characterisation was carried out with SEM image analysis. Four different samples, with various numbers of redox cycles, were tested. In-situ electrochemical performance degradation of Ni infiltrated YSZ scaffold was studied with EIS.

5.2.1 Electrochemical degradation

The response from the impedance data were fitted with an equivalent circuit, shown in Figure 5-3. The ohmic resistance consisted of the sum of the electrolyte resistance and the anode current collection¹⁴⁴. The electrolyte resistance varied with operational temperature, in this case, the resistance from the electrolyte was around 5.3 Ω ; the anode contact resistance could be the main contribution to an observed small ohmic resistance change during each reduction process, which is related to the Ni microstructure change during this early reduction stage. The diffusion resistance is generally constant, as it is attributed to losses by gas conversion and gas diffusion. Finally, the electrochemical reaction polarisation resistance shows, in general, a continuous increase after redox cycling. This is mostly considered to be

related to charge transfer and the activation overpotential of the fuel oxidation process at the active triple phase boundaries (aTPB). The increase in electrochemical reaction polarisation resistance could be due to the loss of aTPB length, which is due to mechanical damage at the electrochemical interfaces⁹⁶.

Table 5-1 Calculated microstructure parameters from the reconstructed 3D tomographic datasets of Ni-YSZ scaffold with different numbers of redox cycles. The datasets of conventional Ni-YSZ were taken from a previous study¹⁰².

		As-reduced state		After 15 redox cycles	
		Ni-YSZ Scaffold	Conventional Ni-YSZ	Ni-YSZ Scaffold	Conventional Ni-YSZ
aTPB Density (Mm^{-2})		28.54	4.63	19.36	2.08
Porosity		0.42	0.442	0.44	0.534
Surface Area Per Total Volume (Mm^{-1})	Ni	3.23	7.90	2.98	6.42
	YSZ	7.65	3.65	7.83	3.82
	Pore	7.45	6.19	7.68	7.54

Figure 5-3b compares the stabilized electrochemical reaction polarisation resistances of the Ni-YSZ scaffold and conventional Ni-YSZ after corresponding numbers of redox cycles. The Ni-YSZ scaffold, with less Ni content (25wt%) and lower operation temperature (550°C), shows smaller initial electrochemical reaction polarisation resistances and relatively slow degradation compared to conventional Ni-YSZ, with 40wt% Ni, at 800°C . This good initial electrochemical reaction polarisation resistances performance could be due to the fact that the YSZ scaffold provides higher surface area and created a large aTPB length between the infiltrated Ni particles. This was also tested using FIB-SEM tomography, as shown in Table 5-1. During redox cycling, there were several factors considered to explain the slower degradation of the Ni-YSZ scaffold compared to conventional Ni-YSZ material: firstly, the lower operating temperature will result in an intrinsically slower degradation; secondly, the relatively stronger

YSZ scaffold provides stable ionic transport by preventing the YSZ framework from breaking down, helping to maintain the aTPB, as shown in Figure 5-4; in addition, the lower nickel volume in the scaffold will also provide less expansion hence less stress on the YSZ scaffold.

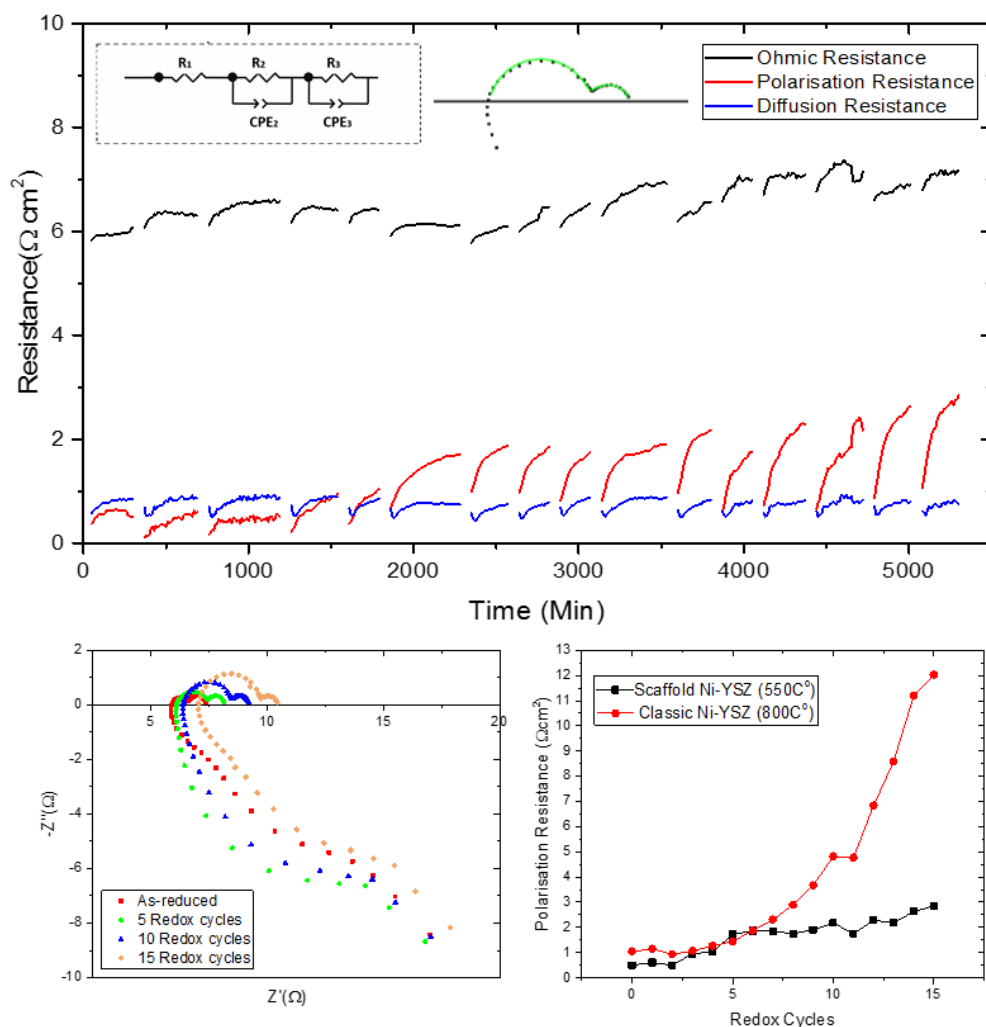


Figure 5-3 Ohmic resistance, Electrochemical reaction polarisation resistance and Diffusion resistance as a function of time during the reduction process (wet 5 vol % H_2) of redox cycling from EIS fitting for the Ni-YSZ scaffold, 550 °C; Comparison of stabilized electrochemical reaction polarisation resistance between conventional Ni-YSZ and Ni-YSZ scaffold, showing that the scaffold material has a good ability to work at lower temperatures with higher performance than Ni-YSZ prepared by powder mixing and sintering (conventional).

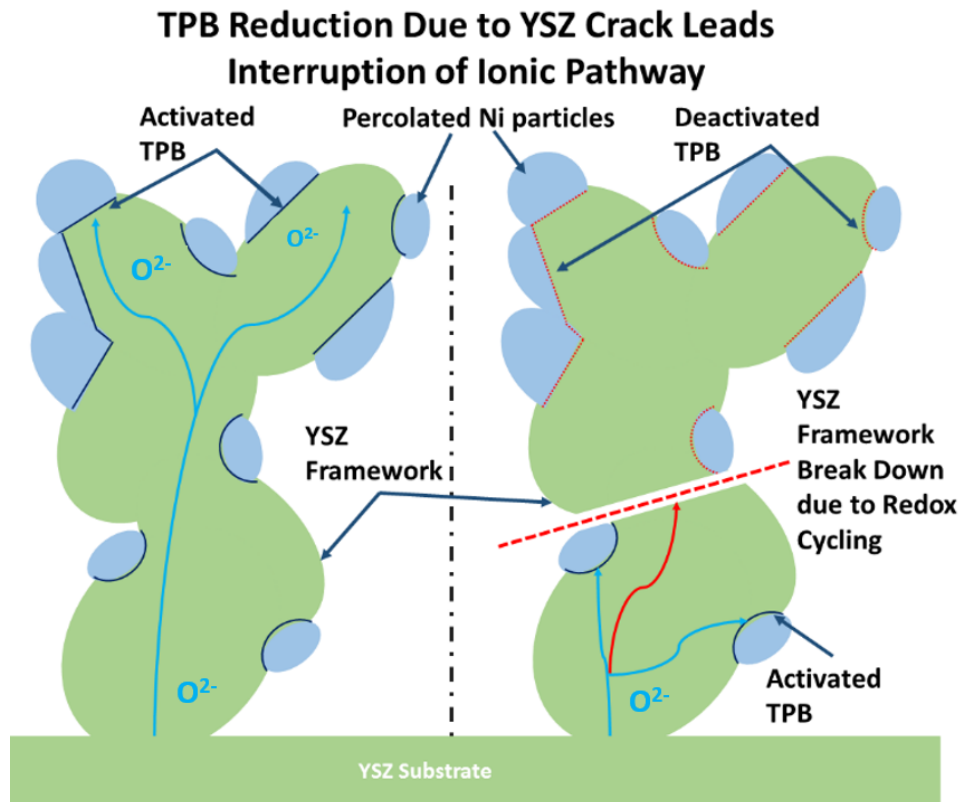


Figure 5-4 visual model of the loss of aTPB by YSZ framework break down. After several redox cycles, the Ni agglomeration accompanied by its volume expansion during oxidation could damage the YSZ structure in conventional Ni-YSZ cermets, but because the YSZ scaffold was stronger, it offers more resistance to mechanical damage from Ni redox volume change.

5.2.2 Microstructure changes

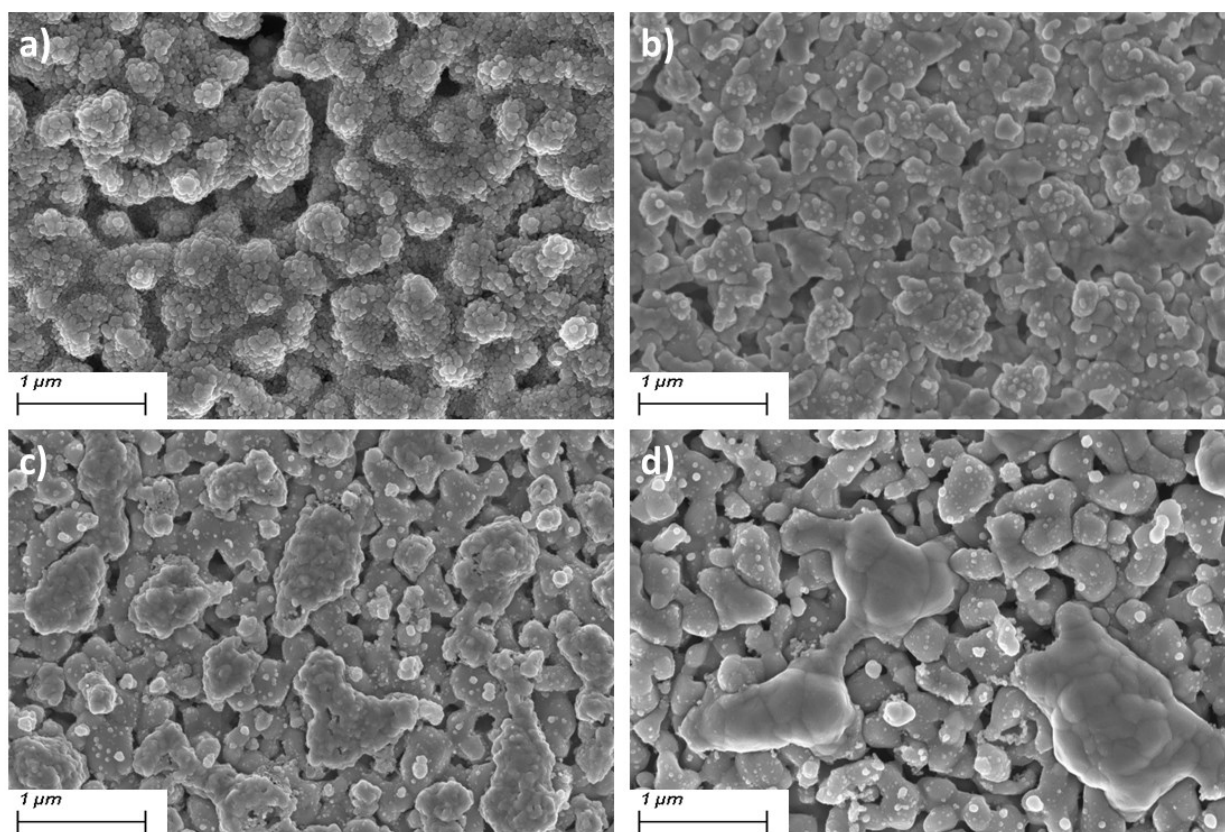


Figure 5-5 Top view of YSZ scaffold after Ni infiltration: a) As- prepared scaffold NiO-YSZ; b) As-reduced scaffold Ni-YSZ; c) the Scaffold Ni-YSZ after 5 redox cycles; d) Scaffold Ni-YSZ after 15 redox cycles

Figure 5-5 and Figure 5-6 show SEM and FIB-SEM images of the scaffold NiO/Ni-YSZ electrode top and cross-sectional views. In the as-prepared sample, the NiO was uniformly distributed both on the YSZ surface and inside the scaffold after 2 hours heat treatment at 550°C. For the as-reduced sample, the NiO has fully reduced to Ni, forming percolated Ni network within the YSZ framework. The detachment between Ni and YSZ scaffolds can also be observed from both SEM and FIB-SEM cross-sectional images, which was caused by the Ni volume shrinkage during the reduction process.

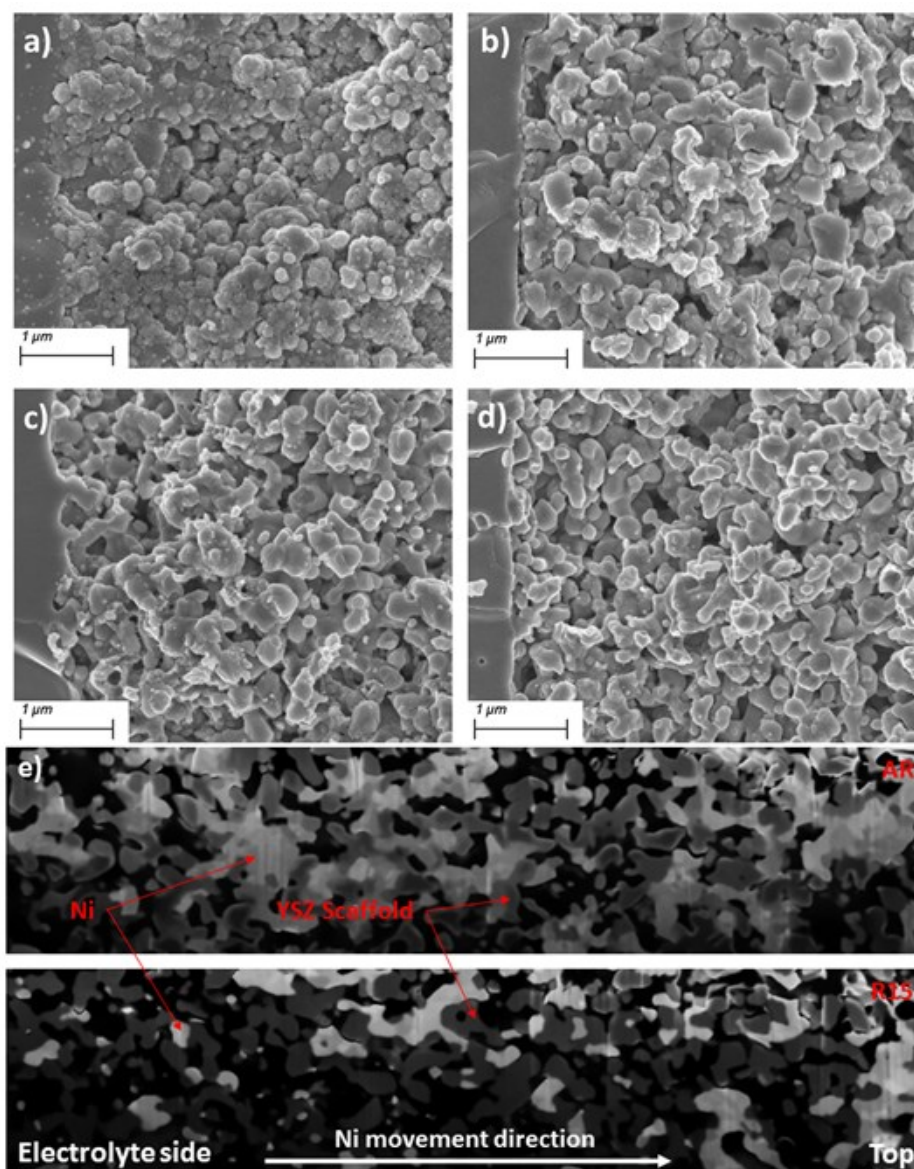


Figure 5-6 Cross-sectional view of YSZ scaffold after Ni infiltration, near the YSZ substrate: a) As- received scaffold NiO-YSZ; b) As-reduced scaffold Ni-YSZ; c) the Scaffold Ni-YSZ after 5 redox cycles; d) Scaffold Ni-YSZ after 15 redox cycles; e) FIB-SEM images shows the Ni movement after 15 redox cycles, the brighter colour indicates Ni, grey is YSZ, black is pore.

A good contrast from FIB-SEM images shows Ni evenly distributed within the YSZ scaffold, Figure 5-6e. For the samples after 5 redox cycles and 15 redox cycles, Ni agglomeration was observed on the top view images and became significant after more redox cycles. Ni nano-

particles were also observed after redox cycling, this could be caused by redox cycling coupled with long-term operation. At the same time, Ni movement was observed from the FIB-SEM images, by comparing the as-reduced sample with the one after 15 redox cycles, which is also consistent with SEM observation. In conventional Ni-YSZ electrodes, YSZ framework break down can be always observed in SEM images after redox cycling¹⁰². In contrast to this, there is no observation of the YSZ scaffold framework breaking down, either from top or cross-sectional images. This supports the view that the YSZ scaffold can better resist structural damage from the Ni volume change during redox cycling.

5.2.3 Mechanical properties change on redox cycling and comparison with the conventional Ni-YSZ anode

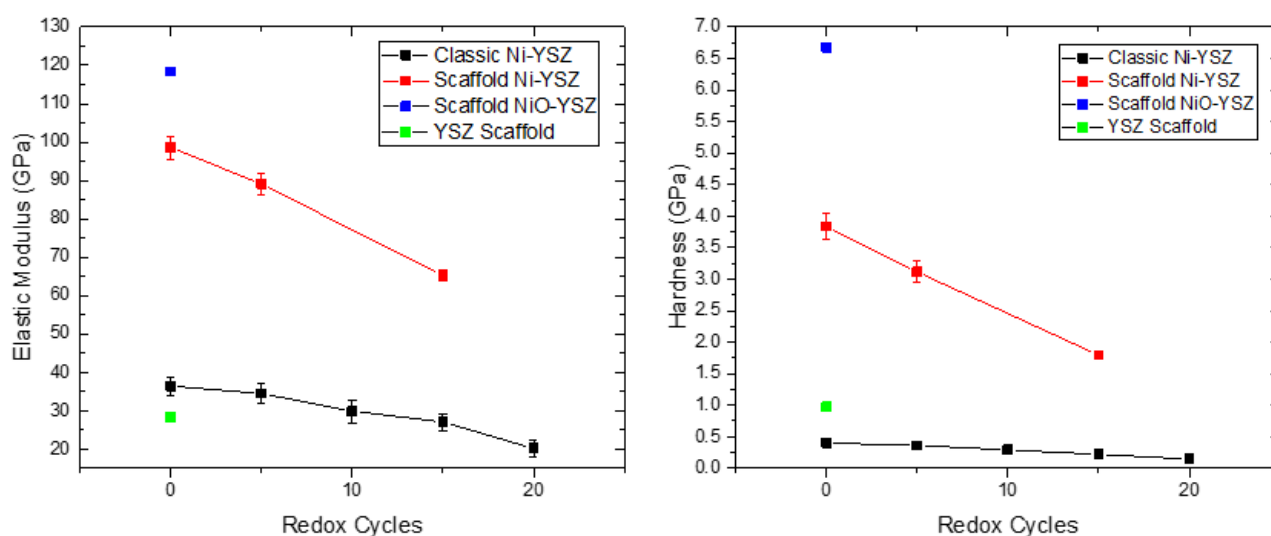


Figure 5-7 Mechanical properties of Ni-YSZ anodes. The redox cycling degradation trend was compared between conventional Ni-YSZ and Ni-YSZ scaffold.

The elastic modulus and hardness of bulk samples measured using nanoindentation are shown in Figure 5-7 plotted against number of redox cycles. The green dot shows the YSZ scaffold with around 45% of porosity, which is similar to the as-reduced Ni-YSZ made from

conventional Ni-YSZ. But, the hardness of the YSZ scaffold was double that of the value of conventional Ni-YSZ^{102,97}, as the YSZ is commonly agreed to be a hard material. Comparing the as-reduced Ni-YSZ scaffold with the as-reduced conventional Ni-YSZ, the initial elastic modulus in the former was tripled, and the hardness increased by a factor of eight. These notable results can be due to the fact Ni infiltration filled the pores within the YSZ scaffold, reducing electrode porosity. A decreasing trend against the number of redox cycles were observed for both the elastic modulus and hardness of the Ni-YSZ scaffold, dropping 33% and 53% respectively, but this was still stronger than the conventional Ni-YSZ after a corresponding numbers of redox cycles. As no YSZ scaffold damage was observed in the SEM images, the drop of hardness and elastic modulus could be caused by Ni agglomeration and increase in porosity (based on FIB-SEM 3D reconstruction measurement) due to extended operation and redox cycling, as observed in last section of nickel migration.

