# MICROSTRUCTURE CHANGES IN SOLID OXIDE FUEL CELL ANODES AFTER OPERATION, OBSERVED USING THREE-DIMENSIONAL RECONSTRUCTION AND MICROCHEMICAL ANALYSIS

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Dedicated to my parents, Amita and Rajendra Parikh and to my wife, Ankur Parikh

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# Microstructure Changes In Solid Oxide Fuel Cell Anodes After Operation, Observed Using Three-Dimensional Reconstruction And Microchemical Analysis

#### Abstract

by

### HARSHIL PARIKH

Solid oxide fuel cells (SOFCs) have great importance as a more efficient source of electrical power than conventional systems. Nonetheless, there is limited understanding of the processes by which their performance decreases with time, especially during long-term operation (>2 kh). This study sought explanations for performance loss in the microstructural changes that take place in the anodes during operation of periods from 2 to 16 kh.

Recently developed three-dimensional (3D) analysis techniques enable the study of aspects of the anode microstructure, such as tortuosity and triple-phase boundary density, that cannot be fully depicted in two-dimensional analyses. The complex multi-phase microstructure of SOFC anodes adds other challenges for applying this technique to study lifetime degradation of SOFCs.

The project is divided into four sections:

 sample preparation and experimentation, including adaptations of standard techniques to the porous microstructures of SOFC anodes;

- 3D reconstruction and results, including development of original computer codes for the determination of active and inactive triple phase boundary density;
- microstructural characterization of anodes tested for up to 16 kh at 800 °C, 860°C or 925 °C, including qualitative analysis of chemical composition of the anodes using energy dispersive x-ray spectroscopy (EDS);
- development of kinetic models of microstructural change in SOFCs during operation, based on the quantitative analysis and calculated microstructure parameters for the tested SOFC anodes, to enable predictions of long-term performance of SOFCs.

Application of 3D reconstruction to SOFC anodes provided insight to the anode microstructure. The microstructural parameters such as volume fractions, particle diameter, active/inactive triple phase boundary, tortuosity; were calculated for the as-reduced cell and cells after operations. Ni and pore phase re-distribution to the anode interfaces were observed during cell operation. The classic relaxation kinetic model was developed to study the long-term Ni growth and reduction in triple phase boundary.

## **Chapter 1: Introduction**

Energy plays a crucial role in sustaining life on earth. Since the middle of the nineteenth century, mankind has depended increasingly on energy from fossil fuels for electricity, transportation, heat etc. In 2012, the total annual energy consumption in USA was 95.0 Quadrillion BTU [1]. The fossil fuels account for 80% of U.S. energy consumption (Fig. 1.1). This demand depletes fossil fuels faster than the geological processes that produce fossil fuels can replace them. With the current rate of consumption, according to some predictions, fossil fuels will not be available in few decades. In addition, their consumption produces greenhouse gases which are detrimental to the environment.



Figure 1.1: Energy Consumption by various sources in US in 2012 [1].

Renewable energy sources are the sources which could be replenished continuously. Traditionally, renewable energy forms are solar, wind, hydro, biomass, geothermal, etc. Fuel cells are not to be a renewable energy technology, but the fuels for them are abundant in nature and could provide power to mankind for prolonged period of time. They are capable of generating electricity with greater efficiencies, and therefore lower emissions, than conventional fossil-fuel-based technologies. Furthermore, unlike traditional renewable energy sources, fuel cell could provide power anytime at the point of use without any constraints.

Of all advanced energy technologies, fuel cells have shown potential as an alternate energy source since Grove demonstrated feasibility of the concept in 1839 [2]. In fact, the fuel cell was invented before the internal combustion engine. By the end of the 19<sup>th</sup> century, the internal combustion engine was invented and the fuel cell was relegated to the status of scientific curiosity. Since its first practical application in the Apollo lunar mission in 1962 for onboard power and drinking water, interest in fuel cells was revived. Other types of fuel cells were explored to overcome some of the challenges for a variety of applications. The timeline for their development is summarized in Fig. 1.2. Unfortunately, none of these fuel cells have achieved commercial success on any major scale.



*Figure 1.2: Development history of fuel cells. SOFC and PEMFC have high potential for large-scale commercialization.* 

Among all types of fuel cells, solid oxide fuel cells (SOFCs) are the most flexible in terms of fuel requirements. SOFCs could be operated with hydrogen, natural gas, carbon monoxides, methanol etc. SOFC converts the chemical energy of the fuel into electrical energy without an intermediate thermal-to-mechanical conversion. So, SOFCs offer intrinsically high efficiency of producing electrical power. Depending on the power rating and stack configuration, the net AC electrical efficiency of the SOFCs varies from 45% - 60% [3]. When combined with the waste-heat recovery cycle, the overall energy conversion efficiency of SOFC systems could reach up to 90% [3]. Very high overall efficiency is one of the prime reasons for the recent research interest in SOFC.