5.3 CHAPTER SUMMARY

In this chapter, a stable YSZ scaffold has been fabricated by using 10 wt% of carbon black as pore former with various sintering temperatures. It has been found from SEM images that different sintering temperatures have a significant influence on YSZ grain size, grain boundary connectivity and pore formation. At sinter temperatures below 1200 °C, YSZ tends to form rather small grains, and poor YSZ grain connectivity important for ionic conductivity and mechanical stability. In the samples sintered above 1200 °C, the YSZ grains were very well connected, and grain size increased with sintering temperature, resulting in improved mechanical properties as high as 136.5 GPa and 7.95 GPa for elastic modulus and hardness respectively. But the high temperature also resulted in a loss in porosity and reduced pore

size; this could lead to difficulty in Ni infiltration and gas phase diffusion. Considering both mechanical stability and scaffold morphology, 1200 °C was selected as the best condition for YSZ scaffold sintering.

The electrochemical and mechanical deterioration of the Ni-YSZ scaffold after up to 15 redox cycles was quantified by a combination of SEM, impedance spectroscopy, nanoindentation and FIB-SEM. It has been found that, after 15 redox cycles, the YSZ scaffold retained its structure well, since improved mechanical properties prevent YSZ failure due to Ni volume expansion during the redox cycling process. That is to say, this stable YSZ framework effectively maintained a considerable number of aTPB, that otherwise could lose effective ionic transport if there was YSZ framework damage. The infiltrated Ni-YSZ scaffold had a better initial performance, with lower Ni content (25 wt%) and a lower operational temperature, compared with conventional Ni-YSZ (40 wt%) sintered under the same condition. For performance during redox cycling, the scaffold electrodes also show a slower degradation than the conventional electrodes.

As in conventional Ni-YSZ anodes, agglomeration still cannot be prevented within Ni-YSZ scaffolds, this is also the main problem for Ni-YSZ material degradation during redox cycling. To further explore this, the wetting properties between Ni and YSZ will be presented in Chapter 7.

CHAPTER 6 CHARACTERIZATION OF THE NICKEL IMPREGNATED YTTRIA-STABILIZED ZIRCONIA FIBRE SCAFFOLD ELECTRODES

The investigations of Ni-infiltrated YSZ scaffolds have shown promising results by reducing the mechanical damage to the YSZ framework while maintaining ionic conductivity^{145,146}. High surface areas of YSZ scaffold and infiltrated Ni contribute to a significantly high TPB density for electrochemical reactions. However, these nano-sized nickel particles lead to faster degradation and dewetting from the scaffold surface^{146,147}. The nickel dewetting leads to nickel vertical movement from inside to the electrode surface, and significant reduction of TPB density^{146,12}. In order to optimize the performance, durability, and cost of the electrode, research is focused on tailoring the electrode microstructure^{148,149}.

Due to its high control and reproducibility, the electrospinning method is widely used for manufacturing well-controlled fibre structures of plastics, metals or ceramics^{150,151}. Many studies focused on enhancing the performance of electrospun carbon nano-fibre electrodes^{152–154}. Nonetheless, its application in SOFCs is very scarce^{34,155,156}. Lee et al. reported that GDC-based thin electrolytes and core/shell fibre structured BSCF-GDC cathodes produced a high and stable performance at low temperatures¹⁵⁷. They attributed the stability of the cathodes to the fibrous structure that provides both mechanical support and excellent interconnectivity for electron and oxygen ion transport. Castkova et al. studied¹⁵⁸ the fabrication methodology for electrospinning 8 mol% yttria-doped zirconia fibres but have not demonstrated the use of the fabricated electrospun fibres in an SOFC application.

6.1 MICROSTRUCTURE CHARACTERIZATION

The microstructure of the Ni-YSZ fibre scaffold was observed by SEM and reconstructive FIB-SEM. Two different magnifications were used for 3D reconstruction – the high magnification images (11.8 nm/ pixel) were used for observing nickel nano particle distribution and agglomeration, and the low magnification (22.1 nm/ pixel) images were used for quantitative analysis, including total TPB, active TPB, interfacial areas, particles size, and particle distribution.

6.1.1 As-prepared NiO-YSZ Fibre Scaffold

Figure 6-1 shows the microstructure of the as-received NiO-YSZ fibre scaffold after 12 infiltration steps and high-temperature decomposition from nickel nitrate. This highly porous YSZ structure allows nickel nitrate to cover both the fibre and scaffold layers. The NiO shows adequate wetting behaviour between the fibre structures, as shown in the SEM and FIB-SEM images. As a result of this behaviour, the nano-NiO particles are evenly distributed upon the YSZ surface, which provides a good foundation for future nickel reduction. The tomography images show a large number of highly porous nanoparticles surrounding and covering the YSZ structures. Due to the resolution limitation, the smallest particles could not be well presented in the 3D reconstructed images, which instead show a layer of NiO covering the fibre.

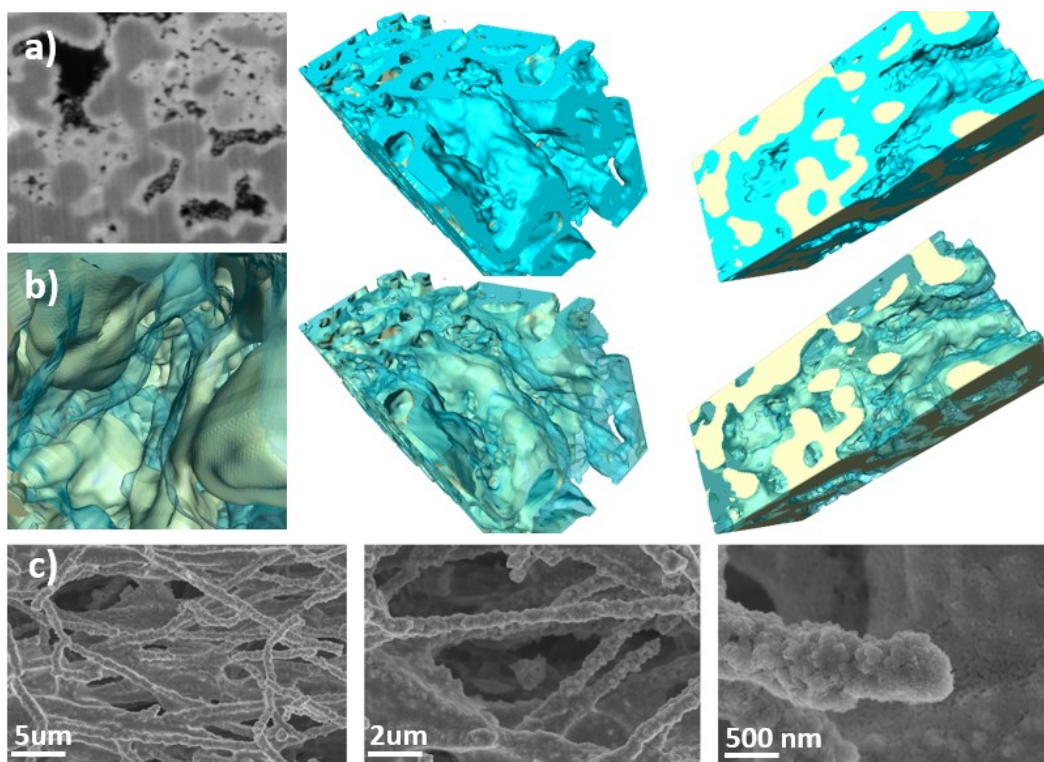


Figure 6-1 the microstructural images for as-received NiO-YSZ Fibre Scaffold, after 12 infiltrations and decomposition from $\text{Ni}(\text{NO}_3)_2$. a) FIB-SEM tomography image and 3D reconstructed structure, blue is NiO and yellow YSZ; b) 3D reconstructed images show transparent NiO covering YSZ structure. c) SEM images of NiO-YSZ fibre scaffold top view, shows NiO nanoparticles covering the YSZ fibre and filling the pores.

6.1.2 As-reduced Ni-YSZ Fibre Scaffold

Figure 6-2 shows the microstructural analysis of the as-reduced Ni-YSZ fibre scaffold. A single YSZ fibre attached to a base YSZ scaffold was observed with a high magnification 3D reconstructed microstructure. Due to the high sintering temperature, multiple areas of contact were formed between the YSZ fibre and the scaffold providing adequate ionic and electronic transport pathways in the fibre layer.

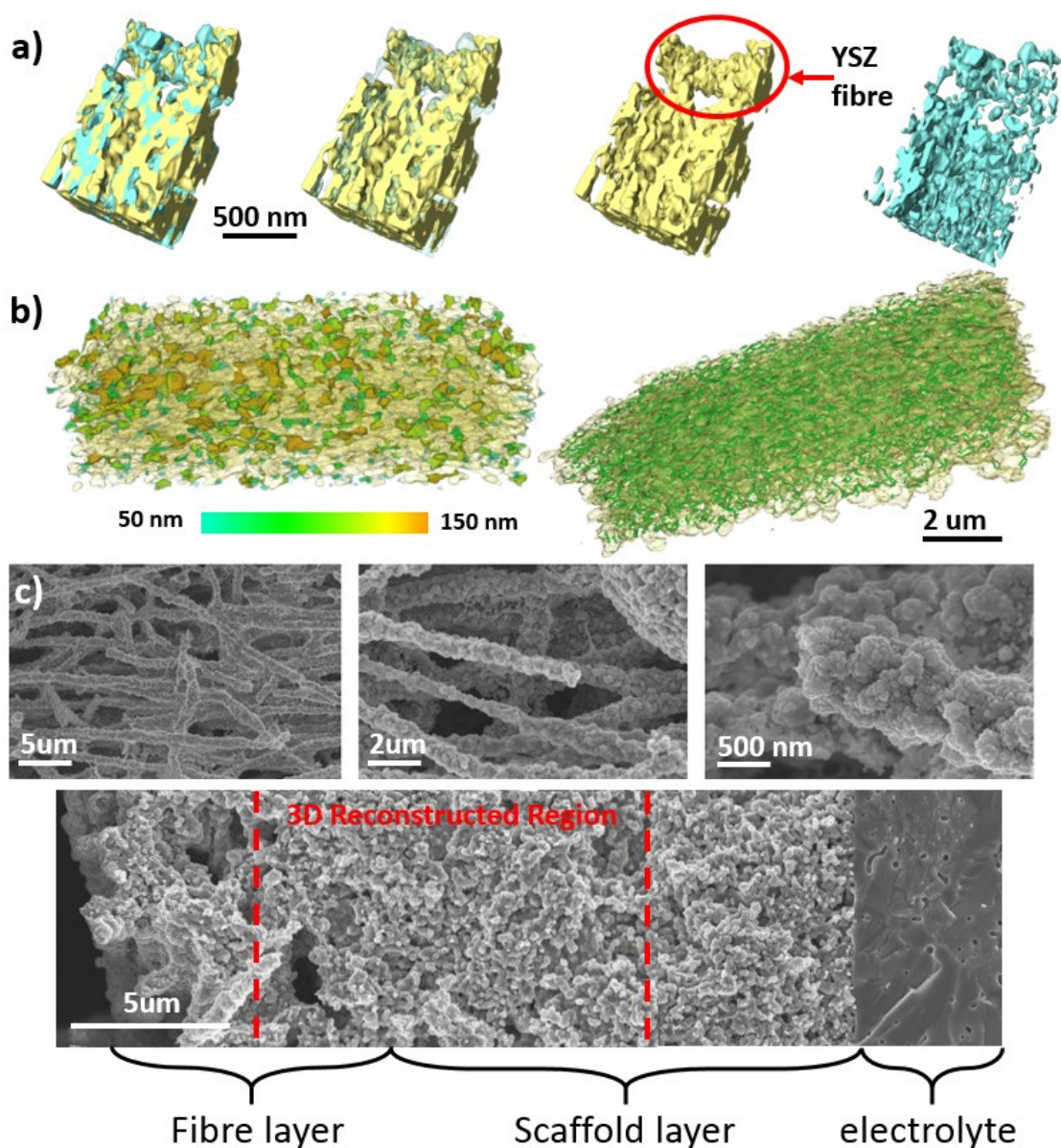


Figure 6-2 the microstructure for the as-reduced Ni-YSZ fibre scaffold: a) the electrode top surface with a single fibre, where the light blue represents nickel particles and yellow represents the YSZ structure. b) Bulk analysis for Ni particle size, presented with a colour code, and the active triple phase boundaries are highlighted with a green line, and YSZ in transparent yellow (due the image resolution limitation, particles below 50 nm could not be presented); c) SEM images for as-reduced Ni-YSZ fibre scaffold top view and cross-sectional view, with indication of the 3D-reconstruction region for all samples.

Due to the different nature of the pore formation mechanism, the YSZ structure showed higher porosity at the top surface (i.e., in the fibre layer), and lower at the inside (i.e. in the scaffold layer). The high porosity from the fibre layer allows for efficient fuel diffusion into the scaffold layer. The nickel nanoparticles are evenly distributed within the scaffold as well on the fibre layer with uniform particle size. The high surface area between nano-sized particles and the scaffold gives rise to a significantly high TPB density of $63.8 \mu\text{m}^{-2}$ based on large volume bulk 3D reconstruction. With the significantly large pore size and high porosity of fibre layer, Figure 6-2, due to lack of contact surface, the nickel particles could not move further from the fibre-scaffold interface, as seen in Figure 6-3 and Figure 6-4.

6.1.3 Aged Ni-YSZ Fibre Scaffold

The same microstructural analysis has also been applied to the 3000 min aged and redox cycled Ni-YSZ fibre scaffold cells, as shown in Figure 6-3 and Figure 6-4 respectively. The YSZ fibre scaffold structure remained mostly intact after 3000 min of operation, as observed in both 3D structure and SEM images. Nickel agglomeration during ageing is only based on nickel solid-state dewetting from the YSZ substrate at an intermediate temperature. Based on this observation, it seems that the percolated nickel particle movement was limited to the fibre-scaffold interface. The agglomeration of the Ni particles, located on the fibre, is prevented by restricting the nickel movement along the fibre geometric structure. This compares favourable to conventional Ni-YSZ scaffolds after a long period of operation, where the nickel particles normally migrate to the electrolyte top surface and show the formation of isolated large particles^{68,159}. By using this highly porous YSZ fibre membrane, the agglomerated nickel particles create new TPBs with the connected YSZ fibre at the fibre-scaffold interface. This

stable microstructure leads to the sustained electrochemical performance of the cell during the isothermal ageing, compared with the Ni infiltrated ScSZ scaffold in the literature, as shown in Figure 6-3.

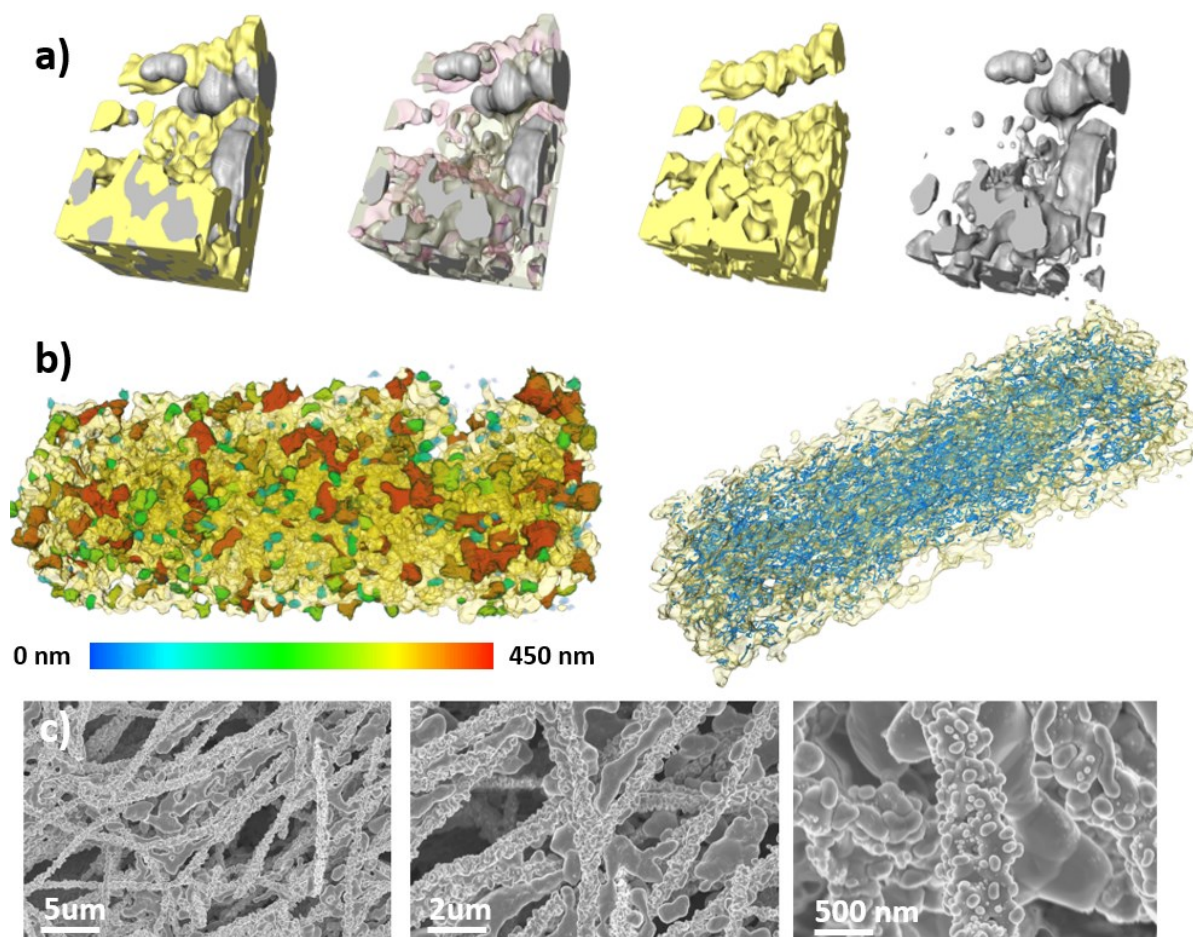


Figure 6-3 the microstructure of the aged Ni-YSZ fibre scaffold, 3000 min, 600 °C: a) the electrode top surface, the grey represents nickel particles and yellow represents YSZ structure. b) bulk analysis for Ni particle size are presented with colour code and the active triple phase boundaries are highlighted in blue, and the YSZ in transparent yellow c) SEM images for Ni-YSZ fibre scaffold top view.

6.1.4 Redox cycled Ni-YSZ Fibre Scaffold

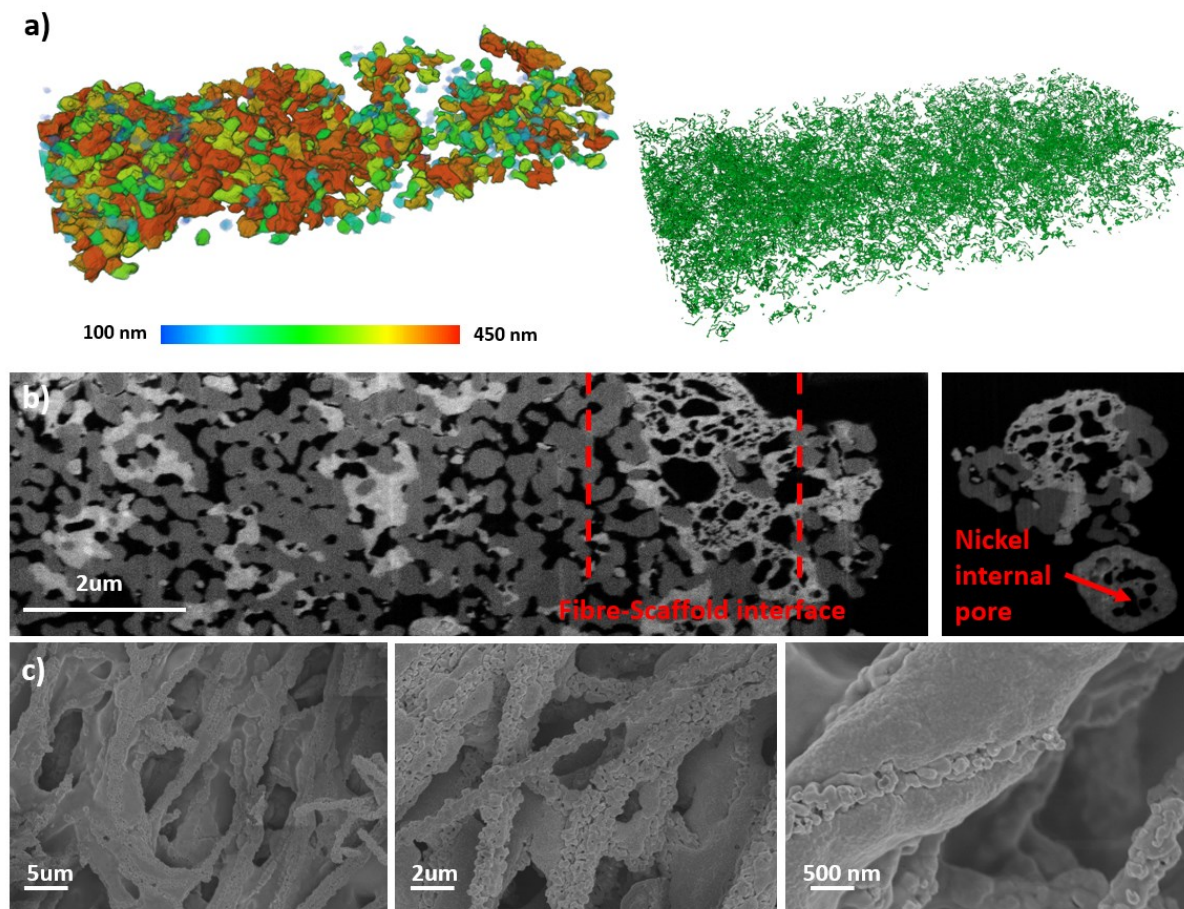


Figure 6-4 the microstructure of the Ni-YSZ fibre scaffold after 20 redox cycles at 600 °C: a) bulk analysis for Ni particle size are presented with colour code and the active triple phase boundaries are highlighted in blue, and the YSZ in transparent yellow; b) FIB-SEM cross-sectional images of the samples, showing nickel agglomeration and internal pore after 20 redox cycles; c) SEM images of the sample top surface.