To achieve the long-term goal of clean energy, department of energy (DOE) has started the Solid-State Energy Conversion Alliance (SECA). One of the objectives of the SECA program is to develop cost-effective, high efficiency SOFCs for residential and commercial applications. The SECA program wants to achieve a cost target of \$140/kW for SOFC stacks (Fig. 1.3) [4]. Additionally, the SECA program has also set a stringent goal of SOFC degradation (power loss) of 0.2%/1000 h of operation for up to 40 kh [5].



Figure 1.3: Reduction in cost of power under SECA program. SECA program has set a cost target of \$140/kW for SOFC stack [4].

The SECA program is partnering with commercial industries, national laboratories and universities to achieve commercial success of SOFCs. One of the industrial partners in SECA program is LG Fuel Cell Systems Inc. (formerly Rolls Royce Fuel Cell Systems). LG fabricated and tested the cells described here, and provided them to Case Western Reserve University for characterization of the microstructure of the electrodes and electrolyte. The focus of the research presented here is the anode.

## **Chapter 2: Background and Literature Review**

#### 2.1 SOFC construction and operation

A fuel cell is an energy conversion device that converts the chemical energy of combustion of a fuel directly to electrical energy and heat. Solid oxide fuel cells (SOFCs) still have to overcome challenges for their long-term performance. Researchers around the world focus on optimization of material selection and processing for both the electrodes and electrolyte to improve the long-term performance of SOFCs.

SOFCs are categorized into two configurations: tubular and planar. Planar SOFC designs can have either a radial configuration or a flat-plate configuration. In this project, the hybrid SOFC design of LG SOFC (formerly Rolls Royce SOFC), which combines elements of tubular and planar designs, is studied. Fig. 2.1 illustrates a simplified version of the LG design [6]. Typically, SOFCs are stacked in series (Fig 2.2) to generate enough power for practical applications



Figure 2.1: Schematic of LG (formerly Rolls Royce) SOFC stack [6]



Figure 2.2: The LGFCS process of forming a stack block of SOFC from the printed tube

Fig. 2.3 shows the operating principle of a SOFC. SOFCs are operated typically at 800 - 1000 °C. Oxygen (usually from air) is carried to the cathode where it dissociates, and picks up electrons from the external circuit to generate O<sup>2-</sup> anions. The O<sup>2-</sup> generated at the cathode migrates through the ceramic electrolyte and reaches the anode. In LG fuel cells, which use reformed methane as the fuel, hydrogen and carbon monoxide at the anode are oxidized by O<sup>2-</sup> and generate H<sub>2</sub>O, CO<sub>2</sub>, and electrons. Flow of electrons through the outer electric circuit provides electrical energy.

The active layers of the LG SOFC are supported on a flat ceramic composite substrate of magnesia and magnesium aluminate (MMA) that contains channels for flow of fuel. A zirconia-based porous anode barrier (PAB) layer is deposited on the substrate. In the LG design the anode (the focus of this research) is the thinnest layer ( $\sim 8 \mu m$ ) and is

a porous composite of Ni and yttria-stabilized zirconia (YSZ). The anode is sandwiched between the electrolyte and the anode current collector (ACC, on top of the PAB). The cathode and the cathode current collector (CCC) are the outermost layers of the cell. The combined thickness of both of these layers is about 100 µm.



Overall reaction:  $2H_2 + O_2 \rightarrow 2H_2O$ 

Possible reforming reactions:  $CH_4 + H_2O \rightarrow 3H_2 + CO$  $CO + H_2O \rightarrow H_2 + CO_2$ 

Figure 2.3: Schematic of the operating principle of SOFC [7]. In certain SOFC designs, the reforming reactions could take place prior to fuel entering the anode. Alternatively, the reforming reaction could happen in the anode.

SOFC Layer	Phases	Typlical Thickness (µm)
Cathode and CCC	La-Mn-Sr-O; YSZ; Porosity	100
Electrolyte	3YSZ	10-15
Anode	Ni; YSZ; Porosity	8
ACC	Ni-Pd; Porosity; Mg-Ni-Al-O spinel	12
PAB	YSZ; Porosity	20
MMA	MgO; Mg-Al-O spinel; Porosity	40

Table 2.1 Summary of layers in SOFC, their composition and typical

thicknesses.

#### 2.2 Importance of the anode

In SOFC, the oxidation of the fuel such as  $H_2$  and natural gas takes place at the anode. The electrochemical oxidation of the  $H_2$  (Figure 2.3) could be written as:

$$H_2 + O_{YSZ}^{-2} = H_2 O + 2e^-$$
(2.1)

The predominance of fuel in the anode atmosphere makes its environment strongly reducing. The anode must not only withstand this environment, it must also meet the following requirements for proper functionality and durability of the SOFCs:

- High catalytic activity to oxidize the fuel and facilitate the electrochemical reaction (equation 2.1).
- High electronic conductivity to transport the electrons generated in equation 2.1 to the external circuit.
- Matched thermal expansion coefficient with the electrolyte and the ACC to reduce thermal stresses at the anode interfaces between room temperature (23 °C) and operational temperature (800 – 1000 °C).
- Chemically stable (itself, and in contact with the electrolyte and the ACC) at room temperature and operational temperature in the anode environment.
- Porous to facilitate the mass transport requirements (fuel in, products out) (equation 2.1).