The fibre-scaffold sample after 20 redox cycles shows similar structure degradation as isothermally aged samples. The double layer YSZ structure maintains a stability after 20 redox cycles. This is due to improvement in the mechanical properties of the scaffold layer, protecting the YSZ framework damage from the volume expansion of the nickel oxidation

process¹⁴⁶. The nickel particles behave differently from that seen during isothermal ageing. The nickel agglomeration behaviour has been observed by FIB-SEM 3D reconstruction. However, during this time, a significant amount of internal pores were generated within these nickel particles, Figure 6-4b. The formation of a nickel inter-porous structure after redox cycling is due to imbalanced mass transport between outward Ni diffusion and inward oxygen diffusion in oxidizing Ni grains at relatively low temperature^{160–163}.

6.2 ELECTROCHEMICAL PERFORMANCE

The electrochemical degradation of the cell was quantified by measuring the impedance upon the introduction of fuel gas. The symmetrical cell was operated at 600 °C in humidified (3% H₂O) diluted hydrogen (5% H₂, 95% N₂). The Ni-YSZ conventional electrode is traditionally operated at around 800 °C while the infiltrated structure significantly reduced the operational temperature to around 600 °C by introducing a large YSZ surface area, and a large number of TPBs per unit area.

Figure 6-5 presents the specific area resistances extracted from the fitting. As shown in Figure 6-5b, the area-specific ohmic resistance (ASR) is 2.8 Ωcm^2 , which is mainly determined by the YSZ electrolyte resistance and current collectors. Due to the high porosity of the YSZ fibre layer and its horizontal orientation, this gives a flexible spring-like contact between the electrode and current collector. The ohmic resistance can be kept at a relatively stable level during a relatively long-term operation and redox cycling. This indicates that nickel percolation has been maintained within the fibre-scaffold structure. The polarization resistance represents the cell electrochemical performance, which is directly linked with the

active TPB density of the cell. Normally, a lower resistance corresponds to higher performance and higher active TPB density. This Ni-YSZ fibre scaffold shows high electrochemical performance at 600 °C, with the polarization resistance stabilising at 0.75 Ωcm^2 for the isothermal ageing process comparing with Ni infiltrated ScSZ operated in 650 °C⁵⁶. The Ni-YSZ fibre scaffold electrode reaches a stable value after 200 min and then stayed relatively constant until the end of the experiment at 3000 min. Similar isothermal experiments have also been examined on other scaffold materials, such as Ni infiltrated ScSZ, which is considered to be a more promising cermet compared to its YSZ analogue. Chen⁵⁶ reported that at 650 °C, Ni infiltrated ScSZ becomes stable around 8 Ωcm^2 after 3000 min operation and 1.4 Ωcm^2 for 800 °C. During the redox cycling process, a polarization resistance improvement has been observed, which is due to the nano-roughness change directly after the nickel reduction process⁶⁹. Encouragingly, the Ni-YSZ fibre-scaffold maintained a stable performance even after 20 redox cycles. This is attributed to the positive effect of the fibre layer on the overall cell stability during nickel agglomeration and particle movement. As reported in Chapter 4, the commercial Ni-YSZ symmetrical cell operated at 800 °C with an initial polarization resistance at 1.04 Ωcm^2 which increased to 23 Ωcm^2 after 20 redox cycles. The regular fluctuation in diffusion resistance, as observed in Figure 6-5b, was established to be due to the lab room temperature changing from day to night. The slightly different temperature leads to a different inlet gas temperature and therefore different water partial pressure, though the polarization resistance stayed stable during this temperature fluctuation and water partial pressure change, which normally strongly depends on water partial pressure for conventional cells.

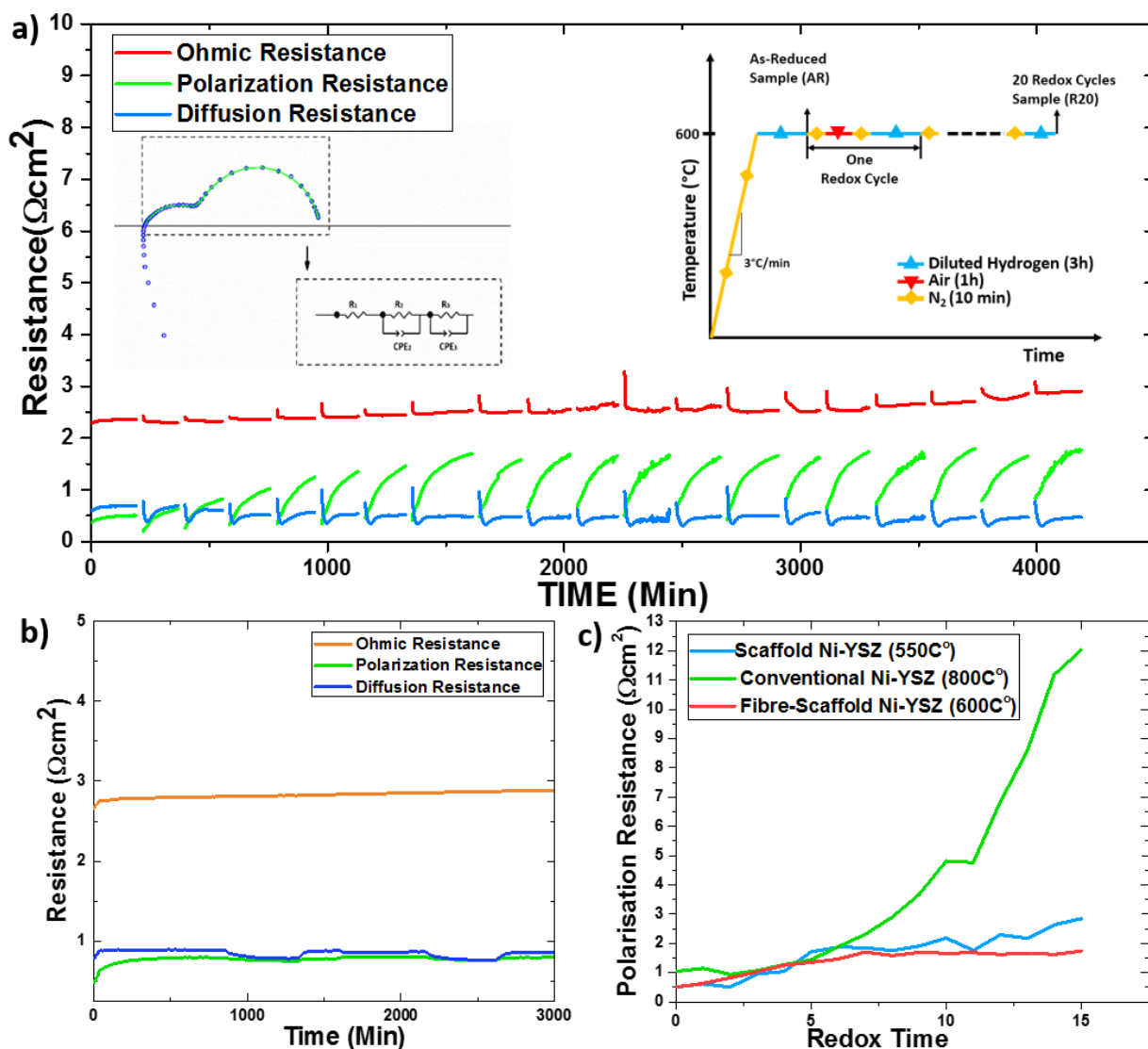


Figure 6-5 a) The specific area resistances for 20 redox cycles of the Ni-YSZ fibre scaffold symmetrical cell operated at 600 $^{\circ}\text{C}$ in diluted wet hydrogen (5% H_2 , 95% N_2); b) the specific area resistances for in-situ isothermal annealing of the Ni-YSZ fibre scaffold symmetrical cell operated at 600 $^{\circ}\text{C}$ in diluted wet hydrogen (5% H_2 , 95% N_2); c) Comparison of the stabilized electrochemical reaction polarisation resistance between conventional Ni-YSZ¹⁰² and Ni-YSZ scaffold¹⁴⁶ and Ni-YSZ Fibre-Scaffold, measured at 800 $^{\circ}\text{C}$, 550 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$, respectively.

Figure 6-5c compares the stabilized electrochemical reaction polarisation resistances of the Ni-YSZ fibre-Scaffold, Ni-YSZ scaffold and conventional Ni-YSZ after corresponding numbers

of redox cycles. The scaffold structure shows a significant advantage in redox stability compared to the conventional structure. This can be because the lower operating temperature and relatively stronger YSZ scaffold provides more stable ionic transport during redox cycles (without fracture, disconnect, etc). The Ni-YSZ Fibre-Scaffold and Ni-YSZ scaffold contain similar Ni contents (25 wt%) and lower operation temperature (600 °C, 550 °C), show smaller initial electrochemical reaction polarisation resistances and similarly slow degradation at their intermediate temperature. The similar electrochemical reaction polarisation resistance between the two samples suggests that the scaffold layer may play an important role in to the electrochemical performance of the Ni-YSZ Fibre-Scaffold. The Ni-YSZ scaffold became unstable after 8 redox cycles, while the fibre-scaffold electrode kept stability even after 20 redox cycles. This stability is considered to be contributed by the additional fibre layer, which maintained aTPB during nickel agglomeration, as described in Figure 6-8.

6.2 QUANTITATIVE ANALYSIS

Table 6-1 Calculated microstructure parameters from the reconstructed 3D tomographic datasets of Ni-YSZ Fibre Scaffold before and after isothermal annealing.

		Ni-YSZ Fibre-Scaffold		
Sample State		As-reduced	Aged (3000 min)	20 Redox Cycles
Total TPB Density (μm^{-2})		63.6	57.52	40.86
Active TPB Density (μm^{-2})		51.9	50.37	29.71
Active TPB Ratio		0.81	0.88	0.73
Interface area per Total Volume (μm^{-1})	Ni-YSZ	4.47	4.21	4.15
	Ni-Pore	0.92	1.09	1.04
	YSZ-Pore	4.95	5.12	5.84

The quantitative analysis results of the 3D microstructure are shown in Table 6-1. The TPB densities and interfacial areas are calculated based on 3D tomography results. Both total TPB density and active TPB density decreased after the ageing and redox cycling. This is consistent with the observed electrochemical performance changes based on EIS measurements, where the polarization resistance of the isothermal ageing sample increased from $0.344\ \Omega\text{cm}^2$ to $0.875\ \Omega\text{cm}^2$ and the polarization resistance of the redox cycling sample increased from $0.375\ \Omega\text{cm}^2$ to $1.768\ \Omega\text{cm}^2$ as reported in the later section. The TPB percolation ratio (ratio between active percolated TPBs and the total number of TPBs) also decreased from 0.81 to 0.73 for the redox cycled sample. This is due to the nickel de-wetting process being accelerated by the volume change during redox cycling⁸⁶. The interfacial area between Ni and YSZ only decreased slightly, suggesting that the ionic and electron transport were stabilized during isothermal ageing and redox cycling. This may be one reason to account for the relatively stable electrochemical performance. During the degradation process, more YSZ was exposed to the pore phase due to the nickel dewetting, as observed by an increase in the calculated YSZ-Pore interface area from $4.95\ \mu\text{m}^{-1}$ to $5.84\ \mu\text{m}^{-1}$. Therefore, the quantitative 3D tomographic analysis confirms the trends detected with SEM analysis regarding Ni agglomeration and loss in total TPB density upon ageing and redox cycling.

The quantitative bulk microstructure evolution between as-reduced, aged and redox cycled samples has been presented in Figure 6-6. The particle size and particle neck size distribution have been presented by using equivalent volume spherical diameters. The nickel particles showed a significant change from an as-reduced sample to a degraded sample. For the as-reduced sample, more than 70% of nickel particles were below 100 nm in diameter, with the largest particle size at around 250 nm. After redox cycling, the formation of inter-porous

nickel led to a much larger particle size when compared with the aged sample. The YSZ structure is considered as the supporting framework of the electrode. The YSZ particle size is similar before and after ageing and redox cycling process. This stability gives a consistent ionic conductivity. The pore size distribution is essential to fuel gas diffusion. In the as-reduced sample, the majority of pores are below 100 nm. This is due to even distribution of the Ni on the YSZ surface after the initial reduction. After ageing and redox cycling, the number pores below 100 nm decreased.

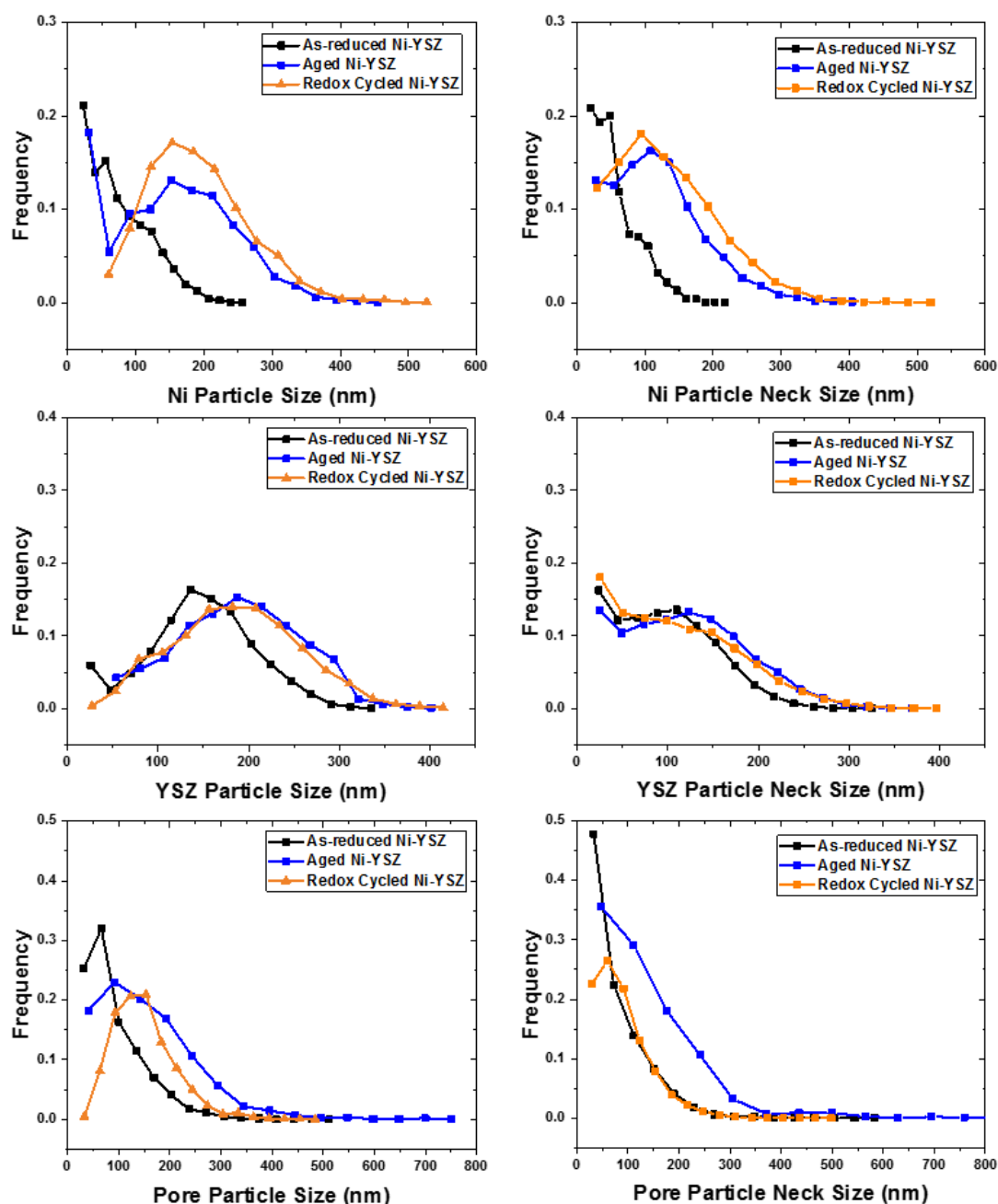


Figure 6-6 Microstructure comparison between as-reduced Ni-YSZ fibre scaffold and aged Ni-YSZ fibre scaffold. a) Ni particle size distribution, Ni neck size distribution and Ni particle distribution from the electrolyte to top surface. b) YSZ particle size distribution, YSZ neck size distribution. c) Pore size distribution, Ni neck size distribution and pore Ni particle distribution from the electrolyte to top surface. d) Active TPB distribution.

6.3 MECHANICAL PROPERTIES CHARACTERISATION

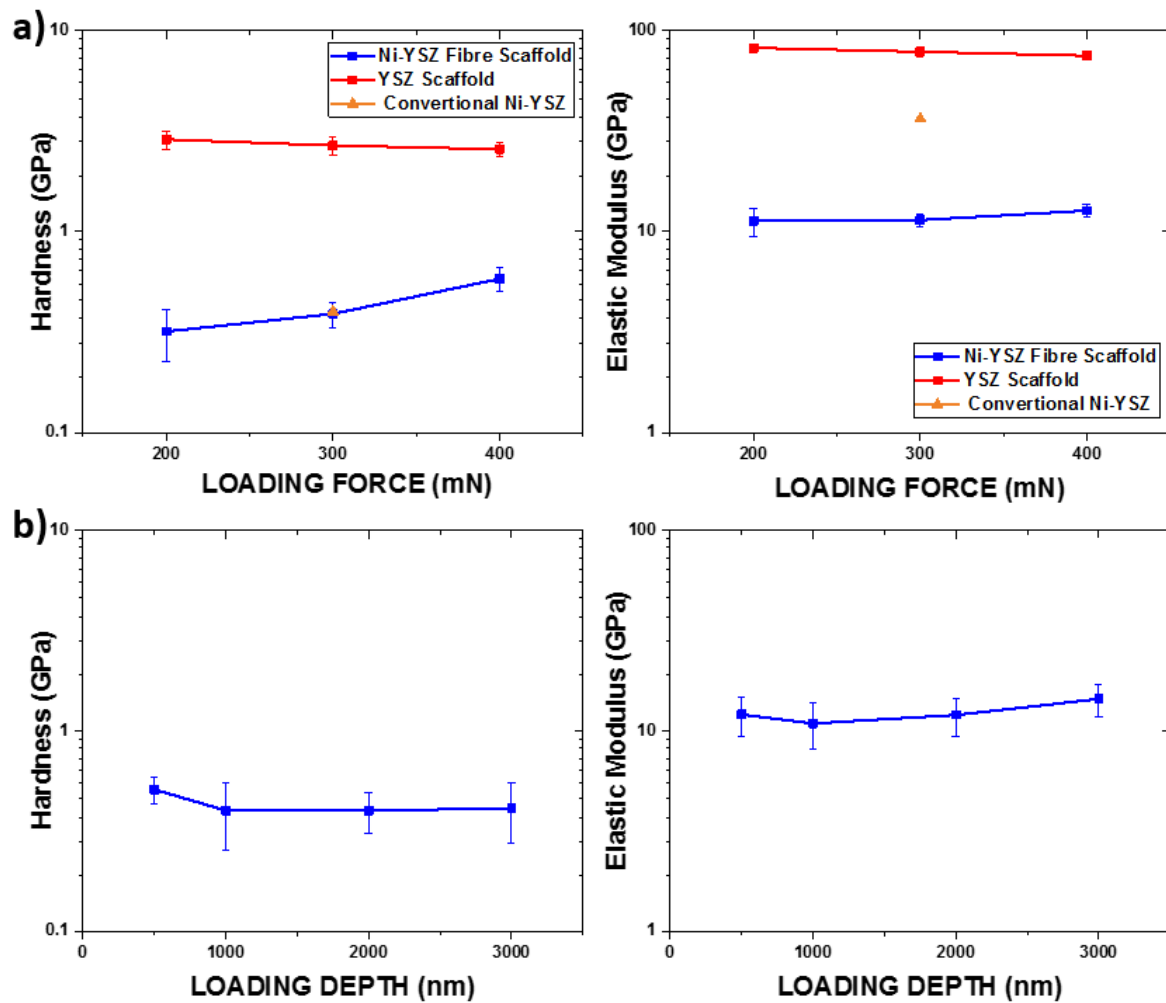


Figure 6-7 the mechanical properties of YSZ fibre layer from the electrode surface, 20 measurements were obtained for each condition. a) The nanoindentation measurement results based on a constant loading force. The elastic modulus and hardness have been compared with the conventional Ni-YSZ electrode and Ni-YSZ scaffold electrode; b) the nanoindentation measurement results based on the maximum loading depth.

The elastic modulus and hardness of the Ni-YSZ fibre scaffold top layer have been measured by using nanoindentation. These results have been used to compare with conventional Ni-YSZ and scaffold Ni-YSZ electrodes measured by the same technique.

Figure 6-7a) shows the hardness and elastic modulus measured by constant loading force, 200 mN, 300 mN and 400 mN. Both hardness and elastic modulus show stable properties at higher loading force, which is considered to be affected by the scaffold layer, as higher loading force could lead to a greater depth. The measurement results from 200 mN show fluctuating mechanical properties. This is considered to be mainly contributed by the fibre layer, the inhomogeneous fibre and pore distribution leading to the difference in local mechanical properties. Because the fibre layer has a thickness of around 5-8 μm , an indentation with controlled depth was performed on the sample top surface. The obtained results are consistent with those results measured from the 200 mN test.