Metallic catalysts such as Mn, Fe, Co, Ni, Ru, and Pt are chemically stable in the harsh reducing environment and have high catalytic activity. Of these catalysts, Ni has the highest activity for H<sub>2</sub> reduction. Ni also has high electrical conductivity (2 ×  $10^4$  S cm<sup>-1</sup> at 1000 °C [8] to transport generated electrons away from the reaction sites. However, the coefficient of thermal expansion of Ni (13.3 × 10<sup>-6</sup> K<sup>-1</sup>) [8] is higher than that of YSZ (10.5 × 10<sup>-6</sup> K<sup>-1</sup>) [8] in the electrolyte. Using Ni/YSZ composite ("cermet") anodes reduces thermal expansion mismatch, and therefore thermal stresses, between the anode and the electrolyte. YSZ also hinders Ni coarsening [9]. The electrical conductivity of the anode strongly depends on the Ni content [10]. Fig. 2.4 shows the electrical conductivity as a function of Ni content in the Ni/YSZ anode. Above 30 vol % Ni, the Ni/YSZ anode has sufficient electrical conductivity to transport electrons to the external circuit (Fig 2.4 (a)). The electrical conductivity of Ni/YSZ also depends on the ratio of particle diameter of YSZ and Ni ( $d_{YSZ}/d_{Ni}$ ). In an anode made from fixed volume fraction of Ni, pores and mixture of fine/coarse YSZ phase, the electrical conductivity of Ni/YSZ anodes increases as the volume fraction of coarse YSZ increases (Fig. 2.4 (b)). Yokokawa et al. [11] proposed that a porosity of 30 – 40 vol% is necessary to transport the fuel to triple-phase boundaries (TPBs) and to remove the reaction products away from TPBs.



Figure 2.4: Change in electrical conductivity with Ni content at temperature up to  $1350 \,^{\circ}C(a)$  and YSZ content at  $1000 \,^{\circ}C(b)$  [10].

Tape casting and screen printing are used commonly to fabricate the functional layers of SOFCs. LG prepared the samples for this study using screen printing. A slurry of materials is prepared for each layer and printed one at a time on the substrate or on the previous layers. The printing process was followed by drying and sintering operations. Screen printing permits precise control over the thickness of the layer to ensure parallel interfaces between the layers, as seen in Fig. 2.5.



Figure 2.5: (a) SEM image of LG SOFC. (b) Magnified view of the anode in LG SOFC with adjacent layers, ACC and electrolyte.

#### 2.3 Three-dimensional analysis of SOFC microstructures

Research on SOFCs has one common goal: understand the SOFC operation better to lower the cost and improve the long-term performance. The cost and performance are the major factors hindering wider implementation of SOFC technology. Microstructural characteristics of SOFC electrodes can be expected to influence SOFC performance. Traditionally, three-dimensional (3D) structural information could be estimated from two-dimensional (2D) images using basic stereology and quantitative microscopy theory [12, 13], such as volume fraction of a phase being estimated from its area fraction in 2D images. Song et al. [14] used the line intercept method to calculate interface area of LSM-YSZ cathodes. Faes et al. used the technique of Tewari et al. [15] to derive 3D particle-size distributions (PSDs) from 2D images of Ni/YSZ electrodes [16]. Triple phase boundaries (TPB), where ionic conductor, electronic conductor, and pore meet in SOFC electrodes, are essential to cell performance. Because the phases themselves are three-dimensional, TPBs likewise are 3D in nature. Zhao et al. [17] estimated TPB density (defined as the curvilinear length of the TPB per unit volume of the electrode) from 2D micrographs. Recently, Wilson and Barnett [18] calculated TPB by performing stereology on 2D micrographs to study the effect of Ni/YSZ composition on anode microstructure and cell performance.

Though 3D microstructural information can be extracted from representative 2D images, the 2D quantitative stereology analysis technique has inherent limitations. The presumption that the section being examined is representative of the three-dimensional structure is not always valid. Even if the section is representative, it is impossible to distinguish *active* from *inactive* TPB and *percolated* from *non-percolated* phase volumes (both discussed in detail in §4.5). The 2D analysis technique additionally has difficulty in quantifying anisotropic or graded microstructures. This deficiency is significant for the present work, as cells studied in this project had developed gradients in Ni and pore volume fractions during operation. Holm and Duxbury [19]expressed the importance of 3D while

studying the percolation and connectivity of grains. Fortunately, recent advances in the instrumentation techniques and computer power allow three-dimensional reconstruction (3DR) of real electrode microstructures.

Wilson et al. [20] was first to use 3DR technique for studying the SOFC anode microstructure. They laid out the procedure for 3DR of the anode using dual focused ion beam sectioning coupled with scanning electron microscopy (FIB/SEM). Using 3DR, it was possible for the first time to measure true *volume fraction, particle diameter* and *tortuosity* of the phases. Other research groups used a similar process for 3DR of SOFC electrodes [21-27].

Phase segmentation — the assignment of a feature to a particular phase in the microstructure (discussed in more detail in \$3.3) — is a labor-intensive process in 3DR. Standard routines are available in image analysis software such as Fiji (open source), Amira<sup>TM</sup> (FEI) etc. However, they are not effective to address artifacts in the images introduced during the sample preparation process. Custom routines to address such artifacts not only reduce the time needed for segmentation, but it also improves the accuracy of true phase identifications [28, 29].

#### 2.4 Microstructural evolution and its effects on SOFC performance

A major issue for SOFCs is their long-term performance degradation. We hypothesize that the performance degradation results in part from microstructural changes of the anode, the cathode, the electrolyte and their interfaces [30]. Coarsening of the nickel (Ni) phase is a prominent feature of microstructure change of a SOFC anode [13, 31, 32]. Two major mechanisms contribute to this phenomenon: transport of volatile nickel species

by evaporation and precipitation [33]; and diffusion by vacancies, driven by different grain sizes and surface curvatures [13].

Ni coarsening is a primary process of microstructural change that often leads to other microstructure changes such as reduction in TPB density [34] and reduction in the percolation of Ni phase [35]. Reduction in the percolation of Ni phase reduces active TPB. Both of the derived microstrural changes reduce cell performance significantly. Faes et al. [16] related Ni coarsening to loss of electrochemical performance through reduction in TPB. Ni coarsening also reduces the conductivity of Ni in the anode [12]. However the effect of reduction in Ni conductance on cell performance is unknown.

Evidence indicates that the mechanisms by which nickel coarsening occurs involve vapor-phase transport and depend on the amount of H<sub>2</sub>O in the anode atmosphere. Du et al. [33] reported transport of Ni via evaporation and condensation of Ni(OH)<sub>2</sub>. Opila (Opila's unpublished work (part2), 2009) used thermodynamic calculations to establish the volatility of Ni under SOFC operating conditions. Ni(OH)<sub>2(g)</sub> is most volatile species in a gas mixture of H<sub>2</sub> and H<sub>2</sub>O. At 950 °C and 1 atm, the partial pressure of Ni(OH)<sub>2(g)</sub> is six orders of magnitude higher than that of pure Ni<sub>(g)</sub> [32]. The formation of Ni(OH)<sub>2</sub> at low concentration of H<sub>2</sub>O could increase the Ni evaporation from SOFC anode significantly.

PSD has wide-reaching effects on one aspect of anode microstructure, the phase percolation [36]. In the SOFC field, researchers have used the spread and shift of PSD to study degradation of anodes. With test duration, PSD widens and shifts towards higher Ni particle diameter. Iwata [34] measured anode degradation of 14  $\mu$ V/h at a current density of 0.3 A/cm<sup>2</sup>. Pore size distribution was studied using mercury intrusion porosimetry (MIP) to understand Ni coarsening. Iwata attributed anode degradation to Ni sintering. More

recently, Munch and Holzer [37] compared the PSD measured with MIP and 3DR to study the differences in PSD in cements. They concluded that the lower diameter predicted by MIP is due to oversimplified model and limited accessibility of the pores because of bottleneck effect. The "discrete PSD" and "continuous PSD" approaches were proposed as an improvement to traditional MIP technique. Later the authors used the proposed approaches in SOFC applications [32].

TPB has been directly related the cell performance. Typically, TPB in the anode is calculated by the stereological method [22, 26, 38]. TPB calculated using this method tend to overestimate TPB length due to step-wise nature of TPB. To understand the overestimation of TPB by the stereological method, Wilson et al. [39] studied the spherical hypothetical model for which accurate TPB can be calculated and applied the stereological method to the structure. TPB angels in 3D space were averaged to calculate the correction factor of 1.455.

Jorgensen et al. [40] proposed an alternate method of polygonization of phase surface to improve the accuracy of TPB. Two schemes of polygonization were studied: voxel accuracy polygonization, nodes of quadrilateral were attached to the voxel vertices and sub-voxel accuracy polygonization, nodes of quadrilateral were not attached to the vertices. The author applied both the polygonization schemes to hypothetical two sphere model and varied the radii of sphere to calculate relative error. The relative error was -0.17% for a sphere radius of 20.

Iwai et al. [22] proposed volume expansion method and centroid method to improve the accuracy of TPB. These methods are discussed in detail in §4.5.2

#### 2.5 Kinetic models for microstructural evolution in SOFCs

DoE's target for the SECA program is to achieve loss of power  $\leq 0.2\%$  per 1000 h of operation under system conditions with a target system life of 40 kh [5]. It is impractical to test a large number of SOFCs for such a long time, especially considering the variety of operational variables that should be evaluated (e.g. temperature, fuel utilization and current density). In absence of 3D reconstructed anode, other groups generated hypothetical anode structures [41]. The hypothetical anode was input to kinetic models to predict long-term performance of SOFCs. As an alternative approach, a 3DR volume of the anode of an asprepared cell was used as a starting point for input to a kinetic model to predict the evolution of its microstructure during operation [9].