6.4 MICROSTRUCTURE EXPLANATION FOR MATERIAL STABILITY

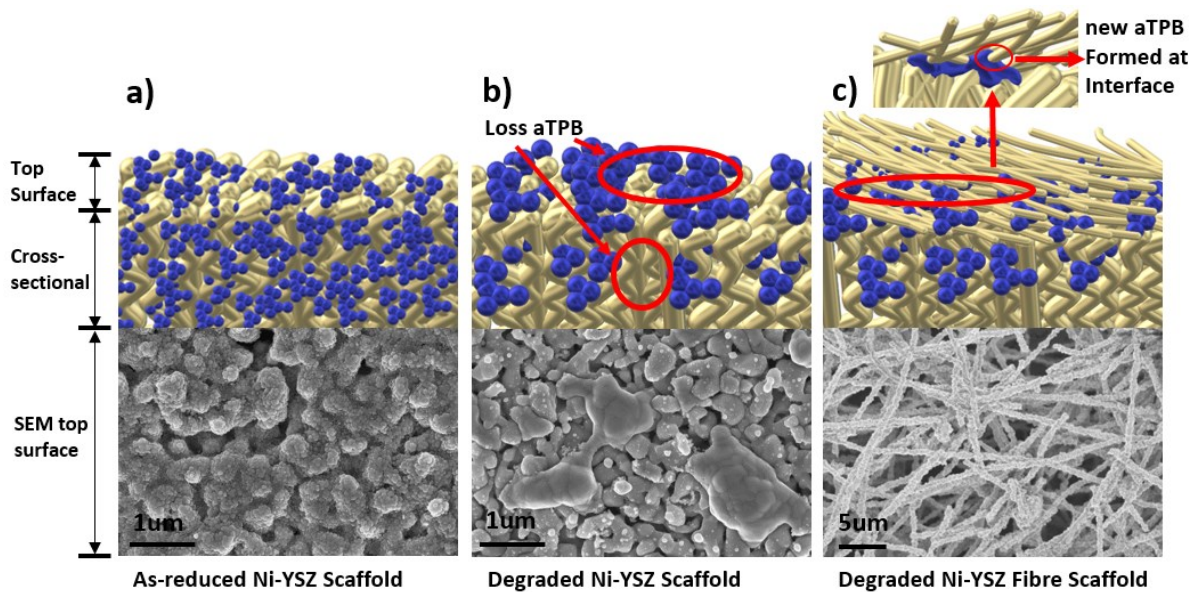


Figure 6-8 sketches coupled with SEM images explaining the nickel control mechanism difference between the Ni-YSZ scaffold and Fibre-Scaffold.

Figure 6-8a shows SEM images and a conceptual sketch of the as-reduced nickel infiltrated YSZ scaffold electrode, where nickel nanoparticles are evenly distributed on the surface of the scaffold structure and generate large numbers of TPBs. Figure 6-8b shown the degraded

scaffold electrode, where nickel moved to the electrode top surface and formed large nickel particles, which led to a TPB reduction. However, by adding an additional highly porous YSZ fibre layer, those large nickel particles reconnect with the fibre and form a new aTPB. Due to the large pore size and limited nickel-fibre contact within this fibre layer, further nickel migration was restricted, as there was no observation of nickel particles on top of the fibre layer.

6.5 CHAPTER SUMMARY

In this chapter, a fibre microstructure has been used for solid oxide fuel cell anode structure design to enhance the stability of scaffold structures. Several advantages have been identified, including:

1. The significant porosity difference between the scaffold and fibre layers appeared to maintain nickel particles at the interfacial layer. Simultaneously, the highly porous fibre layer allowed sufficient fuel flow from the surrounding atmosphere. This contributes to more stable electrochemical performance compared to current conventional nickel infiltrated scaffold materials.
2. The horizontal single direction YSZ fibre structures effectively limit the nickel agglomeration pathway within the fibre layer. This may help stabilise the electrochemical performance with time.
3. The highly porous fibre layer, on top of the scaffold, provides a flexible contact with the current collector. This application improved the ohmic resistance stability in impedance measurements in the experiments. Furthermore, in SOFC stacks, the

flexibility of the fibre layer could potentially minimize both material redox cycling and thermal expansion impact on the structural damage.

4. Under the compliant fibre layer, the mechanically strong scaffold layer provides not only an extremely high surface area for the electrochemical reaction but also a stable structure to resist redox damage.
5. The high electrochemical performance at the low temperature is mainly contributed by the scaffold layer of the electrode. This low operational temperature enables slower cell degradation during both isothermal ageing and redox cycling processes.

This work is a novel concept for the anode electrode structure design. There are still some improvements that can be implemented such as controlling single fibre diameter, modifying YSZ suspension concentration and sintering temperature.

CHAPTER 7 STUDY OF NI DEWETTING AND PORE FORMATION FROM THE 2D NI-YSZ ELECTRODE

7.1 BACKGROUND OF NI DEWETTING

Dewetting describes the transformation of a thin film into an energetically favoured set of droplets or particles. Solid-state dewetting occurs at temperatures well below the melting temperature of the bulk material⁷⁰. As described in previous chapters and literature, a wide range of experimental evidence has proven that Ni dewetting can accelerate electrochemical performance degradation, by damaging the cermet microstructure and reducing the active triple phase boundary length^{102,164}. The investigation of Ni dewetting is also driven by the increasing interest in nanostructured infiltrated electrodes^{62–65}, whose initial performance before Ni dewetting makes this technology very promising for intermediate and low-temperature operation^{67–69}. In addition to this, it also has been observed that isolated nickel particles have appeared outside the electrode region after long term redox cycling operation at high temperature, as shown in Figure 7-1, which may be formed by nickel evaporation-condensation at high temperature in humidified atmospheres. However, due to the large dimensional disparity between nickel nanoparticles and the complicated YSZ structure, the dewetting mechanism itself remains challenging to investigate in the electrode.

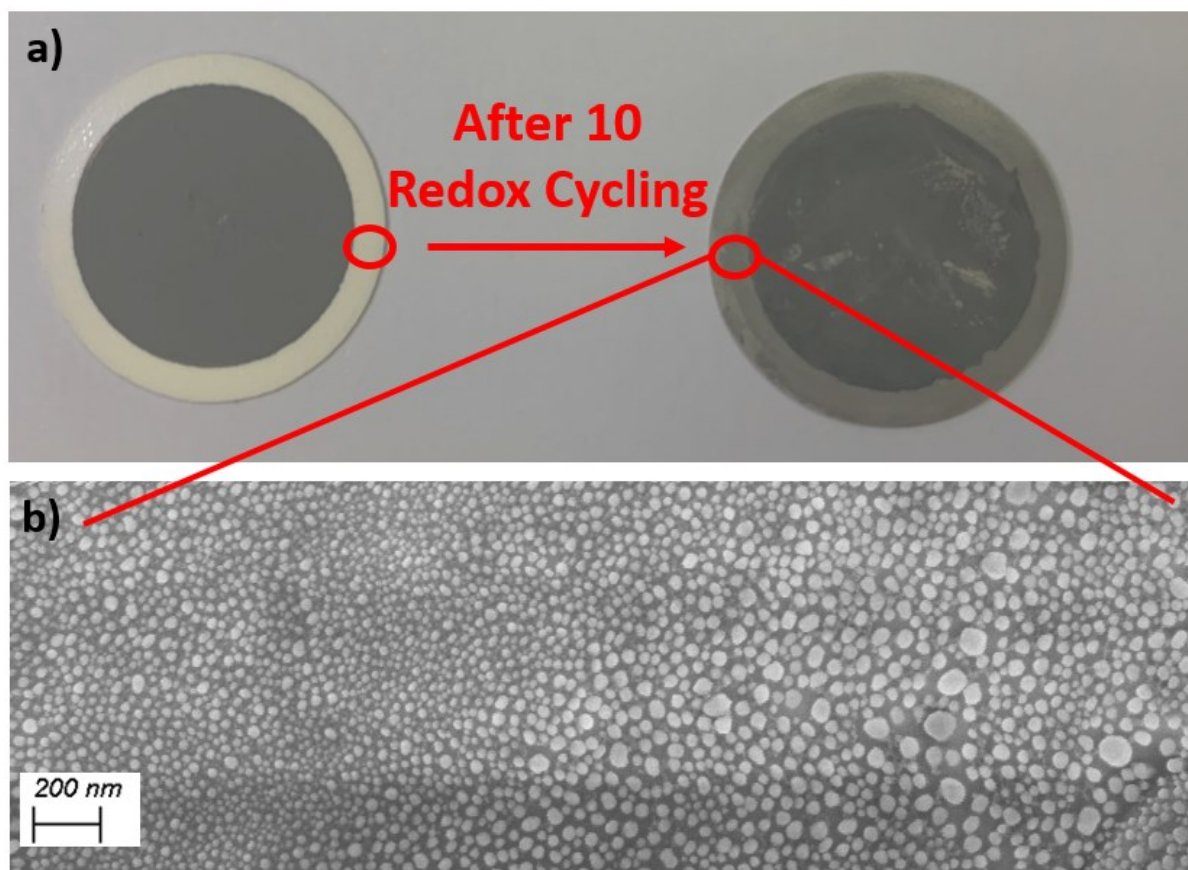


Figure 7-1 a) the conventional Ni-YSZ observed before and after 10 redox cycling; b) The SEM image shows the grey region (from a)) in high magnification.

In this chapter a 2D Ni-YSZ electrode, consisting of a 40 nm Ni film sputtered on a YSZ substrate, was designed to study the in-situ anode degradation affected by Ni dewetting and de-percolation, without any influence from other geometric factors. This dimensional reduction significantly simplifies the experimental setup for an in-situ environmental observation of nickel behaviour at high temperature and under a controlled gas atmosphere^{70,165,166}, allowing for more robust and representative analysis compared to interrupted annealing^{78,167,168}. The investigation uses a wide range of techniques, including in-situ environmental scanning electron microscopy (E-SEM), electrochemical impedance spectroscopy (EIS), focused ion beam-scanning electron microscopy (FIB-SEM) and atomic

force microscopy (AFM). These experimental techniques are complemented by simulations of the Ni film evolution, electrochemical models and advanced tools for image analysis. For the first time, a thorough investigation is performed to quantify the nature of morphological changes of Ni thin films and their electrochemical performance, highlighting the capability of predicting this important aspect of SOFC anode degradation.

7.2 PRE-EXPERIMENT

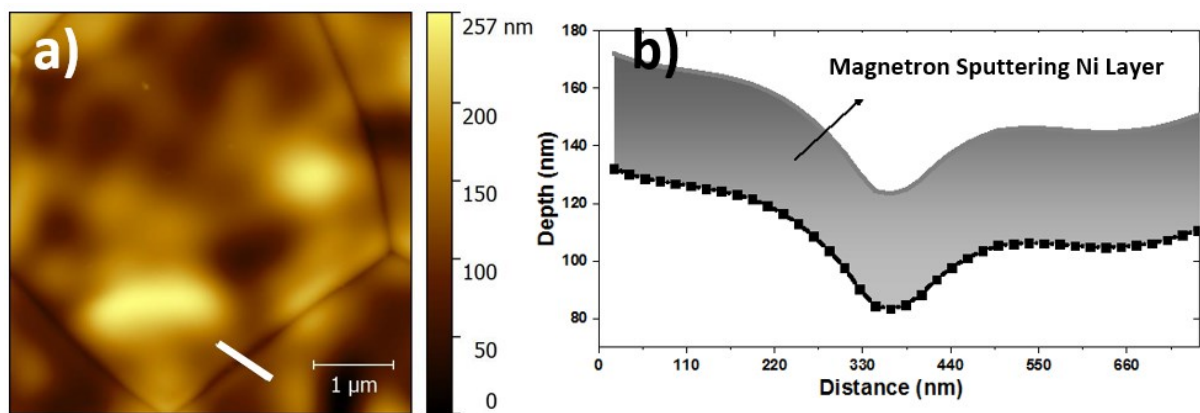


Figure 7-2 a) Map of the YSZ surface as measured by AFM before Ni deposition. b) Depth of the YSZ grain boundary measured along the line shown in a). A fictitious nickel layer of 40 nm is also illustrated in b).

The depth of the grain boundaries of the YSZ substrate was mapped in advance of the experiment using AFM, Figure 7-2. The characteristic grain boundary depth ranges between 30nm and 50nm. Due to the small and uniform thickness (~40 nm) of the nickel film, the morphology of the nickel film reflects the surface features of the YSZ substrate. The grain boundary grooves on the YSZ substrate are clearly observed on the Ni layer. The morphology of nickel film in the initial stage (Figure 7-5 a) shows clearly the grain boundary grooves on

zirconia substrate. This is because the grain boundary groove depth on YSZ is comparable to the film thickness (which is only 40 nm).

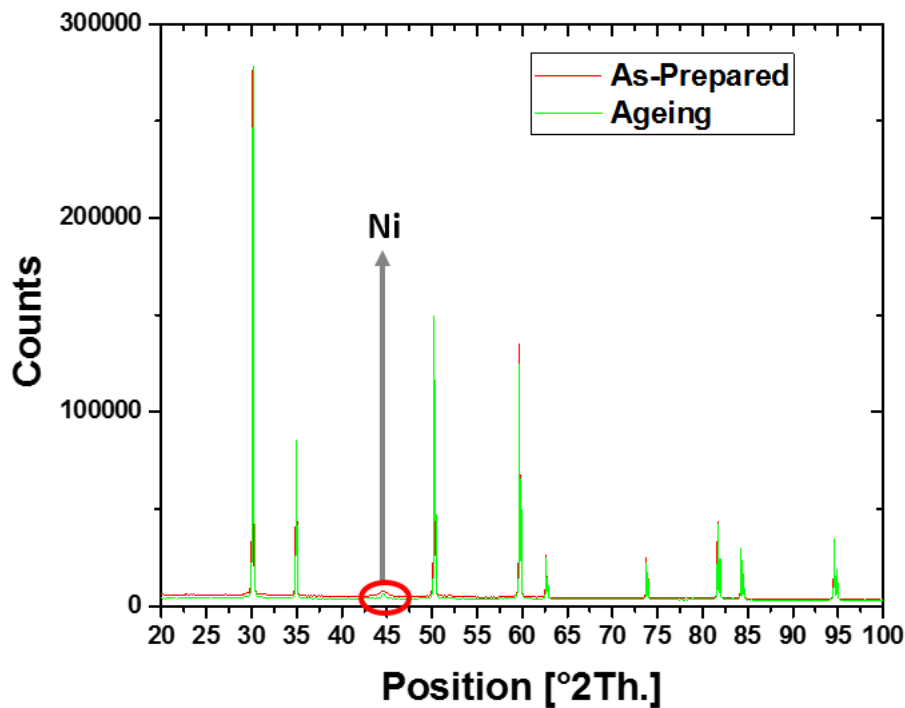


Figure 7-3 XRD of as-prepared and aged 100 nm Ni thin film on YSZ substrate. The indicated peak is from Ni, all the rest are YSZ.

Ni deposition was carried out at room temperature so the nickel film is very likely in an amorphous state, which was further confirmed by using XRD, as shown in Figure 7-3. In order to perform the morphology study by XRD, a thicker nickel film (100 nm) has been used. It has been found that the nickel nanoparticles lay on the YSZ substrate layer by layer. The residual diffraction contrast causes the grains to show a bright contrast⁷⁰. When the temperature is raised above 450 °C, the self-diffusion of Ni atoms in the Ni layer is activated and nickel atoms start to become mobile. This leads to crystallization of the nickel layer as reported in Figure 7-4. Crystallization is accompanied by a volume shrinkage, which can lead to a tensile stress in the film. In the experiments, it was found that cracking occurs first in grooves and valleys

(see Figure 7-5a). This is because of the stress concentration that magnifies tensile stress and the maximum stress concentration factor appears at the most concave surface locations¹⁶⁹.

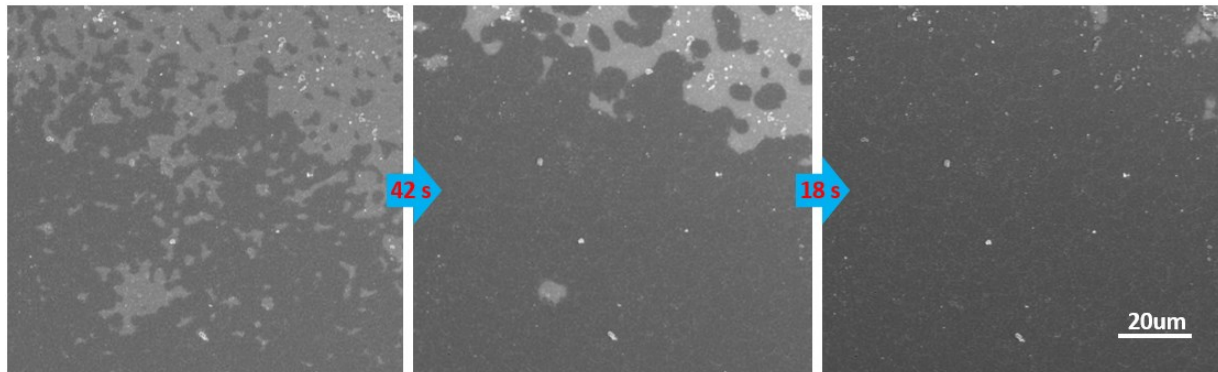


Figure 7-4 the images sequence of the change in charging effect observed from E-SEM during heating up, the bright colour indicates those nickel particles in an amorphous state, and the darker region indicates the nickel crystallization process is finished, where amorphous nickel nanoparticles become the thin layer.

7.3 SURFACE MORPHOLOGY EVOLUTION

7.3.1 High magnification images: morphology of Ni dewetting

The local morphology of the nickel layer was scrutinized at higher magnification ($\times 10,000$), as shown in Figure 7-5. The nickel thin film geometric transformation progress was recorded at two different temperatures (560 °C and 600 °C). The film appeared to be separated along the YSZ grain boundary, which could be a result of shrinkage of the coherent film at some stage before the temperature reached the highest point.

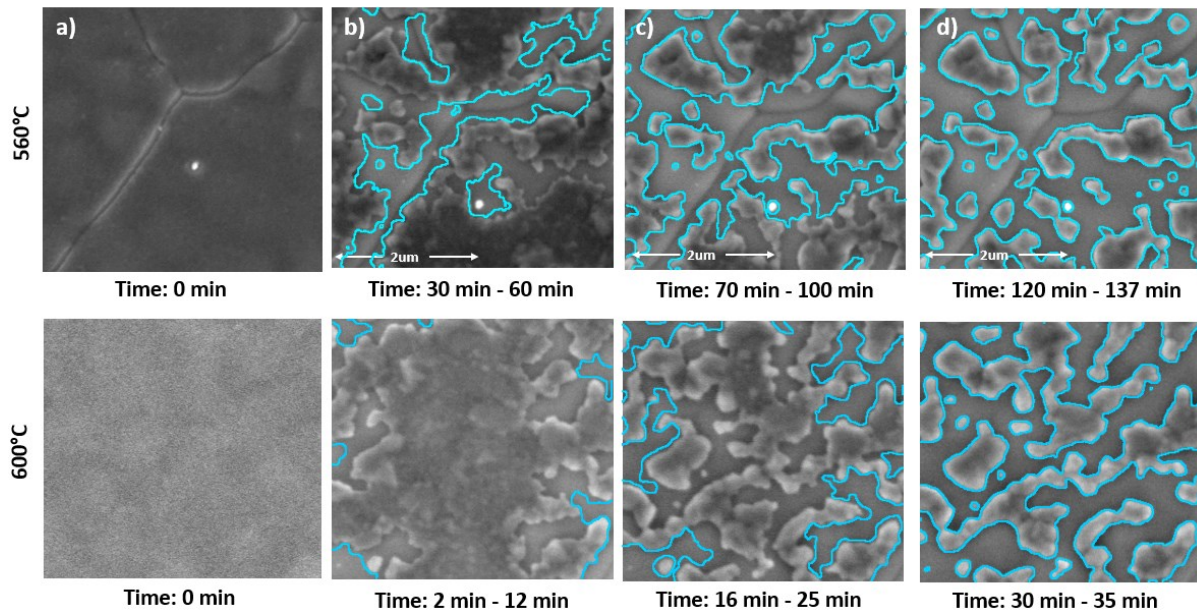


Figure 7-5 experimental results of zirconia supported nickel film top surface morphology at 560 °C and 600 °C in the controlled gas mixture. Light blue represents the nickel particle boundaries at the initial time and the background SEM image is the real morphology at the ending time, as indicated under each image.

The dewetting of the nickel film is apparently sensitive to the pre-existing defects along the YSZ grain boundaries. Figure 7-5b clearly shows that dewetting preferentially starts from a YSZ grain boundary: the film retracts from the YSZ boundary and multiple pores are formed along the grain boundary lines. This stage involves the generation of pores, the formation of TPBs and an increase in TPB length. The nickel particles are well percolated and all TPBs contribute to the electrochemical reaction. The nucleation and growth of the pores on flat and coherent film area take place at a much later stage (as shown in Figure 7-5c). During dewetting, some of nickel particles gradually became isolated from the large clusters. As a result of this, the overall connectivity of the film decreased with time. Once small particles become isolated, their size and shape become very stable. The surface energy minimization

process leads to the reduction of surface roughness. The coupled observations from Figure 7-5, Figure 7-6 and Figure 7-9 help understanding of the nickel behaviour under such a controlled environment. In contrast the microstructure of the large clusters continued to evolve.

7.3.2 Low magnification images: General behaviour of the Ni layer migration

The low magnification ($\times 5,000$) images were segmented and used for quantitative analyses of parameters that are characteristic of the general features of the Ni layer dewetting. These parameters are total TPB density, nickel surface coverage ratio and nickel percolation ratio. As shown in Figure 7-6, a higher operating temperature could lead to faster nickel evolution. This is due to thermal activation that leads to an increase in the atomic mobility. The increase in total TPB density that was observed at the initial stage was associated with the nickel thin film dewetting process, leading to pore generation and to a significant nickel coverage reduction. After 110 min and 25 min for 560 °C and 600 °C respectively, the total TPB density from both experiments reached a relatively stable level around $5.5 \mu\text{m}^{-1}$. This indicates the start of the nickel agglomeration stage (i.e., stage d in Figure 7-5). During this time, isolated nickel islands are formed and the gradual agglomeration leads to a reduction in surface coverage ratio and nickel surface roughness.

At the nickel coverage point of 0.63, the thin film has a significant de-percolation rate, where the intermediate phase between dewetting and agglomeration has been reached. It has been also found that under the different temperatures, the nickel area coverage ratio stabilized at c. 0.49. This may indicate that nickel particles can reach a stable state even below 600 °C,

which is characterized by a particle thickness of $\sim 80\text{nm}$, assuming that the volume of Ni remains constant during the dewetting process.