Researchers have tried to model TPB density [16], Ni coarsening and electrochemical performance [16] to predict long-term performance of SOFC. As discussed in §2.3, Ni coarsening is at the heart of microstructural changes. Simwonis et al. first attempted to model Ni coarsening with a 'grain growth model' [12]. The model predicted the Ni particle diameter of 4.2  $\mu$ m after 40 kh of cell operation. However the authors believed the data basis for the model was poor and many effects were neglected in the cell operation.

The grain size predicted by 'grain growth model' is very large compared to experimental measurement [16]. The difference is due to the fact that presence of YSZ in anode restricts the growth of the Ni particles [9]. In Ni-YSZ anodes, Ni particles grow much faster in the beginning and reach a plateau.

Vasen et al. proposed a two-particle model for Ni coarsening [13]. Two particles with different curvature have different pressures and vacancy concentrations. Transport of

vacancies due to this concentration gradient increases the size of larger particle at the expense of smaller particle. A special term in the model was introduced to account for the slow growth of Ni particles at long times.

Yakal-Kremski et al. [42] attempted to develop a mechanistic model based on accelerated degradation of the anode. The cell was tested for up to 500 h at 1100 °C to accelerate the anode degradation. The degradation of the cathode was studied by firing the cathode for 1 h up to 1325 °C. The hypothesis of the study was that the elevated temperature has the same effect on microstructure as the long cell operation. However, the correlation between time and temperature on microstructural change was not reported.

The other approach to predict the long-term performance is by fitting the experimental data with kinetic models. Shah et al. tried to fit the measured cathode resistance to a model that relates resistance to cathode surface area based on surface diffusion coarsening [43]. Faes et al. [16] attempted to fit the measured Ni coarsening data with to Ostwald ripening growth kinetics, the exponential growth model, and the classical relaxation kinetics model. A good fit was found between experimental data and the relaxation kinetics model up to 4 kh. Nelson et al. [44] used the same model to predict the long-term performance and found good agreement.

Surface diffusivity of Ni is three orders of magnitude higher than the bulk surface diffusivity at  $1100 \,^{\circ}$  [9]. That leads to believe, surface diffusion might be driving the solid-state diffusion mechanism. Recently, Gao et al. [45] proposed a two-parameter, surface-diffusion-based Ni coarsening model. The proposed model fit well with the experimental data of Faes et al. [16], Simwonis et al. [12] and Tanasini et al.[46] In the same work, the
two parameter model was simplified to a one-parameter model. However, the authors found that the two-parameter model fit better to the literature data.

### 2.6 Research hypothesis

The processing of a material affects its microstructure, properties, and performance. Material science and engineering seeks understanding of these relationships to predict and improve the performance of the material in specific applications.

The effect of two variables, operating temperature and time, on the SOFC anode microstructures was studied in this research. During the testing, the current density and fuel utilization were kept constant. The samples studied here were an untested ("as-reduced") sample and samples tested at three temperatures — 800 °C, 860 °C, and 925 °C — for up to 16 kh.

The chemical composition of the anode was analyzed using energy-dispersive X-ray spectroscopy (EDS). The intent of the EDS study was to verify the initial composition (table 2.1) and established the grey scale basis for subsequent 3D reconstruction work. The EDS study was limited to qualitative analysis of the anode composition.

To study the anode microstructure, the microstructures of the actual anode were virtualized by reconstructing them in 3D. The dual-beam FIB/SEM technique was developed to collect the data (images) for 3D anode reconstruction. The images were synthesized to form virtual 3D anodes. Chapter 3 covers the details of the 3D reconstruction procedure.

Microstructural parameters such as volume fractions, particle diameters, and tortuosity were calculated using Amira<sup>TM</sup> (FEI). MatLab (The MathWorks Incorporated) codes were developed to calculate derived microstructural parameters such as the phase percolated volumes and TPB densities. The results from tested samples were compared to those of the as-reduced sample results to study the evolution of the anode microstructure during operation. Chapter 4 lays out the details for microstructure analysis.

# **Chapter 3: 3D Reconstruction of the anode**

### **3.1 Introduction**

Interest in 3D reconstructions of materials' microstructures has grown in the last decade. Available analytical techniques for this type of study are serial sectioning – TEM (ss-TEM), micro – x-ray tomography ( $\mu$ -xCT) and FIB/SEM. With ss-TEM it would be difficult to analyze regions as large as the representative sample volumes of the SOFC anodes studied here (see §4.4).  $\mu$ -xCT is a non-destructive technique. However, the sample preparation time is more than 30 h per section and the highest image resolution is in the micrometer range [47], too coarse for the feature sizes in SOFC electrodes. The spatial resolution of FIB/SEM is between t-TEM and  $\mu$ -xCT. FIB/SEM allows reconstruction of sufficiently large volumes for microstructure analysis. Fig. 3.1 [48] compares FIB/SEM with competing 3DR analytical techniques for spatial resolution and size of the sample volume.