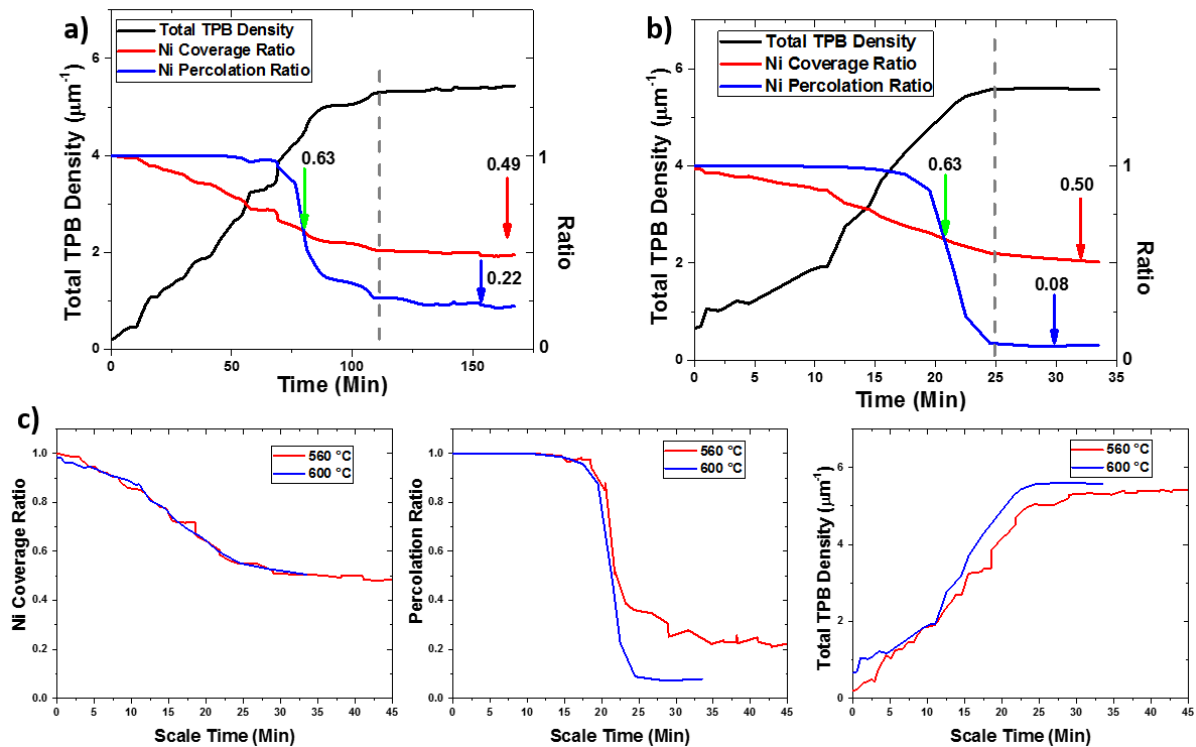


Figure 7-6 TPB density, Ni area coverage ratio and Ni percolation ratio data based on segmented images. a) Data obtained from HT-ESEM image series recorded at $T=560\text{ °C}$. b) Data obtained from HT-ESEM image series recorded at $T=600\text{ °C}$. c) Superposition of data at $T=560\text{ °C}$ (blue lines) and $T=600\text{ °C}$ (red lines) after scaling the time of the data at $T=560\text{ °C}$ according to the ratio of times corresponding to a coverage fraction of 0.63. The vertical dashed lines indicate the start of the agglomeration stage.

Figure 7-6c shows the superposition of the nickel coverage ratio, Ni percolation ratio and total TPB density of the two datasets after scaling the time of data at 560 °C by a factor equal to the ratio of times corresponding to a coverage fraction of 0.63. Figure 7-6c shows that all the relevant microstructural properties are successfully rescaled with sufficient precision. This

indicates that the dewetting and agglomeration phenomena proceed according to the same mechanisms irrespective of temperature within the temperature range 560-600 °C⁷⁰.

The calculated time scaling factor used in Figure 7-6c is equal to 3.91, which is comparing the time spent of the changing in coverage ratio, this means that the rate of dewetting and agglomeration becomes roughly four times faster from $T = 560\text{ °C}$ to $T = 600\text{ °C}$. Assuming thermal activation of the kinetics of the Ni dewetting phenomena, the time scaling factor enables estimation of the activation energy of the characteristic rate of the dewetting mechanism⁷⁰, equal to 0.71 eV for a 40 nm Ni film on YSZ. This value is lower than the activation energies of the characteristic dewetting rate reported by Niekiet et al.⁷⁰, equal to 1.04 eV and 1.42 eV for 15 nm and 22 nm Au films on silicon nitride substrate, respectively.

7.4 ACTIVE TPB ESTIMATION

The TPB densities of the E-SEM images were calculated from the segmented data using an in-house code which treated the edges of the square pixels as the interface between the nickel and YSZ. Special care was given to the evaluation of the aTPB density, which is the TPB belonging to Ni clusters connected to the Pt mesh current collector used in impedance measurements. Since the opening of the Pt mesh current collector ($\sim 300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$) was significantly larger than the area imaged by FEG-ESEM, Ni percolation and aTPB assessed on the imaged area had to be scaled up to the open area of the Pt mesh, which is representative of the entire electrode area. Two different approaches were used: a wire-based model and a lattice-based model.

7.4.1 Lattice model for TPB estimation

This model was fully developed by Dr. Antonio Bertei.

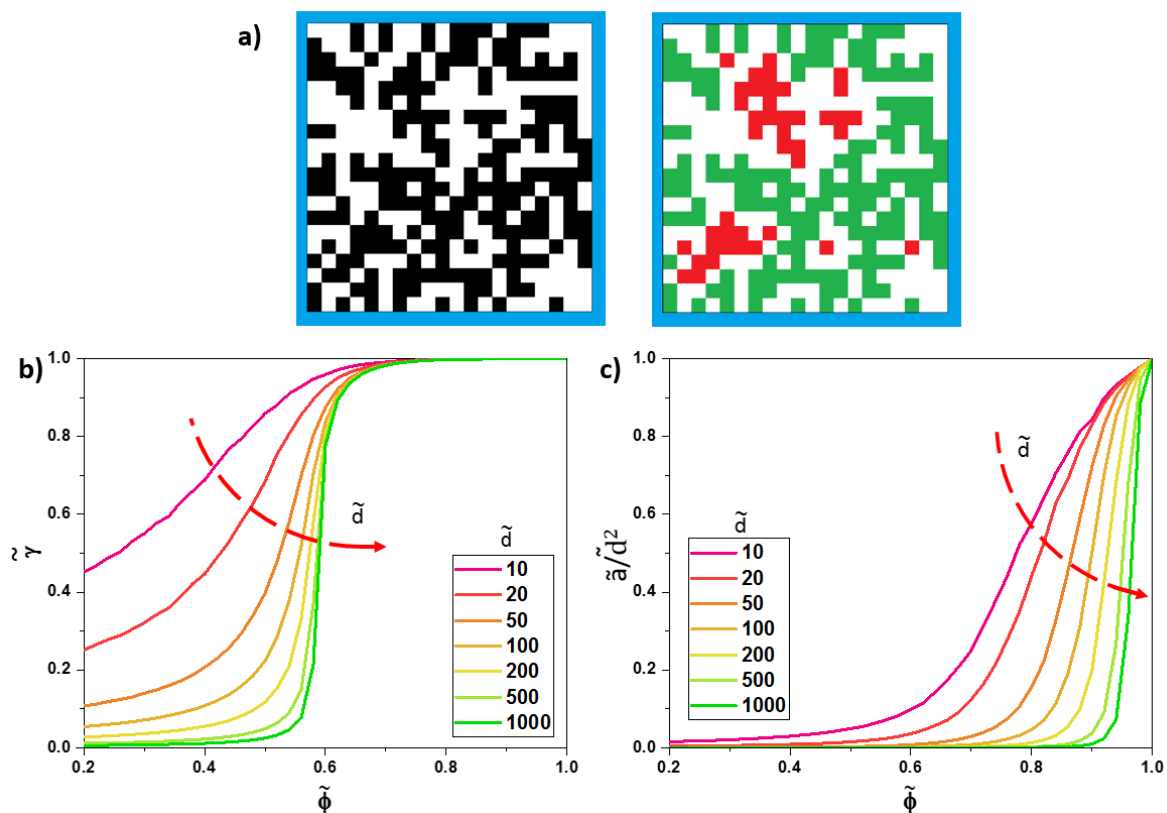


Figure 7-7 Lattice-based model. a) A random realisation of a square lattice, with clusters of percolated green pixels connected to the external boundaries and isolated red pixels. In this presented case: $\tilde{d} = 20$, $\tilde{\phi} = 0.5$, $\tilde{\alpha} = 200/26 \approx 7.69$, $\tilde{\gamma} = 159/200 = 0.795$. b) Percolation fraction $\tilde{\gamma}$ as a function of coverage fraction $\tilde{\phi}$ for different side lengths $\tilde{d}$. c) Normalised mean cluster area $\tilde{\alpha}/\tilde{d}^2$ as a function of coverage fraction $\tilde{\phi}$ for different side lengths $\tilde{d}$.

This lattice-based model is used to scale up the aTPB from the imaged area to the electrode area, which combined random lattice simulations with the scaling laws of percolation theory in finite domains¹⁷⁰. A C++ program was developed to randomly fill in square lattices, as shows in Figure 7-7. In these simulations the black pixels represented the Ni phase and the white

pixels are the uncovered YSZ phase. The percolation ratio ($\tilde{\gamma}$) is represents the ratio of black pixels are connected to the blue boundaries and the mean cluster area ($\tilde{a}$) of the black phase were evaluated over 1000 random realisations for different values of coverage ratio ($\tilde{\phi}$) and side length ($\tilde{d}$), as reported in Figure 7-7.

The equivalence between random lattices and imaged areas was performed by using segmented images with side length d obtained from E-SEM, the Ni coverage fraction ϕ , the mean Ni cluster area a and the Ni percolation fraction γ with external boundaries were evaluated by image analysis. According to Figure 7-7c, the length $\tilde{d}_1$ was determined by ϕ and a/d^2 of the segmented images, based on the equivalent random lattice having $\tilde{\phi}_1 = \phi$ and $(\tilde{a}/\tilde{d}^2)_1 = (a/d^2)$. This allows for the evaluation of the percolation fraction $\tilde{\gamma}_1$ of such an equivalent lattice according to Figure 7-7b. Then, the ratio $\delta = d_m/d$ between the side length of the Pt mesh opening ($d_m = 300 \mu m$) and the E-SEM image side length (d) was used to scale up the equivalent random lattice to the side length $\tilde{d}_2 = \delta \cdot \tilde{d}_1$, for which the percolation fraction $\tilde{\gamma}_2$ is obtained. Finally, the aTPB density referred to the entire electrode area was evaluated as:

$$\rho_{aTPB} = \gamma \frac{L_{TPB}}{A_{image}} \cdot \frac{\tilde{\gamma}_2}{\tilde{\gamma}_1} \quad \text{Equation 11}$$

that is, by scaling up the percolating TPB density per unit of imaged area ($\gamma L_{TPB}/A_{image}$) for the ratio of Ni percolation fractions in the equivalent random lattices ($\tilde{\gamma}_2/\tilde{\gamma}_1$). Notably, this lattice-based model allows for the extrapolation of the active TPB density evaluated by image analysis up to the size of the Pt mesh according to the scaling laws of percolation in finite lattices.

7.4.2 Wire model for TPB estimation

This model was a collaboration with Dr. Sam Cooper, where he has contributed Matlab coding.

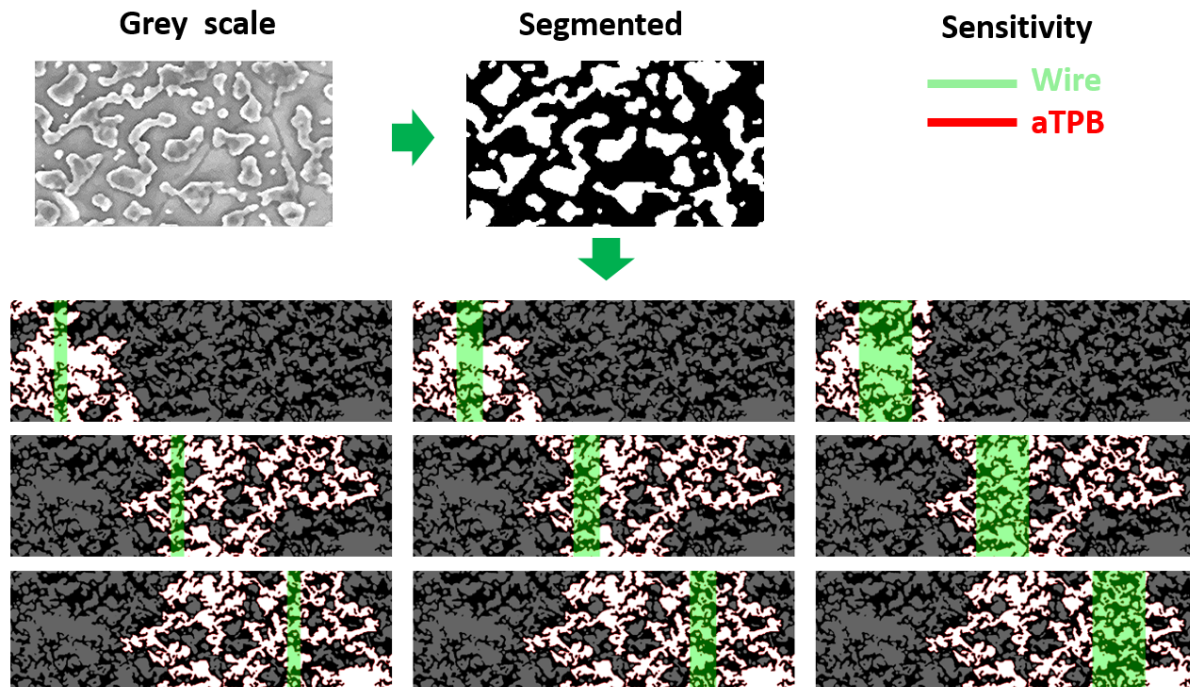


Figure 7-8 the image segmentation and wire based model used for aTPB statistics. The green line represents the wire current collector located at the different region with different width. The white area is the percolated nickel in contact with the current collector and the red line surrounding the white particle represents the corresponding active triple phase boundaries.

In the wire-based model a 'wire' location was assigned across the images. Due to the uncertainty around the quality of the contact between the current collector and the nickel layer, a two-part sensitivity analysis was performed to investigate the degree of lateral percolation in the nickel phase so that the aTPB density could also be approximated. Percolation was assessed by placing an initial "wire" column, representing the contact from a section of the current collector mesh, and then counting only those TPBs which belong to the

Ni clusters connected to the wire. The first part of the sensitivity study involved placing the wire at a range of equally spaced horizontal locations and the second part varied the width of the wire column as illustrated by Figure 7-8.

Percolation across the full width of the imaged area was used to assess the global percolation of the nickel layer with the Pt mesh. If the nickel percolated across the whole imaged area, the imaged active TPB density was assumed to be available to the entire electrode area. However, once Ni percolation from wire to image side stopped, the active TPB density was assumed to scale with the length of current collector mesh per unit area. Thus, the following equations were used for Ni percolation across the whole imaged area:

$$\rho_{aTPB} = \frac{L_{aTPB}}{A_{image}} \quad \text{Equation 12}$$

and once Ni percolation was lost from the fictitious wire location to the image side:

$$\rho_{aTPB} = \frac{L_{aTPB}}{L_{wire-micro}} \times \frac{L_{wire-macro}}{A_{cell}} \quad \text{Equation 13}$$

where, ρ_{aTPB} is the active TPB density per unit of total cell area, L_{aTPB} is total active TPB length measured in the image area, A_{image} is the image area, $L_{wire-micro}$ is the wire length observed in the image area, $L_{wire-macro}$ is total Pt current collector length and A_{cell} is the total cell area.

7.4.3 Active TPB density obtained from Image analysis

The wire model and the lattice model described above were used for estimating aTPB per unit of entire electrode area as shown in Figure 7-9. The variations of aTPB with time show the

same trends in both models. First, the early stage is characterized by an increase of aTPB with time that corresponds to the dewetting progress from a dense nickel thin film to a highly porous network. Secondly, the intermediate stage begins when the aTPB generation rate slows down until aTPB reaches a peak. The two models show a consistent time value match when aTPB reaches a maximum value. Around this peak point, the aTPB was affected by both pore generation and de-percolation, resulting in a temporary maximum. In addition to that, this peak aTPB density shows a consistent time step with coverage point of 0.63, as described in Figure 7-6. Finally, the agglomeration stage starts when both the total TPB and aTPB became stable. The final minimum aTPB values are directly controlled by the active nickel particles that are directly in contact with the current collector. Prolonging the heat treatment at high temperature leads to a further decrease in the aTPB values.

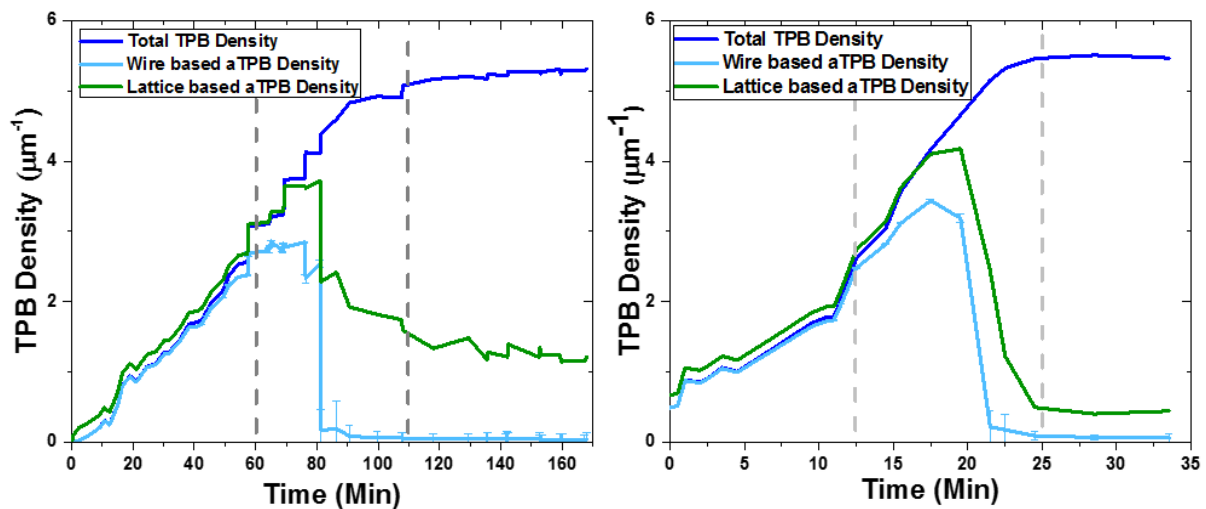


Figure 7-9 the aTPB estimation based on wire model and lattice model for the two samples recorded within wet 5 vol % H_2 at $T = 560^\circ\text{C}$ (left) and $T = 600^\circ\text{C}$ (right). The dark blue line shows the total TPB, light blue line shows the calculated results from wire model and green line represent the calculation results from the lattice model.

7.5 ELECTROCHEMICAL PERFORMANCE

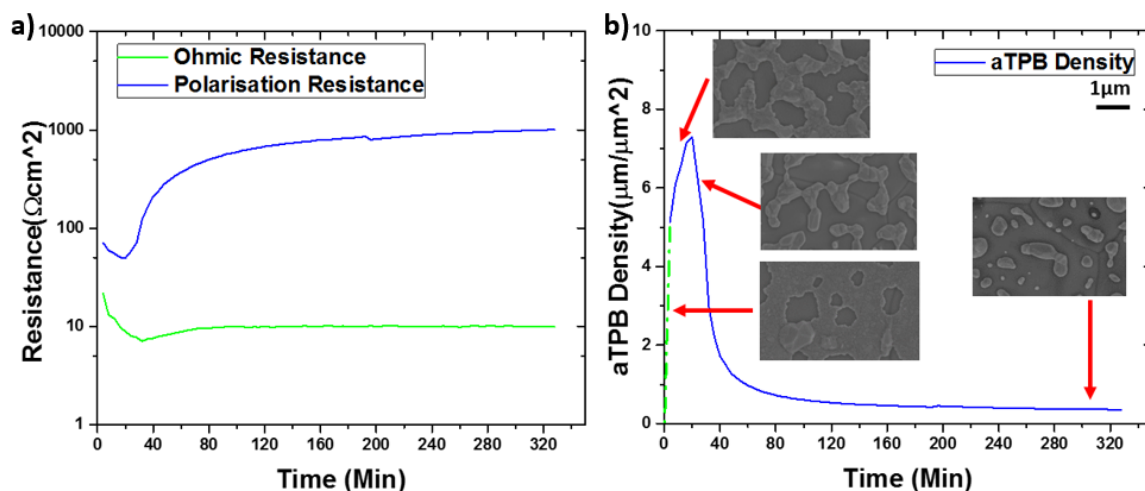


Figure 7-10 a): the Ohmic resistance and electrochemical reaction polarisation resistance as a function of time as measured from impedance spectroscopy data at 600 °C; b): the active area ratio ω_{act} and active TPB density per unit of electrode area ρ_{aTPB} or active percolating area ρ_{aTPB}^{act} obtained according to Equations 12 and 13, respectively.

Theoretically, only one temperature was sufficient for EIS investigation because the microstructural evolution at different temperatures can be rescaled with a single scaling factor (Figure 7-6). The electrochemical behaviour of the 2D Ni/YSZ electrode is reported in Figure 7-10a shows that, within the first 20 minutes of operation, the electrode gives high values of ohmic resistance (R_1) and electrochemical reaction polarisation resistance (R_2). According to the image analysis reported before, within the first minutes the electrode corresponds to a dense Ni layer with a few defects/pores. In this situation, the electrochemical reaction occurs only at the sparsely dispersed TPBs, thus the ionic current flows in the electrolyte only underneath the projected area of these defects, resulting in large values of ohmic and polarization resistance.

As soon as de-wetting begins, some "holes" are generated, which create TPBs. At a certain point, it could be assumed that holes (and aTPB) are uniformly distributed over the entire electrode planar area. In this situation, the whole electrode area is active and so the electrolyte ohmic resistance is minimum. According to Figure 7-10a, this situation occurs after ca. 20 min at 600 °C. Notably, at this point the long-range percolation of Ni is not yet lost since the Ni percolation ratio in the imaged area is equal to 1 for up to 15 min (see Figure 7-6a). So, when the ohmic resistance is minimum ($R_1^{\min}$), the whole electrode area can be considered covered by a homogeneous layer of nickel with holes (and TPBs). Therefore, any subsequent increase in R_1 is attributed to the loss in long-range percolation that causes a decrease in active area as described in Figure 7-7.

Figure 7-10b also shows the active TPB density evaluated according to Equation 12&13 from the temporal evolution of the polarization resistance R_2 reported in Figure 7-10a. The increasing and then decreasing stages of R_2 produce a maximum in the ρ_{aTPB} , which is in qualitative agreement with that obtained from image analysis in Figure 7-9. After roughly 30 minutes of operation, the loss in nickel percolation leads to the significant increase in R_2 , resulting in an abrupt decrease in ρ_{aTPB} .

7.6 MICROSTRUCTURE SIMULATION

7.6.1 Nickel Wetting Angle and Dihedral Angle

For the nickel thin film supported on YSZ substrate, a simulation was used to simulate the microstructure evolution of the nickel film. It has been found that the microstructure evolution is strongly dependent on the wetting angle between Ni and YSZ, and the dihedral

angle between two neighbour nickel grains at the surface. The simulation results reported in the later section are based on a wetting angle of 121° (determined based on FIB cross section images) and a dihedral angle of 129°. The dihedral angle is calculated from the ratio of the grain boundary energy to the surface energy of nickel (reported to be 0.37¹⁷¹).

$$\alpha = \arctan\left(\frac{\tan\beta}{\cos 36^\circ}\right)$$

Equation 14

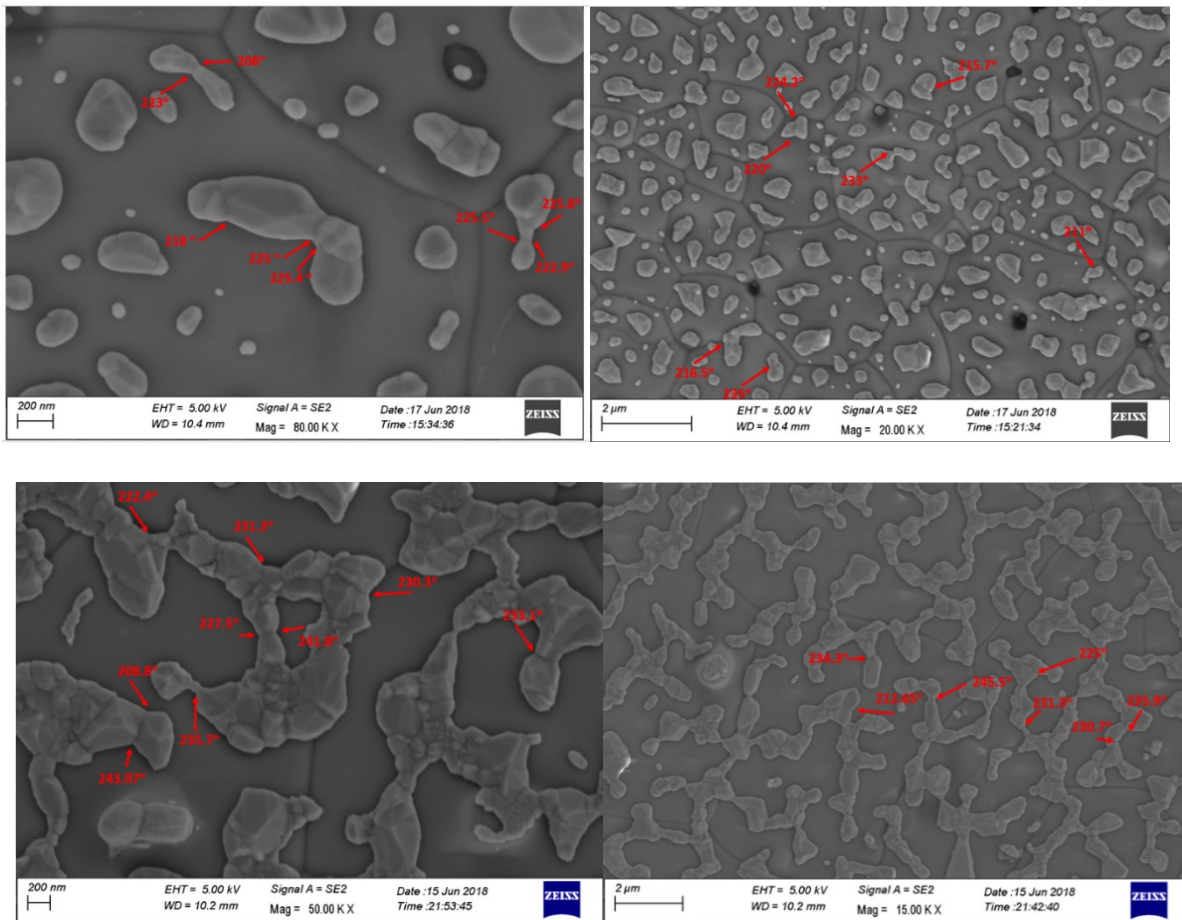


Figure 7-11 a) SEM images 2D Ni-YSZ after degradation at 600 °C, with dihedral angle measurements. Dihedral angle= 152°±7.2°; b) SEM images 2D Ni-YSZ after degradation at 500 °C, with dihedral angle measurements. Dihedral angle= 129°±10.2°

The wetting angle of nickel particles was measured with FIB-SEM cross-sectional views. A wetting angle correction was considered due to the sample tilt of 54° for FIB milling. Here α is the real wetting angle, β is the observed angle from SEM images, as shown in Figure 7-12. The contact point is a cross-section of a TPB (i.e., the intersection of gas/Ni/YSZ). From the SEM image, $\beta = 126^\circ \pm 13^\circ$; therefore, after correction via Eq. 12, the contact angle results equal to $\alpha = 121^\circ \pm 12^\circ$.

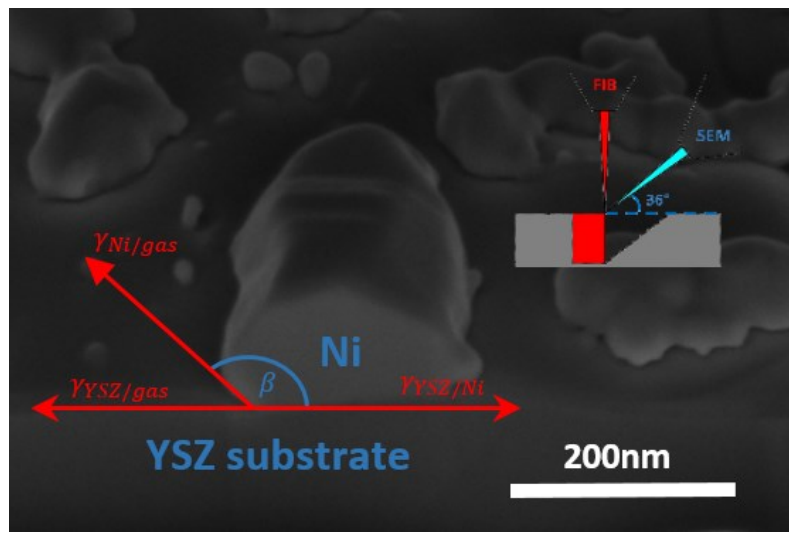


Figure 7-12 FIB-SEM cross-sectional images for Ni wetting angle measurements.

7.6.2 Nickel Dewetting Simulation

In order to obtain a mechanistic insight into the mechanisms that govern Ni dewetting, cellular automata simulations were performed by Dr. Xin Wang, and compared with the image analysis of experimental E-SEM images discussed above.

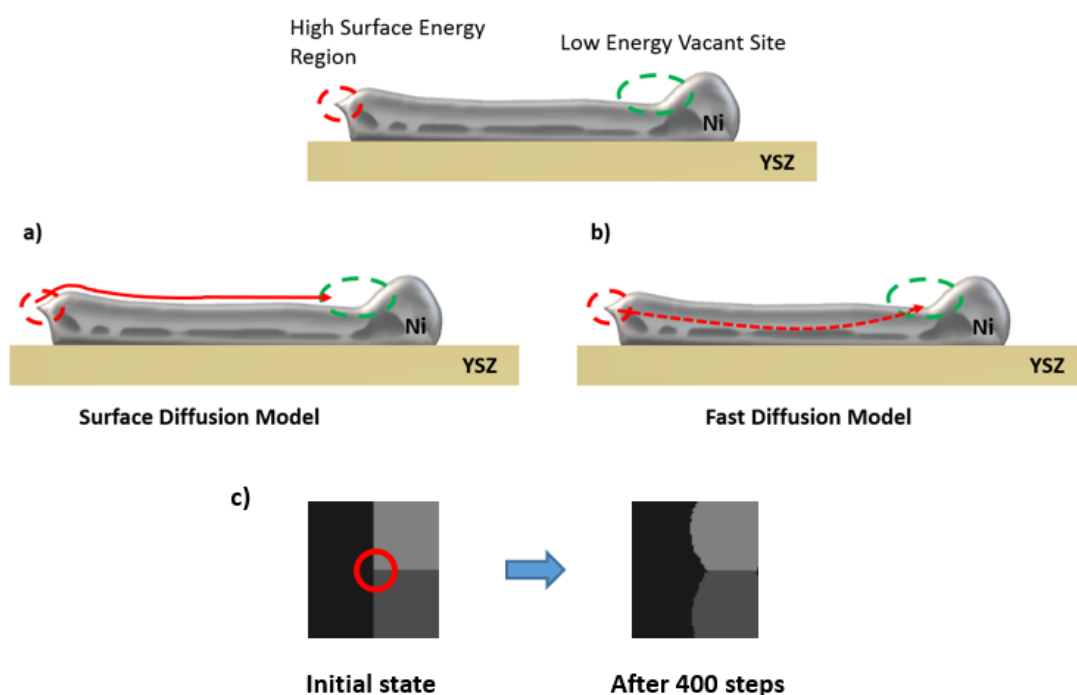


Figure 7-13 Schematic representation of surface diffusion and fast diffusion models. a) Mass transport takes place along the nickel surface, step-by-step, until the matter voxel reaches the low energy vacant site; b) the high energy matter voxel can jump into the low energy vacant site in a single step; c) a grain boundary migration model presented that the higher energy voxels region (light grey and dark grey) change to lower energy voxels region (black) near the triple grain junction.

It used to be generally accepted that the process of solid-state dewetting is governed by surface self-diffusion⁷¹. While, this does not seem to be true according to recent studies^{72,81,166}. It was found that other mechanisms such as grain boundary⁷³ and interface diffusion^{79,80} can play a crucial role. For example, the metal self-diffusion along the metal–ceramic interface was found to be faster than mass-transport self-diffusion along a surface of the same metal⁷¹.

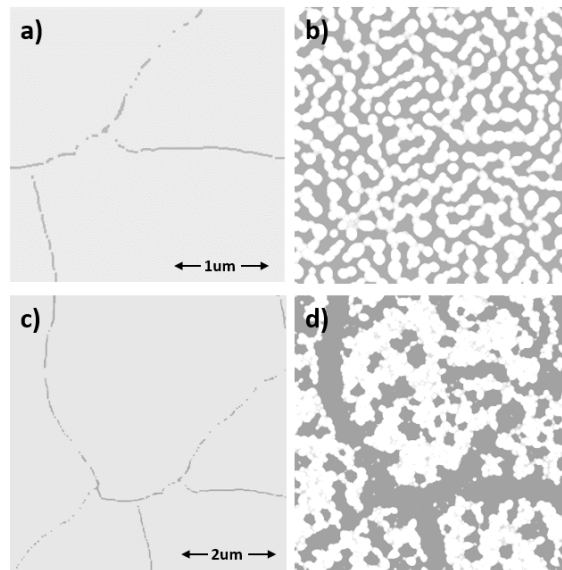


Figure 7-14 a) the initial microstructure of a representative area of nickel film b) the simulated microstructure evolved by using the surface diffusion model when nickel coverage is reduced to about 60%; c) a slightly larger area of nickel film than a), d) the simulated microstructure evolution from c) by employing a fast diffusion model, at this point the nickel coverage area is also reduced to about 60%.

Figure 7-13 shows a Ni cluster with a high surface energy region and low energy vacant site. These two conditions have been assigned to each individual model. a) According to the surface diffusion model, mass transport takes place along the surface, step-by-step, until the matter voxel reaches the low energy vacant site. b) According to the fast diffusion model, the high energy matter voxel can jump into the low energy vacant site in a single step. In both cases, mass transport takes place only within the same Ni cluster. c) Grain boundary migration model: each grain boundary voxel is allowed a chance of changing its state to that of one of its neighbours, with a probability proportional to the local energy difference; for example, at a triple junction (within the red circle in c), the energy of light grey and dark grey voxels is higher than that of black voxels. Therefore those voxels initially belong to light grey and dark

grey grains near the triple grain junction will be more likely to change to black. As a result of this evolution, the triple junction will become more balanced when the angle becomes roughly 120° (by assuming isotropic grain boundary energy).

In order to investigate how initial defects affect the microstructure changes, crack like defects were introduced in the initial microstructure. Figure 7-14 a-d show the simulated microstructure evolution by using the surface diffusion model. The simulated microstructure evolution (shown in Figure 7-14 a and b) is significantly different from the experimental observation. Since the surface diffusion simulation is more expensive in computational cost, a relatively small area ($3.2\mu\text{m}$ by $3.2\mu\text{m}$) of nickel film is simulated. The major discrepancy between simulation and experimental results is that the simulation failed to reflect the preferential pore growth or expansion from the pre-existent defects. Also the pore growth and the shrinkage of the nickel clusters shown in the simulation are very limited as compared to the experimental observation. Therefore, the nickel film dewetting is unlikely to be controlled by surface diffusion. This is consistent with the study from Amram⁷², which shows surface diffusion cannot be used to interpret the fact that if no rim or hillock on both sides of grain boundary groove.

In contrast, the microstructure evolution simulated by the fast diffusion model is fairly close to what was observed in experiment (shown in Figure 7-14 c & d). Both experimental and simulation results predict that the de-percolation occurs at about 60% nickel coverage rate (i.e., the threshold for 2D nickel cluster percolation is about 60%), but different mechanisms show very different phase sizes and TPB density at the percolation threshold. Figure 7-15 lists these parameters at the point of de-percolation obtained by experiment and simulations. The

phase size (measured by using interception length) and TPB density are obtained from the 2D images. Figure 7-15 shows that while the fast diffusion model matches the experimental results fairly well, the surface diffusion model severely deviates from the experimental results.

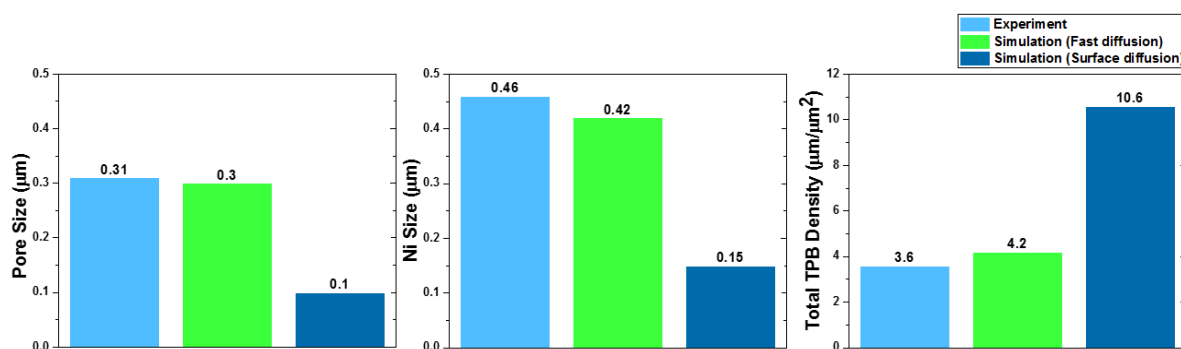


Figure 7-15 Microstructural parameters (pore size, Ni size and TPB density) at the Ni percolation threshold obtained by different simulation models and evaluated in experimental E-SEM observations. In this graph, TPB values were calculated on a subset of the image area, thus they differ from those evaluated on the large dataset due to statistical variation.

In the fast diffusion model, nickel transport is only allowed to occur within one cluster: i.e., the nickel is not allowed to move from one isolated particle to another isolated particle. This is based on the in-situ experimental observation that the small nickel particles do not change size once detached from a large cluster to which they originally connected, which indicates that nickel transport along the YSZ surface is very limited, if not impossible. It also rules out the possibility of evaporation-condensation in dewetting.

7.7 ACTIVE TPB COMPARISON

The link between microstructural evolution and electrochemical response of the Ni film was assessed by comparing image analysis, simulations and impedance spectroscopy data, which

is reported in Figure 7-10a for 600 °C and 1 atm. Notably, E-SEM imaging and EIS data refer to two nominally equal but distinct samples, thus some variations are expected due to variance in sample fabrication and differences in operating conditions.

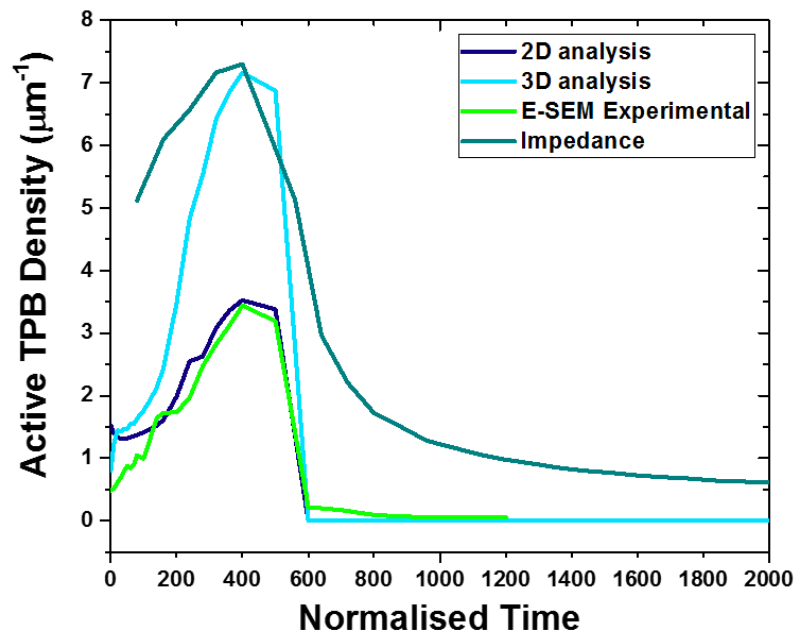


Figure 7-16 the active TPB density obtained from 3D analysis and 2D image analysis on simulated microstructure evolution, compared with the experimental results (2D analysis).

Since the wetting angle of nickel is $> 90^\circ$, the actual TPB is hidden under nickel particles. Therefore the TPB density obtained from 2D images may not to reflect the actual TPB density. Simulation provides both 3D data sets and 2D images which allow the comparison of the percolated TPB density obtained from 2D analysis with that from 3D analysis. As shown in Figure 7-16 the 3D analysis gives much higher percolated TPB density than that obtained from 2D analysis. In Figure 7-16, the time is normalised against the de-percolation time so that the simulation result can be compared (the de-percolation occurs at about 550 time steps in simulation whereas the experiment at 600 °C shows the de-percolation occurs at 22 min). The aTPB obtained from simulations show a fairly good match with experimental results. The E-

SEM result is consistent to the 2D analysis, due to the nature of the top-view hiding the actual TPBs. The aTPB calculated from electrochemical impedance data shows a reasonable match with 3D analysis result, except that the aTPB estimated from 3D analysis shows a narrower peak than the aTPB estimated from EIS. Such a difference mainly comes from four reasons: firstly, each impedance measurement takes 2 mins, which could provide a real-time degradation for a short period of time; the presence of any nickel nanoparticle and nano roughness are limited by observation resolution for the computational analysis, but counted for electrochemical performance; thirdly, due to the significant computation load, only a small area has been analysed, this simulation only provided a general analysis of the local nickel dewetting; lastly, in the impedance measurement, the isolated nickel particles could still provide the aTPB by in contact with Pt mesh current collector. While, in the both simulation and E-SEM observation, nickel isolation leads to de-percolation and aTPB reduction.

7.8 CHAPTER SUMMARY

In this chapter, the morphological and microstructural evolution of 40 nm thick nickel films on a YSZ substrate has been studied in-situ using E-SEM with humidified (3%) diluted hydrogen at 560 °C and 600 °C. The rate of dewetting is decrease with nickel thickness, and increases with temperature. The solid-state dewetting process is interpreted and discussed in terms of microstructure migration and statistical analysis. The dewetting of the nickel thin films originated from the YSZ grain boundaries, which may be due to the stress concentration. This suggests that bigger YSZ grains with minimized grain boundaries could potentially increase the initial nucleation point that is required for nickel solid-state dewetting. Two

models were developed and used to estimate the aTPB density changes to predict the nickel evolution in the overall cell. The dewetting process under two temperatures shows a consistent trend, including TPB density, nickel surface coverage and percolation ratio. The sufficient precision of rescaled relevant microstructural properties indicates that the dewetting and agglomeration phenomena proceed according to the same mechanisms, irrespective of temperature over the range 560-600 °C.

Impedance spectroscopy data has been also acquired under the same gas mixture operating condition at 600 °C. The EIS data was used to estimate aTPB density based on the electrochemical performance of the 2D symmetrical cell. The estimated aTPB density shows a good match with the morphological change confirmed by the image observation, as well as the aTPB densities calculated by two models.

The nickel dewetting simulation was developed for further studies, which considered thickness, wetting angle, dihedral angle, nickel surface diffusion, grain growth and temperature for a given operational gas mixture. It has been clearly identified that nickel dewetting is not driven by surface diffusion, nor by evaporation-condensation. Rather, the energetics of pore nucleation appears to be the most important energy barrier to trigger dewetting. This implies that reducing the number of nucleation points, for example by removing defects, dust and controlling the purity of materials, may significantly slow down the rate of dewetting. For the same experimental parameters, the dewetting time and nickel morphological change showed good correspondence between the simulation and E-SEM observation. By comparing the aTPB simulation results with experimental data, the 2D analysis shows consistent trend and results with E-SEM statistical analysis. Furthermore, by

adding the wetting angle to the simulation, a 3D analysis was established. This result shows a good match with aTPB values obtained from the cell electrochemical impedance.