*Figure 3.1: FIB/SEM tomography technique in relationship with other tomography techniques* [48]

3D reconstruction can be divided into three sub-processes: sample preparation, data generation, and image processing. Proper attention is required at each step to preserve the original microstructure and to obtain the high-resolution images with excellent contrast, both of which are essential to achieving successful 3D reconstructions.

Sample preparation using the dual beam FIB/SEM is well documented [20, 22, 38]. Differential density of the phases, and the presence of non-conductive phases, can reduce the fidelity of the data generated. Impregnating pores with epoxy, and applying relatively thick conductive coatings on samples with anode exposed on two faces, improved the quality of the images analyzed in the current work.

The dual-beam FIB/SEM is now widely used for material characterization and topology studies. These instruments combine a focused ion beam for milling of the specimen with a scanning electron beam for imaging. A dual-beam FIB/SEM consists of a vacuum system, liquid metal ion source, electron and ion-column systems, stage, computer controls and detectors (Fig. 3.2).

When the electron beam impinges on the sample, it excites electrons in atoms within a certain depth, causing emission of Auger electrons (AE), secondary electrons (SE), and backscattered electrons (BE), as well as various types of electromagnetic radiation (Fig. 3.3). The depth of the excited region depends on the acceleration voltage of the beam. SEs are produced by inelastic interactions of the incident electrons with valence electrons of the atoms in the specimen. A significant level of the contrast in images formed from the detection of SEs, arises from differences in the atomic number (Z) of the elements, with low-Z elements generating fewer SEs and therefore appearing darker. This aspect of electron microscopy is central not just to the detection of elements using energy-dispersive

x-ray spectroscopy (EDXS) but also provides the main means of differentiating between different phases during 3DR of a multi-phase microstructure.



Figure 3.2: Schematic of FIB/SEM system
[http://www.brucherseifer.com/html/sem\_\_\_fib.html]

Low acceleration voltage (below ~ 5kV) results in a small interaction volume, and most of the secondary electrons emerge from a surface depth of 0.1 µm or less, yielding high-resolution images. Low beam energies also reduce damage to the sample from the electron beam and reduce the charge deposited in insulating or poorly conducting specimens [49].



Figure 3.3: Interaction volumes in specimens under an electron beam. The incident beam penetrates into the specimen, which emits Auger electrons, secondary electrons, backscattered electrons, characteristic X-rays, continuous X-rays and fluorescent X-rays. [http://mee-inc.com/sem.html]

To achieve the best combination of image quality and data-collection efficiency, the complementary strengths of two dual beam systems were leveraged for this project. The large working distance (15 mm) afforded by the Quanta 200 3D offers great flexibility during milling. The capability of the Quanta to mill large volumes (due to its enhanced gas chemistry technology) at high milling current (65 nA) reduced the trench-preparation time. In contrast, Helios NanoLab<sup>™</sup> 360 has a short working distance and precise FIB slicing combined with a high-precision piezo stage. This instrument's three SE detectors — an Elster in-lens SE detector, an Everhart-Thornley SE detector, and a high-performance SE and secondary ion detector — allowed collection of high-resolution and high-contrast images.

#### **3.2: Experimental procedure**

The cells were fabricated and tested by LG Fuel Cell Systems Inc. Specimens from nine cells, one as-reduced and eight after operation at 800 °C, 860 °C and 925 °C for duration up to 16 kh at an overpressure 6.4 bar, were studied (Table 3.1).

<b>Test Duration</b>	t = 2 kh	t = 4 kh	t = 8 kh	t = 16 kh
as-reduced	NA	NA	NA	NA
800 °C	800 °C / 2 kh	800 °C / 4 kh	800 °C / 8 kh	Not Studied
860 °C	Not Studied	860 °C / 4 kh	860 °C / 8 kh	860 °C / 16 kh
925 °C	925 °C / 2 kh	925 °C / 4 kh	Not Studied	Not Studied

*Table 3.1: Summary of the samples studied in the research. The variables were test temperatures and test durations.* 

Cell fabrication entailed screen printing and firing the anodes (and all the other functional layers) on ceramic substrates (§2.1) in a single-cell configuration. The cells were first exposed to a reducing atmosphere for 2 h at 925 °C to reduce nickel oxide (NiO) in the anode to metallic Ni. During operation, fuel utilization < 2% and current density 380 mA/cm<sup>2</sup> were kept constant. The cathode gas consisted of 12% O<sub>2</sub>, 1% H<sub>2</sub>O, balanced with N<sub>2</sub>. The anode gas consisted of reformate fuel with 40 – 45% H<sub>2</sub> balanced with CO, CO<sub>2</sub> and H<sub>2</sub>O.