Since the YSZ surface morphology, film preparation method, film thickness, operational atmosphere and temperature have significant influence on the dewetting process, a further study can focus on verifying different individual parameters, such as investigating the proper nickel particle size for lower dewetting rates at relatively high temperatures, different humidification, or hydrogen partial pressure. The novel technique of using the 2D cell could significantly simplify the SOFC material studies for other research work as well, including: material selection, redox cycling, catalyst poisoning, carbon deposition, etc.

CHAPTER 8 CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

Ni-YSZ has been considered as one of most reliable and cost-effective anode materials for SOFC applications. The motivation of the present research was to investigate the redox cycling impact on Ni-YSZ electrodes and nickel dewetting behaviour on YSZ substrates, in order to improve the material structure for more reliable performance. The results combine the evolution of electrochemical performance, microstructure and mechanical properties (elastic modulus and hardness) to demonstrate the material change under redox condition.

Firstly, the electrochemical and mechanical deterioration of Ni-YSZ anodes after up to 20 redox cycles was quantified by a combination of FIB-SEM tomography, impedance spectroscopy, nanoindentation and modelling. The fractures at the YSZ grain boundaries, Ni-YSZ detachment, continuous nickel agglomeration and increasing porosity after each redox cycle were observed, all of which lead to the mechanical properties deterioration and seem to be irreversible. The electrochemical degradation was measured by impedance spectroscopy and a physically-based model was used to infer the TPB length from the temporal evolution of the electrochemical reaction polarisation resistance, revealing a good match with TPB density obtained through FIB-SEM tomography. In particular, the model fits very well the initial, 5 redox and 10 redox samples, with a less satisfactory fit for higher redox cycles, attributed to changes in the effective conductivity of the composite caused by YSZ fractures and nickel agglomeration. It is also observed that the electrochemical reaction

polarisation resistance decreased temporarily by a factor ca. 2 upon each re-reduction, probably due to the transient generation of Ni nanoparticles around the TPB coming from the volume shrinkage from NiO to Ni. Although this causes a temporary decrease in electrochemical reaction polarisation resistance, after each redox cycle the degradation rate is even faster due to the promoted Ni agglomeration. This results in an overall increase in electrochemical reaction polarisation resistance by about an order of magnitude as a consequence of a reduction in active TPB density (from $4.63 \mu\text{m}^{-2}$ to $1.06 \mu\text{m}^{-2}$) and fragmentation of the YSZ network along its grain boundaries due to Ni expansion upon oxidation.

To try to improve the microstructure to resist redox cycling and prevent YSZ damage, Ni infiltrated YSZ scaffolds were studied. It has been found that, at sintering temperatures below 1200°C , YSZ tends to form rather small grains, with poor YSZ grain connectivity important for ionic conductivity and mechanical stability. In the samples sintered above 1200°C , the YSZ grains were very well connected, and grain size increased with higher sintering temperature, resulting in improved mechanical properties as high as 136.5 GPa and 7.95 GPa for elastic modulus and hardness, respectively. But the high sintering temperature also resulted in a loss of porosity and reduced pore size; this could lead to difficulty in Ni infiltration and gas phase diffusion.

The electrochemical and mechanical deterioration of Ni infiltrated YSZ scaffolds after up to 15 redox cycles was determined by a combination of SEM, impedance spectroscopy, nanoindentation and FIB-SEM. It has been found that after 15 redox cycles the YSZ scaffold retained its structure well, since improved mechanical properties prevent the YSZ break down

against Ni volume expansion during the oxidation cycle. This stable YSZ framework effectively maintained considerable numbers of aTPB, that otherwise could lose effective ionic conductivity if there were YSZ framework damage. The infiltrated Ni-YSZ scaffold has a better initial performance and stable performance, with lower Ni content (25 wt%) and a lower operational temperature, compared with conventional Ni-YSZ (40 wt%) sintered under the same condition but operated at a higher temperature.

However, as in conventional Ni-YSZ anodes, nickel agglomeration still cannot be minimized within Ni-YSZ scaffolds, leading to nickel migration from the electrode to the top surface, and resulting in a significant loss of nickel content within electrodes. As this could not be prevented, a multi-porosity layered electrode has been designed to try to trap the nickel within the interface of the fibres and the scaffold.

Under the compliant fibre layer, the mechanically strong YSZ scaffold layer provides not only an extremely high surface area for the electrochemical reaction but also a stable structure to resist degradation induced by redox cycling. It has been identified that, the high electrochemical performance at the low temperature is mainly contributed by the scaffold layer of the cell, as compared with Ni-YSZ Scaffold. This low operational temperature enables slower cell degradation during both isothermal ageing and redox cycling processes. The horizontal single direction YSZ fibre structure effectively limits the nickel agglomeration pathway within the fibre layer. This may help stabilise the electrochemical performance (electrochemical reaction polarisation resistance) in the longer term. At the same time, the highly porous YSZ fibre layer, on top of the scaffold, provides compliant contact with the

current collector. This application improved the ohmic resistance stability as attested by impedance measurements.

Apart from the electrode redox cycling study, additional work has been focused on the nickel wetting properties between Ni and YSZ. E-SEM observations revealed that film dewetting originated from pre-existing film cracks at the YSZ grain boundaries. Microstructural evolution occurred only within connected Ni clusters, no mass transport was observed among isolated Ni particles. Additional pore nucleation in the bulk of Ni film took place only at a late stage. The high energy barrier of pore nucleation was confirmed by cellular automata simulations, which revealed that neither surface diffusion nor evaporation-condensation mechanisms were compatible with the observed film evolution. On the contrary, the energetics of pore nucleation represents the dominant energy barrier, with an apparent activation energy of 2.1 eV.

The analysis of the active triple phase boundary density revealed that 2D images underestimate the real aTPB. Nevertheless, 2D image analysis showed that aTPB density initially increased and then dropped as soon as the Ni coverage ratio approached 0.63, which identified the start of the de-percolation stage. Both the peak and the abrupt drop in aTPB density were satisfactorily correlated to the impedance response, linking the microstructural evolution to the electrochemical degradation of 2D Ni-YSZ electrodes.

8.2 Future Work

The experiments revealed that redox cycling impacts in different ways on different forms of Ni-YSZ electrodes, and that the electrochemical performance and mechanical properties of the Ni-

YSZ electrode can be improved through microstructural design. Therefore, the nickel agglomeration behaviours under multi-porosity electrodes and data found in this study must be further explored and interpreted.

The introduction of the 2D Ni on YSZ electrodes offers a promising new methodology to study nickel behaviour on YSZ under operational conditions. The quantitative link between microstructural evolution and electrochemical response enables prediction of electrochemical degradation via in-situ microstructural observation and, vice versa, the investigation of microstructural evolution phenomena through EIS. From a technological perspective, as pore nucleation represents the most important energy barrier of dewetting, reducing the number of nucleation points by removing defects and dust, controlling the purity and surface properties of materials, or by increasing the YSZ grain size, may significantly slow down the dewetting rate. While all these points require specific individual studies, the proposed methodology provides a platform to investigate other phenomena, such as redox cycling, poisoning and carbon deposition in simplified and controlled conditions, thus supporting material and technological research.

LIST OF PUBLICATIONS

Journal Papers

1. **Song, B.***, Ruiz-Trejo, E., Bertei, A. & Brandon, N. P. Quantification of the degradation of Ni-YSZ anodes upon redox cycling. *J. Power Sources* 374, 61–68 (2018)
2. Liu X, Naylor Marlow M, Cooper S, **Song B**, Chen X, Brandon NP, Wu B*, Flexible all-fiber electrospun supercapacitor, *Journal of Power Sources*, ISSN:0378-7753
3. **Song B.***, Ruiz-Trejo E., Brandon N. P., Enhanced mechanical stability of Ni-YSZ scaffold demonstrated by nanoindentation and Electrochemical Impedance Spectroscopy, *Journal of Power Sources*, 395C (2018) pp. 205-211, ISSN:0378-7753
4. **Song B.**, Bertei A.* , Wang X., Cooper S.J., Ruiz-Trejo E., Chowdhury R., Podor R., Brandon N. P., Unveiling the mechanisms of solid-state dewetting in Solid Oxide Fuel Cells with novel 2D Ni-YSZ electrodes, under 2nd review
5. **Song B.***, Tariq F., Ruiz-Trejo E., Liu X., Yufit V., Chen X., Stevenson G. R., Brandon N. P., Novel Nickel Impregnated Yttria-stabilized Zirconia Fibre Electrodes for Performance Stabilization, submitted

Conference Presentations

1. *Presented at The Hydrogen & Fuel Cell Researcher Conference (Supergen),
14-16th Dec 2015, University of Bath, UK. (Poster)*
2. *Presented at 12th European SOFC and SOE Forum 2016,
1-4th July 2016, Lucerne, Switzerland. (Poster)*
3. *Presented at The Hydrogen & Fuel Cell Researcher Conference (Supergen),
14-16th Dec 2016, Ulster University, UK. (Poster)*
4. *Presented at The Hydrogen & Fuel Cell Researcher Conference (Supergen),
11-13th Dec 2017, University of St. Andrews, UK. (Oral)*
5. *Presented at The 3rd International Conference on New Energy and Future Energy System,
21-24th August 2018, Shanghai, China. (Oral) **Awarded for best presentation in Energy
Storage Material Session***

REFERENCES

1. Morris, C. & Pehnt, M. *Energy Transition Outlook 2017*. [Http://Energytransition.De/](http://Energytransition.De/) (DNV.GL, 2017).
2. US Department of Energy. Fuel Cells. *US Department of Energy* Available at: <https://www.energy.gov/eere/fuelcells/fuel-cells>. (Accessed: 23rd July 2018)
3. UNFCCC. KP Introduction. *United Nations* Available at: <https://unfccc.int/process/the-kyoto-protocol>. (Accessed: 23rd July 2018)
4. Mench, M. M. *Fuel cell engines*. (John Wiley & Sons, 2008).
5. Baur, E. & Preis, H. Über Brennstoff-Ketten mit Festleitern. *Berichte der Bunsengesellschaft für Phys. Chemie* **43**, 727–732 (1937).
6. Davtyan, O. K. Direct conversion of chemical energy of fuel into electrical energy. *Br. Electr. Allied Ind. Res. Assoc.* (1949).
7. Jiang, S. P. & Chan, S. H. A review of anode materials development in solid oxide fuel cells. *J. Mater. Sci.* **39**, 4405–4439 (2004).
8. Brandon, N. P., Skinner, S. & Steele, B. C. H. Recent Advances in Materials for Fuel Cells. *Annu. Rev. Mater. Res.* **33**, 183–213 (2003).
9. McIntosh, S. & Gorte, R. J. Direct Hydrocarbon Solid Oxide Fuel Cells. *Chem. Rev.* **104**, 4845–4866 (2004).
10. Solid Oxide Fuel Cells: Technologies and Global Markets. Available at:

<http://www.prnewswire.com/news-releases/solid-oxide-fuel-cells-technologies-and-global-markets-300296479.html>.

11. Basu, S. *Recent Trends in Fuel Cell Science and Technology*. (Springer-Verlag New York, 2007). doi:10.1007/978-0-387-68815-2
12. EG&G Technical Services, I. *Fuel Cell Handbook (Seventh Edition)*. (2004). doi:Under Contract No. DE-AM26-99FT40575
13. Irvine, J. T. S. *et al.* Evolution of the electrochemical interface in high-temperature fuel cells and electrolyzers. *Nat. Energy* **1**, 15014 (2016).
14. Liu, B., Zhang, Y., Tu, B., Dong, Y. & Cheng, M. Electrochemical impedance investigation of the redox behaviour of a Ni–YSZ anode. *J. Power Sources* **165**, 114–119 (2007).
15. Fergus, J. W. Oxide anode materials for solid oxide fuel cells. *Solid State Ionics* **177**, 1529–1541 (2006).
16. Cassidy, M., Lindsay, G. & Kendall, K. The reduction of nickel/zirconia cermet anodes and the effects on supported thin electrolytes. *J. Power Sources* **61**, 189–192 (1996).
17. Singhal, S. Advances in solid oxide fuel cell technology. *Solid State Ionics* **135**, 305–313 (2000).
18. Sakurambo. Diagram of a solid oxide fuel cell. (17000). Available at: https://commons.wikimedia.org/wiki/File:Solid_oxide_fuel_cell.svg. (Accessed: 5th July 2018)
19. Bi, L., Da'as, E. H. & Shafi, S. P. Proton-conducting solid oxide fuel cell (SOFC) with Y-

- doped BaZrO₃ electrolyte. *Electrochem. commun.* **80**, 20–23 (2017).
20. da Silva, F. S. & de Souza, T. M. Novel materials for solid oxide fuel cell technologies: A literature review. *Int. J. Hydrogen Energy* **42**, 26020–26036 (2017).
 21. Ivers-Tiffée, E., Weber, A. & Herbstritt, D. Materials and technologies for SOFC-components. *J. Eur. Ceram. Soc.* **21**, 1805–1811 (2001).
 22. Tao, S. & Irvine, J. T. S. Discovery and characterization of novel oxide anodes for solid oxide fuel cells. *Chem. Rec.* **4**, 83–95 (2004).
 23. Liu, J., Madsen, B. D., Ji, Z. & Barnett, S. A. A Fuel-Flexible Ceramic-Based Anode for Solid Oxide Fuel Cells. *Electrochem. Solid-State Lett.* **5**, A122 (2002).
 24. Mogensen, M. & Kammer, K. Conversion of Hydrocarbons in Solid Oxide Fuel Cells. *Annu. Rev. Mater. Res.* **33**, 321–331 (2003).
 25. Kim, H., Lu, C., Worrell, W. L., Vohs, J. M. & Gorte, R. J. Cu-Ni Cermet Anodes for Direct Oxidation of Methane in Solid-Oxide Fuel Cells. *J. Electrochem. Soc.* **149**, A247 (2002).
 26. Zhu, W. . & Deevi, S. . A review on the status of anode materials for solid oxide fuel cells. *Mater. Sci. Eng. A* **362**, 228–239 (2003).
 27. Sarantaridis, D. & Atkinson, A. Redox cycling of Ni-based solid oxide fuel cell anodes: A review. *Fuel Cells* **7**, 246–258 (2007).
 28. Hibino, T. *et al.* High Performance Anodes for SOFCs Operating in Methane-Air Mixture at Reduced Temperatures. *J. Electrochem. Soc.* **149**, A133 (2002).
 29. Steele, B. C. H. Appraisal of Ce_{1-y}Gd_yO_{2-y/2} electrolytes for IT-SOFC operation at

- 500°C. *Solid State Ionics* **129**, 95–110 (2000).
30. Singhal, S. C. & Kendall, K. *High-temperature solid oxide fuel cells : fundamentals, design, and applicatons*. (Elsevier Advanced Technology, 2003).
 31. Fabbri, E. *et al.* Design and fabrication of a chemically-stable proton conductor bilayer electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs). *Energy Environ. Sci.* **1**, 355 (2008).
 32. Chen, J. *et al.* Characterization of Degradation in Nickel Impregnated Scandia-Stabilize Zirconia Electrodes during Isothermal Annealing. *J. Electrochem. Soc.* **164**, F935–F943 (2017).
 33. Vohs, J. M. & Gorte, R. J. High-Performance SOFC Cathodes Prepared by Infiltration. *Adv. Mater.* **21**, 943–956 (2009).
 34. Enrico, A. *et al.* La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} nanofiber cathode for intermediate-temperature solid oxide fuel cells by water-based sol-gel electrospinning: Synthesis and electrochemical behaviour. *J. Eur. Ceram. Soc.* **38**, 2677–2686 (2018).
 35. Fleig, J. Solid Oxide Fuel Cell Cathodes: Polarization Mechanisms and Modeling of the Electrochemical Performance. *Annu. Rev. Mater. Res.* **33**, 361–382 (2003).
 36. Tarancón, A. *et al.* GdBaCo₂O_{5+x} layered perovskite as an intermediate temperature solid oxide fuel cell cathode. *J. Power Sources* **174**, 255–263 (2007).
 37. Shao, Z. & Haile, S. M. in *Materials for Sustainable Energy* 255–258 (Co-Published with Macmillan Publishers Ltd, UK, 2010). doi:10.1142/9789814317665_0036

38. Malzbender, J. & Steinbrech, R. W. Advanced measurement techniques to characterize thermo-mechanical aspects of solid oxide fuel cells. *J. Power Sources* **173**, 60–67 (2007).
39. Milewski, J. & Lewandowski, J. Analysis of Design and Construction of Solid Oxide Fuel Cell in Terms of their Dynamic Operation. *Arch. Combustionis* **30**, 145–154 (2010).
40. Minh, N. Q. Solid oxide fuel cell technology—features and applications. *Solid State Ionics* **174**, 271–277 (2004).
41. Mahata, T., Nair, S. R., Lenka, R. K. & Sinha, P. K. Fabrication of Ni-YSZ anode supported tubular SOFC through iso-pressing and co-firing route. *Int. J. Hydrogen Energy* **37**, 3874–3882 (2012).
42. Electrochemical Society., D., Choi, B. & Tsutsumi, A. *Journal of the Electrochemical Society*. (Electrochemical Society, 1948).
43. Panthi, D. & Tsutsumi, A. Micro-tubular solid oxide fuel cell based on a porous yttria-stabilized zirconia support. *Sci. Rep.* **4**, 5754 (2015).
44. Sammes, N. M., Du, Y. & Bove, R. Design and fabrication of a 100W anode supported micro-tubular SOFC stack. *J. Power Sources* **145**, 428–434 (2005).
45. Wilson, J. R. *et al.* Three-dimensional reconstruction of a solid-oxide fuel-cell anode. *Nat. Mater.* **5**, 541–4 (2006).
46. Faes, A., Hessler-Wyser, A., Presvytes, D., Vayenas, C. G. & Van herle, J. Nickel-Zirconia Anode Degradation and Triple Phase Boundary Quantification from Microstructural Analysis. *Fuel Cells* **9**, 841–851 (2009).

47. Tanasini, P. *et al.* Experimental and Theoretical Investigation of Degradation Mechanisms by Particle Coarsening in SOFC Electrodes. *Fuel Cells* **9**, 740–752 (2009).
48. Zhu, W., Ding, D. & Xia, C. Enhancement in Three-Phase Boundary of SOFC Electrodes by an Ion Impregnation Method: A Modeling Comparison. *Electrochem. Solid-State Lett.* **11**, B83 (2008).
49. Heenan, T. M. M. *et al.* Three-Phase Segmentation of Solid Oxide Fuel Cell Anode Materials Using Lab Based X-ray Nano-Computed Tomography. *Fuel Cells* **17**, 75–82 (2017).
50. Bertei, A. *et al.* Validation of a physically-based solid oxide fuel cell anode model combining 3D tomography and impedance spectroscopy. *Int. J. Hydrogen Energy* **41**, 22381–22393 (2016).
51. Faes, A. *et al.* RedOx study of anode-supported solid oxide fuel cell. *J. Power Sources* **193**, 55–64 (2009).
52. Hanasaki, M. *et al.* SOFC Durability against Standby and Shutdown Cycling. *J. Electrochem. Soc.* **161**, 850–860 (2014).
53. Tao, S. & Irvine, J. T. S. A redox-stable efficient anode for solid-oxide fuel cells. *Nat. Mater.* **2**, 320–3 (2003).
54. Laurencin, J., Delette, G., Sicardy, O., Rosini, S. & Lefebvre-Joud, F. Impact of ‘redox’ cycles on performances of solid oxide fuel cells: Case of the electrolyte supported cells. *J. Power Sources* **195**, 2747–2753 (2010).
55. Brus, G., Miyoshi, K., Iwai, H., Saito, M. & Yoshida, H. Change of an anode’s

- microstructure morphology during the fuel starvation of an anode-supported solid oxide fuel cell. *Int. J. Hydrogen Energy* **40**, 6927–6934 (2015).
56. Chen, J., Ruiz-Trejo, E., Atkinson, A. & Brandon, N. P. Microstructural and Electrochemical Characterisation of Degradation in Nickel Impregnated Scandia-Stabilised Zirconia Electrode during Isothermal Annealing. *ECS Trans.* **78**, 1125–1137 (2017).
57. Pihlatie, M. H., Kaiser, A., Mogensen, M. & Chen, M. Electrical conductivity of Ni–YSZ composites: Degradation due to Ni particle growth. *Solid State Ionics* **189**, 82–90 (2011).
58. WALDBILLIG, D., WOOD, A. & IVEY, D. Thermal analysis of the cyclic reduction and oxidation behaviour of SOFC anodes. *Solid State Ionics* **176**, 847–859 (2005).
59. Khan, M. S. *et al.* Fundamental mechanisms involved in the degradation of nickel-yttria stabilized zirconia (Ni-YSZ) anode during solid oxide fuel cells operation: A review. *Ceram. Int.* (2015). doi:10.1016/j.ceramint.2015.09.006
60. Vaßen, R., Simwonis, D. & Stöver, D. Modelling of the agglomeration of Ni-particles in anodes of solid oxide fuel cells. *J. Mater. Sci.* **36**, 147–151 (2001).
61. Ruiz-Trejo, E., Atkinson, A. & Brandon, N. P. Metallizing porous scaffolds as an alternative fabrication method for solid oxide fuel cell anodes. *J. Power Sources* **280**, 81–89 (2015).
62. Jiang, S. P. A review of wet impregnation—An alternative method for the fabrication of high performance and nano-structured electrodes of solid oxide fuel cells. *Mater. Sci. Eng. A* **418**, 199–210 (2006).

63. Liu, Z. *et al.* Fabrication and modification of solid oxide fuel cell anodes via wet impregnation/infiltration technique. *J. Power Sources* **237**, 243–259 (2013).
64. Gorte, R. J. & Vohs, J. M. Nanostructured anodes for solid oxide fuel cells. *Curr. Opin. Colloid Interface Sci.* **14**, 236–244 (2009).
65. Joong Yoon, K. *et al.* Nano-tailoring of infiltrated catalysts for high-temperature solid oxide regenerative fuel cells. *Nano Energy* **36**, 9–20 (2017).
66. Klemensø, T., Thydén, K., Chen, M. & Wang, H.-J. Stability of Ni–yttria stabilized zirconia anodes based on Ni-impregnation. *J. Power Sources* **195**, 7295–7301 (2010).
67. Keyvanfar, P. & Birss, V. Optimization of Infiltration Techniques Used to Construct Ni/YSZ Anodes. *J. Electrochem. Soc.* **161**, F660–F667 (2014).
68. Keyvanfar, P., Hanifi, A. R., Sarkar, P., Etsell, T. H. & Birss, V. Enhancing the Stability of Infiltrated Ni/YSZ Anodes. *ECS Trans.* **68**, 1255–1263 (2015).
69. Bertei, A. *et al.* The fractal nature of the three-phase boundary: A heuristic approach to the degradation of nanostructured solid oxide fuel cell anodes. *Nano Energy* **38**, 526–536 (2017).
70. Niekel, F., Schweizer, P., Kraschewski, S. M., Butz, B. & Spiecker, E. The process of solid-state dewetting of Au thin films studied by in situ scanning transmission electron microscopy. *Acta Mater.* **90**, 118–132 (2015).
71. Thompson, C. V. Solid-State Dewetting of Thin Films. *Annu. Rev. Mater. Res* **42**, 399–434 (2012).