The "slice and view" reconstruction methodology of Vivet et al. [38] (Fig. 3.4) and others [20, 23, 26] were followed, with modifications (explained below) to improve the images and to expedite the SEM imaging and the FIB serial-sectioning procedure. Impregnation of the pores with a low-viscosity epoxy under vacuum reduced the differences in densities between the pores and the solid phases, thus reducing the effects of preferential milling and improving the open pore phase contrast in 2-D images.



Figure 3.4: Methodology for creating 3D reconstruction volume: sample preparation, preparation for region of interest (ROI), data collection and data processing [38].

As an improvement to the standard process, the mounted specimen was cut as shown in Fig. 3.5 such that the anode was exposed on two faces of the mold. Both of the faces were polished down to 1  $\mu$ m roughness to produce flat, smooth surfaces perpendicular to the interfaces between the active layers.

Poor conductivity of the ceramic phase and pores would create an imbalance between the incoming and emitted electrons, causing negative charge to accumulate on the specimen. Commonly a carbon (C), gold (Au) or palladium (Pd) coating is applied to such specimens. For this project, the polished surfaces were coated with palladium (Pd), ~200 nm thick, using Danton Vacuum (LLC) Desk IV.



*Figure 3.5: Schematic of mounted specimen. The layers of the fuel cell are visible from two orthogonal surfaces of the mount after polishing.* 

A second improvement to the standard technique entailed mounting the specimen on a  $45^{\circ}$  stub with carbon tape such that the two faces with exposed anode were at  $45^{\circ}$  to the electron beam and at 7° to the ion beam (Fig. 3.6). Strips of silver (Ag) paint were applied, connecting the end of the sample in the mount to the stub, to drain incident electrons from the specimen. Mounting at  $45^{\circ}$  eliminated the need to cut a trench in the front, and enabled viewing of the depth of the side trenches (next paragraph) without moving the FIB-SEM stage. This significantly reduced the time needed for serial sectioning and imaging.



Figure 3.6: Schematic of dual beam SEM-FIB system with specimen mounted on 45° stub. The angle between two incident beams, electron beam, and ion beam was 52°.

A platinum strip (40  $\mu$ m × 40  $\mu$ m × 1  $\mu$ m thick) was applied on the surface above the area of interest to protect it from being damaged during trench cutting and serialsectioning. Trenches were cut on either side of the area of interest to isolate it from the rest of the sample. The trenches needed to be deep enough to prevent the re-deposition of the milled material on the area of interest during serial sectioning. The depth of the trench depends on the number of slices that need to be collected. For this project, typical side trench dimensions were 70  $\mu$ m (length) × 20  $\mu$ m (width) × 40  $\mu$ m (depth) (Fig. 3.7). The high milling current (65 nA max) of the FEI Quanta reduced the Pt deposition and the trench-cutting time considerably.



Figure 3.7: SEM image of the area of interest after Pt deposition and trench cutting. Pt deposition:  $40 \ \mu m \times 40 \ \mu m \times 1 \ \mu m$ ; trenches:  $70 \ \mu m \times 40 \ \mu m \times 20 \ \mu m$ .

A different FIB/SEM (FEI Helios) with automated "Slice and View" capability was used for serial sectioning and imaging. A fiducial mark in a clean surface of the trench served as a reference for the dual beam system to confirm its position before milling. For serial sectioning, the accelerating voltage was 30 kV and the ion beam current was 15 nA. A Ga<sup>+</sup> liquid source was used for high-resolution milling. For imaging, the acceleration voltage was 2 kV and the electron beam current was 1.6 nA. The field emission gun SEM was utilized to image the freshly milled surface with a through-lens detector (TLD). The TLD's charging contrast was used to distinguish between the phases. Imaging with this instrument offers the high resolution and high contrast needed to distinguish the three anode phases during the segmentation process. The surface to be imaged was rotated perpendicular to the electron beam. Images taken in this manner did not require a scale correction factor for the subsequent 3D reconstruction. Based on the feature size and shapes of the three phases (Ni, yttria-stabilized zirconia (YSZ) and pores), typically 120 - 150 slices, 0.15 µm thick were made, generating a stack of images (Fig. 3.8).



Figure 3.8: Stack of anode slices prior to combining for 3D reconstruction (as-reduced specimen).

# **3.3 Segmentation and reconstruction**

The images from serial sectioning were preprocessed using the open source software Fiji. Typically, this entailed aligning features from one image to the next, and cropping images to exclude the anode/electrolyte and the anode/anode current collector (ACC) interfaces from first image to last image. The total thickness of these anodes was about 8  $\mu$ m. The cropped images showed 5–6  $\mu$ m of the anode thickness. Finally, contrast in the images was enhanced using standard routines available in Fiji.