72. Amram, D., Klinger, L., Gazit, N., Gluska, H. & Rabkin, E. Grain boundary grooving in thin films revisited: The role of interface diffusion. *Acta Mater.* **69**, 386–396 (2014).
73. Simrick, N. J., Kilner, J. A. & Atkinson, A. Thermal stability of silver thin films on zirconia substrates. *Thin Solid Films* **520**, 2855–2867 (2012).
74. Wu, Y., Fowlkes, J. D. & Rack, P. D. The optical properties of Cu-Ni nanoparticles produced via pulsed laser dewetting of ultrathin films: The effect of nanoparticle size and composition on the plasmon response. *J. Mater. Res.* **26**, 277–287 (2011).
75. Randolph, S. J. *et al.* Controlling thin film structure for the dewetting of catalyst nanoparticle arrays for subsequent carbon nanofiber growth. *Nanotechnology* **18**, 465304 (2007).
76. Geissler, A., He, M., Benoit, J.-M. & Petit, P. Effect of Hydrogen Pressure on the Size of Nickel Nanoparticles Formed during Dewetting and Reduction of Thin Nickel Films. *J. Phys. Chem. C* **114**, 89–92 (2010).
77. Ye, J. & Thompson, C. V. Mechanisms of complex morphological evolution during solid-state dewetting of single-crystal nickel thin films. *Appl. Phys. Lett.* **97**, 071904 (2010).
78. Simrick, N. J., Kilner, J. A. & Atkinson, A. Thermal stability of silver thin films on zirconia substrates. *Thin Solid Films* **520**, 2855–2867 (2012).
79. Toghan, A., Khodari, M., Steinbach, F. & Imbihl, R. Microstructure of thin film platinum electrodes on yttrium stabilized zirconia prepared by sputter deposition. *Thin Solid Films* **519**, 8139–8143 (2011).
80. Galinski, H. *et al.* Agglomeration of Pt thin films on dielectric substrates. *Phys. Rev. B*

- 82**, 235415 (2010).
81. Kosinova, A., Kovalenko, O., Klinger, L. & Rabkin, E. Mechanisms of solid-state dewetting of thin Au films in different annealing atmospheres. *Acta Mater.* **83**, 91–101 (2015).
 82. Thydén, K. & Danmarks Tekniske Universitet. Risø DTU. *Microstructural degradation of Ni-YSZ anodes for solid oxide fuel cells*. (Risø National Laboratory for Sustainable Energy, Technical University of Denmark, 2008).
 83. Vaßen, R., Simwonis, D. & Stöver, D. Modelling of the agglomeration of Ni-particles in anodes of solid oxide fuel cells. *J. Mater. Sci.* **36**, 147–151 (2001).
 84. Simwonis, D., Tietz, F. & Stöver, D. Nickel coarsening in annealed Ni/8YSZ anode substrates for solid oxide fuel cells. *Solid State Ionics* **132**, 241–251 (2000).
 85. Shimura, T., Jiao, Z., Hara, S. & Shikazono, N. Quantitative analysis of solid oxide fuel cell anode microstructure change during redox cycles. *J. Power Sources* **267**, 58–68 (2014).
 86. Faes, A., Hessler-Wyser, A., Zryd, A. & Van herle, J. A Review of RedOx Cycling of Solid Oxide Fuel Cells Anode. *Membranes (Basel)*. **2**, 585–664 (2012).
 87. Weast, R. C. CRC Handbook of Chemistry and Physics. *Book E-93, F-4-F40* (1989). doi:10.5860/CHOICE.29-0016
 88. Atkinson, A. & Selçuk, A. Mechanical behaviour of ceramic oxygen ion-conducting membranes. *Solid State Ionics* **134**, 59–66 (2000).

89. Selçuk, A. & Atkinson, A. Strength and Toughness of Tape-Cast Yttria-Stabilized Zirconia. *J. Am. Ceram. Soc.* **83**, 2029–2035 (2004).
90. Atkinson, A., Kim, J.-S., Rudkin, R., Taub, S. & Wang, X. Stress Induced by Constrained Sintering of 3YSZ Films Measured by Substrate Creep. *J. Am. Ceram. Soc.* **94**, 717–724 (2011).
91. Morales, M., Roa, J. J., Capdevila, X. G., Segarra, M. & Piñol, S. Mechanical properties at the nanometer scale of GDC and YSZ used as electrolytes for solid oxide fuel cells. *Acta Mater.* **58**, 2504–2509 (2010).
92. Meixner, D. L. & Cutler, R. A. Sintering and mechanical characteristics of lanthanum strontium manganite. *Solid State Ionics* **146**, 273–284 (2002).
93. Gutierrez-Mora, F., Ralph, J. . & Routbort, J. . High-temperature mechanical properties of anode-supported bilayers. *Solid State Ionics* **149**, 177–184 (2002).
94. Yu, J. H., Park, G. W., Lee, S. & Woo, S. K. Microstructural effects on the electrical and mechanical properties of Ni–YSZ cermet for SOFC anode. *J. Power Sources* **163**, 926–932 (2007).
95. Radovic, M. & Lara-Curzio, E. Mechanical properties of tape cast nickel-based anode materials for solid oxide fuel cells before and after reduction in hydrogen. *Acta Mater.* **52**, 5747–5756 (2004).
96. Laurencin, J., Delette, G., Morel, B., Lefebvre-Joud, F. & Dupeux, M. Solid Oxide Fuel Cells damage mechanisms due to Ni-YSZ re-oxidation: Case of the Anode Supported Cell. *J. Power Sources* **192**, 344–352 (2009).

97. Pihlatie, M., Kaiser, A. & Mogensen, M. Mechanical properties of NiO/Ni-YSZ composites depending on temperature, porosity and redox cycling. *J. Eur. Ceram. Soc.* **29**, 1657–1664 (2009).
98. Selcuk, A. & Atkinson, A. Elastic Properties of Ceramic Oxides Used in Solid Oxide Fuel Cells (SOFC). *J. Eur. Ceram. Soc.* **17**, 1523–1532 (1997).
99. Radovic, M., Lara-Curzio, E. & Riester, L. Comparison of different experimental techniques for determination of elastic properties of solids. *Mater. Sci. Eng. A* **368**, 56–70 (2004).
100. Stone, D. S. *et al.* Hardness and elastic modulus of TiN based on continuous indentation technique and new correlation. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **9**, 2543–2547 (1991).
101. ANSTIS, G. R., CHANTIKUL, P., LAWN, B. R. & MARSHALL, D. B. A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: I, Direct Crack Measurements. *J. Am. Ceram. Soc.* **64**, 533–538 (1981).
102. Song, B., Ruiz-Trejo, E., Bertei, A. & Brandon, N. P. Quantification of the degradation of Ni-YSZ anodes upon redox cycling. *J. Power Sources* **374**, 61–68 (2018).
103. Chen, S. J., Duan, W. H., Li, Z. J. & Sui, T. B. New approach for characterisation of mechanical properties of cement paste at micrometre scale. *JMADE* **87**, 992–995 (2015).
104. Chen, Z., Wang, X., Atkinson, A. & Brandon, N. Spherical indentation of porous ceramics: Elasticity and hardness. *J. Eur. Ceram. Soc.* **36**, 1435–1445 (2016).

105. Clément, P., Meille, S., Chevalier, J. & Olagnon, C. Mechanical characterization of highly porous inorganic solids materials by instrumented micro-indentation. *Acta Mater.* **61**, 6649–6660 (2013).
106. Chen, Z., Wang, X., Giuliani, F. & Atkinson, A. Microstructural characteristics and elastic modulus of porous solids. *Acta Mater.* **89**, 268–277 (2015).
107. Oliver, W. C. & Pharr, G. M. Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. (2016). doi:10.1557/jmr.2004.19.1.3
108. Chen, Z. & Brandon, N. Inkjet printing and nanoindentation of porous alumina multilayers. *Ceram. Int.* **42**, 8316–8324 (2016).
109. Chen, Z., Wang, X., Bhakhri, V., Giuliani, F. & Atkinson, A. Nanoindentation of porous bulk and thin films of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$. *Acta Mater.* **61**, 5720–5734 (2013).
110. Fukui, T. *et al.* Morphology control of Ni-YSZ cermet anode for lower temperature operation of SOFCs. *J. Power Sources* **125**, 17–21 (2004).
111. Itoh, H. *et al.* Configurational and Electrical Behavior of Ni-YSZ Cermet with Novel Microstructure for Solid Oxide Fuel Cell Anodes. *J. Electrochem. Soc.* **144**, 641 (1997).
112. Tariq, F. *et al.* 3D imaging and quantification of interfaces in SOFC anodes. *J. Eur. Ceram. Soc.* **34**, 3755–3761 (2014).
113. Shearing, P. R., Golbert, J., Chater, R. J. & Brandon, N. P. 3D reconstruction of SOFC anodes using a focused ion beam lift-out technique. *Chem. Eng. Sci.* **64**, 3928–3933 (2009).

114. Shearing, P. R., Brett, D. J. L. & Brandon, N. P. Towards intelligent engineering of SOFC electrodes: a review of advanced microstructural characterisation techniques. *Int. Mater. Rev.* **55**, 347–363 (2010).
115. Wilson, J. R. *et al.* Three-dimensional reconstruction of a solid-oxide fuel-cell anode. *Nat. Mater.* **5**, 541–544 (2006).
116. Gostovic, D., Smith, J. R., Kundinger, D. P., Jones, K. S. & Wachsman, E. D. Three-Dimensional Reconstruction of Porous LSCF Cathodes. *Electrochem. Solid-State Lett.* **10**, B214 (2007).
117. Wilson, J. R. *et al.* Three-Dimensional Analysis of Solid Oxide Fuel Cell Ni-YSZ Anode Interconnectivity. *Microsc. Microanal.* **15**, 71–77 (2009).
118. Izzo, J. R. *et al.* Nondestructive Reconstruction and Analysis of SOFC Anodes Using X-ray Computed Tomography at Sub-50 nm Resolution. *J. Electrochem. Soc.* **155**, B504 (2008).
119. Wilson, J. R., Cronin, J. S. & Barnett, S. A. Linking the microstructure, performance and durability of Ni-yttria-stabilized zirconia solid oxide fuel cell anodes using three-dimensional focused ion beam–scanning electron microscopy imaging. *Scr. Mater.* **65**, 67–72 (2011).
120. Shearing, P. R. *et al.* Exploring microstructural changes associated with oxidation in Ni–YSZ SOFC electrodes using high resolution X-ray computed tomography. (2012). doi:10.1016/j.ssi.2011.10.015
121. Kubota, M., Okanishi, T., Muroyama, H., Matsui, T. & Eguchi, K. Microstructural

- Evolution of Ni-YSZ Cermet Anode under Thermal Cycles with Redox Treatments. *J. Electrochem. Soc.* **162**, F380–F386 (2015).
122. Pecho, O. *et al.* 3D Microstructure Effects in Ni-YSZ Anodes: Influence of TPB Lengths on the Electrochemical Performance. *Materials (Basel)*. **8**, 7129–7144 (2015).
 123. Schuh, C. A. Nanoindentation studies of materials. *Mater. Today* **9**, 32–40 (2006).
 124. Liu, X. *et al.* Flexible all-fiber electrospun supercapacitor. *J. Power Sources* **384**, 264–269 (2018).
 125. Kishimoto, M., Lomberg, M., Ruiz-Trejo, E. & Brandon, N. P. Enhanced triple-phase boundary density in infiltrated electrodes for solid oxide fuel cells demonstrated by high-resolution tomography. *J. Power Sources* **266**, 291–295 (2014).
 126. Zhou, Y. *et al.* Performance and degradation of metal-supported solid oxide fuel cells with impregnated electrodes. *Int. J. Hydrogen Energy* **39**, 2279–2285 (2014).
 127. Liu, Z. *et al.* Fabrication and modification of solid oxide fuel cell anodes via wet impregnation/infiltration technique. *J. Power Sources* **237**, 243–259 (2013).
 128. Lee, S., Kim, G., Vohs, J. M. & Gorte, R. J. SOFC Anodes Based on Infiltration of La_{0.3}Sr_{0.7}TiO₃. *J. Electrochem. Soc.* **155**, B1179 (2008).
 129. Podor, R., Pailhon, D., Ravoux, J. & Brau, H.-P. Development of an Integrated Thermocouple for the Accurate Sample Temperature Measurement During High Temperature Environmental Scanning Electron Microscopy (HT-ESEM) Experiments. *Microsc. Microanal.* **21**, 307–312 (2015).

130. Oliver, W. C. C. *et al.* An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* **7**, 1564–1583 (1992).
131. Gadag, S., Subbarayan, G. & Barker, W. Thermo-elastic properties of dense YSZ and porous Ni-ZrO₂ monolithic and isotropic materials. *J. Mater. Sci.* **41**, 1221–1232 (2006).
132. Sakharova, N. A. A., Fernandes, J. V. V., Antunes, J. M. M. & Oliveira, M. C. C. Comparison between Berkovich, Vickers and conical indentation tests: A three-dimensional numerical simulation study. *Int. J. Solids Struct.* **46**, 1095–1104 (2009).
133. Jiao, Z. & Shikazono, N. Simulation of the reduction process of solid oxide fuel cell composite anode based on phase field method. *J. Power Sources* **305**, 10–16 (2016).
134. Holzer, L. *et al.* Microstructure degradation of cermet anodes for solid oxide fuel cells: Quantification of nickel grain growth in dry and in humid atmospheres. *J. Power Sources* **196**, 1279–1294 (2011).
135. J. Chen, A. Bertei, E. Ruiz-Trejo, A. Atkinson, N. P. B. Characterisation of degradation in nickel impregnated scandia-stabilised zirconia electrodes during isothermal annealing. *J. Electrochem. Soc.* (in Press. doi:10.1149/2.0821709jes
136. Tariq, F. *et al.* Advanced 3D Imaging and Analysis of SOFC Electrodes. *ECS Trans.* **64**, 81–86 (2014).
137. Bertei, A., Mertens, J. & Nicolella, C. Electrochemical simulation of planar solid oxide fuel cells with detailed microstructural modeling. *Electrochim. Acta* **146**, 151–163 (2014).

138. Simwonis, D., Thülen, H., Dias, F. . J., Naoumidis, A. & Stöver, D. Properties of Ni/YSZ porous cermets for SOFC anode substrates prepared by tape casting and coat-mix® process. *J. Mater. Process. Technol.* **92–93**, 107–111 (1999).
139. Holzer, L. *et al.* Redox cycling of Ni–YSZ anodes for solid oxide fuel cells: Influence of tortuosity, constriction and percolation factors on the effective transport properties. *J. Power Sources* **242**, 179–194 (2013).
140. Cheng, Y.-T. & Cheng, C.-M. Scaling, dimensional analysis, and indentation measurements. *Mater. Sci. Eng. R Reports* **44**, 91–149 (2004).
141. Buyukaksoy, A., Kammampata, S. P. & Birss, V. I. Effect of porous YSZ scaffold microstructure on the long-term performance of infiltrated Ni-YSZ anodes. *J. Power Sources* **287**, 349–358 (2015).
142. Lee, J. H. *et al.* Quantitative analysis of microstructure and its related electrical property of SOFC anode, Ni-YSZ cermet. *Solid State Ionics* **148**, 15–26 (2002).
143. Atul Tiwari , Sridhar Natarajan. *Applied Nanoindentation in Advanced Materials*. (Wiley).
144. Suzuki, T. *et al.* Impact of anode microstructure on solid oxide fuel cells. *Science* **325**, 852–5 (2009).
145. Atkinson, A. *et al.* Advanced anodes for high-temperature fuel cells. *Nat. Mater.* **3**, 17–27 (2004).
146. Song, B., Ruiz-Trejo, E. & Brandon, N. P. Enhanced mechanical stability of Ni-YSZ

- scaffold demonstrated by nanoindentation and Electrochemical Impedance Spectroscopy. *J. Power Sources* **395**, 205–211 (2018).
147. Welander, M. M., Zachariasen, M. S., Hunt, C. D., Sofie, S. W. & Walker, R. A. Operando Studies of Redox Resilience in ALT Enhanced NiO-YSZ SOFC Anodes. *J. Electrochem. Soc.* **165**, F152–F157 (2018).
 148. Shri Prakash, B., Senthil Kumar, S. & Aruna, S. T. Properties and development of Ni/YSZ as an anode material in solid oxide fuel cell: A review. *Renew. Sustain. Energy Rev.* **36**, 149–179 (2014).
 149. Connor, P. A. *et al.* Tailoring SOFC Electrode Microstructures for Improved Performance. *Advanced Energy Mater.* **1800120**, 1–20 (2018).
 150. Inagaki, M., Yang, Y. & Kang, F. Carbon Nanofibers Prepared via Electrospinning. *Adv. Mater.* **24**, 2547–2566 (2012).
 151. Liu, K. *et al.* Electrospun core-shell microfiber separator with thermal-triggered flame-retardant properties for lithium-ion batteries. *Sci. Adv.* **3**, e1601978 (2017).
 152. Chen, L.-F., Lu, Y., Yu, L. & Lou, X. W. (David). Designed formation of hollow particle-based nitrogen-doped carbon nanofibers for high-performance supercapacitors. *Energy Environ. Sci.* **10**, 1777–1783 (2017).
 153. Zhang, L. & Hsieh, Y.-L. Carbon nanofibers with nanoporosity and hollow channels from binary polyacrylonitrile systems. *Eur. Polym. J.* **45**, 47–56 (2009).
 154. Yin, Y.-B., Xu, J.-J., Liu, Q.-C. & Zhang, X.-B. Macroporous Interconnected Hollow Carbon Nanofibers Inspired by Golden-Toad Eggs toward a Binder-Free, High-Rate, and Flexible

- Electrode. *Adv. Mater.* **28**, 7494–7500 (2016).
155. Enrico, A. *et al.* Parameter Optimization for the Electrospinning of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ Fibers for IT-SOFC Electrodes. *Fuel Cells* **17**, 415–422 (2017).
 156. Enrico, A., Aliakbarian, B., Perego, P. & Costamagna, P. Micro-Modelling of IT-SOFC Electrodes Manufactured through Electrospinning. *ECS Trans.* **68**, 857–865 (2015).
 157. Lee, J. G., Park, J. H. & Shul, Y. G. Tailoring gadolinium-doped ceria-based solid oxide fuel cells to achieve 2 W cm^{-2} at 550°C . *Nat. Commun.* **5**, 4045 (2014).
 158. Castkova, K., Maca, K., Sekaninova, J., Nemcovsky, J. & Cihlar, J. Electrospinning and thermal treatment of yttria doped zirconia fibres. *Ceram. Int.* **43**, 7581–7587 (2017).
 159. Mogensen, M. B. *et al.* Relation Between Ni Particle Shape Change and Ni Migration in Ni-YSZ Electrodes - a Hypothesis. *Fuel Cells* **17**, 434–441 (2017).
 160. Jeangros, Q. *et al.* In situ redox cycle of a nickel–YSZ fuel cell anode in an environmental transmission electron microscope. *Acta Mater.* **58**, 4578–4589 (2010).
 161. Waldbillig, D., Wood, A. & Ivey, D. G. Thermal analysis of the cyclic reduction and oxidation behaviour of SOFC anodes. *Solid State Ionics* **176**, 847–859 (2005).
 162. Shearing, P. R. *et al.* Exploring microstructural changes associated with oxidation in Ni–YSZ SOFC electrodes using high resolution X-ray computed tomography. *Solid State Ionics* **216**, 69–72 (2012).
 163. Liu, B., Zhang, Y., Tu, B., Dong, Y. & Cheng, M. Electrochemical impedance investigation of the redox behaviour of a Ni–YSZ anode. *J. Power Sources* **165**, 114–119 (2007).

164. Tao, S. & Irvine, J. T. S. A redox-stable efficient anode for solid-oxide fuel cells. *Nat. Mater.* **2**, 320–3 (2003).
165. Atiya, G., Chatain, D., Mikhelashvili, V., Eisenstein, G. & Kaplan, W. D. The role of abnormal grain growth on solid-state dewetting kinetics. *Acta Mater.* **81**, 304–314 (2014).
166. Kosinova, A., Klinger, L., Kovalenko, O. & Rabkin, E. The role of grain boundary sliding in solid-state dewetting of thin polycrystalline films. *Scr. Mater.* **82**, 33–36 (2014).
167. Mutoro, E., Günther, S., Luerßen, B., Valov, I. & Janek, J. Electrode activation and degradation: Morphology changes of platinum electrodes on YSZ during electrochemical polarisation. *Solid State Ionics* **179**, 1835–1848 (2008).
168. Utz, A., Störmer, H., Gerthsen, D., Weber, A. & Ivers-Tiffée, E. Microstructure stability studies of Ni patterned anodes for SOFC. *Solid State Ionics* **192**, 565–570 (2011).
169. Gao, H. Stress concentration at slightly undulating surfaces. *J. Mech. Phys. Solids* **39**, 443–458 (1991).
170. Jiao, Z. & Shikazono, N. Study on the effects of polarization on local morphological change of nickel at active three-phase-boundary using patterned nickel-film electrode in solid oxide fuel cell anode. *Acta Mater.* **135**, 124–131 (2017).
171. Kovalenko, O., Greer, J. R. & Rabkin, E. Solid-state dewetting of thin iron films on sapphire substrates controlled by grain boundary diffusion. *Acta Mater.* **61**, 3148–3156 (2013).