Further processing of the stack of anode images was carried out in the commercially available program Amira<sup>TM</sup> (FEI). Amira divides the reconstructed volume into small volumes called voxels. Length (*x*-direction) and width (*y*-direction) of the voxel will be the same in a stack, as both are based on the resolution and field of view in the SEM image. Depth (*z*-direction) of the voxel is the spacing between the consecutive slices (0.15  $\mu$ m). Table 3.2 summarizes the voxel dimensions for the analyzed samples. The as-reduced sample had much smaller depth (0.050  $\mu$ m) than the other samples. The feature sizes in the

as-reduced sample was much bigger than 0.050  $\mu$ m. To reduce the data collection time in FIB/SEM experimentation, the spacing between the FIB slicing were increased to 0.150  $\mu$ m for all the tested samples. In all samples the *x*- and *y*-dimensions were much smaller than the microstructural features being analyzed, which is necessary for accuracy of the microstructural parameters (Fig 3.9).

	x, y (μm)	z (µm)	Total Volume (μm <sup>3</sup> )
As-Reduced	0.027	0.050	1130.6
800 °C / 2 kh	0.009	0.150	1407.6
800 °C / 4 kh	0.009	0.150	1558.0
800 °C / 8 kh	0.009	0.150	1130.0
860 °C / 4 kh	0.008	0.150	994.3
860 °C / 8 kh	0.019	0.150	1364.3
860 °C / 16 kh	0.008	0.150	1599.2
925 °C / 2 kh	0.018	0.150	1445.0
925 °C / 4 kh	0.007	0.150	1253.7

Table 3.2: Voxel size and reconstructed anode volume summary for the as-reduced

samples and the samples after operation.



*Figure 3.9: SEM image of Sample 925 °C / 2kh anode. Three phases of the anode: Ni (white/light grey), YSZ (dark grey) and pore (black).* 

The stack of images was auto-segmented in Amira based on the grey scale of the three phases. Artifacts such as curtaining (dark streaks in the images that result from preferential milling), bright spots due to localized charging of the sample, small particles from milling etc. (Fig. 3.10) are inevitable in the images obtained by serial sectioning. Manual segmentation of all images in the stack is required to reassign the affected voxels to their appropriate phases. Fig. 3.11 shows an image before and after segmentation.











Figure 3.10: Common image artifacts (indicated by arrows) in SEM images obtained by serial sectioning: (a) curtaining, due to preferential milling; (b) air bubbles trapped in epoxy; (c) charging; (d) pores not filled by epoxy, showing particles below the cutting plane.



Figure 3.11: Image of the as-reduced specimen before (a) and after (b) segmentation. The phases of the anode: Ni (white), YSZ (grey) and pore (black).

Finally, the segmented images are combined in Amira to reconstruct the anode in 3D (Fig. 3.12).

### **3.4.** Elemental analysis by X-ray energy-dispersive spectroscopy (XEDS)

SEM images are grey-scale images. These differentiate the various phases by their Z values only. However, to establish the link between the grey scale images to the anode phases, it is important to verify the chemical composition of the different intensity of the grey scale in SEM images. X-ray energy-dispersive spectroscopy (XEDS) was used to study the composition of phases observed the anodes.

The metal phase of the anodes was Ni. The ACC consisted of a Ni-Pd alloy and an Mg-Al spinel oxide. Since Pd was one of the elements in the ACC, samples for elemental analysis were coated with gold (~30 nm). XEDS was performed on all samples using the Quanta 200 3D. The as-reduced specimen and two other specimens were also analyzed using the Helios Nano 360 to compare results from the two systems. The acceleration

voltage was 20 kV and current was 2.9 nA for all samples. The high acceleration voltage increased the depth of the interaction volume, allowing collection of data from well below the surface of the material.



Figure 3.12: Reconstructed 3D volume of sample 925 °C / 2 kh. Three phases of the anode: Ni (green), YSZ (yellow) and pore (red). Top surface of the volume was close to the anode/electrolyte interface and the bottom surface (only the front edge of which is visible) was close to the anode/ACC interface.

Elemental maps of the as-reduced specimen confirmed the presence of Ni and YSZ in the anode (Fig. 3.13) as expected. However, Pd was detected in the same locations as Ni throughout the anode. At 925 °C (sintering temperature), Pd evidently diffused into the anode from the ACC and formed a Ni-Pd solid solution. No separate Pd or Ni particles are seen in either layer (Fig. 3.13 (b), (c)). The elemental maps were similar for the cell after operation (Fig. 3.14), where Ni and Pd were also detected in the pores of the porous anode barrier (PAB). The presence of Ni and Pd in isolated spots in the PAB could be due to volatization and precipitation of these elements during cell operation. The line profiles of Ni and Pd across the anode and ACC confirm the higher concentration of both elements in these layers compared to the adjacent electrolyte and PAB.

### **3.5 Conclusion**

The dual beam FIB/SEM was used to reconstruct SOFC anodes for microstructure analysis. The spatial resolution of the technique was well suited to reconstruct large anode volumes  $(1000 - 1600 \ \mu m^3)$  without compromising the details of the microstructure. The instrument times required for FIB/SEM experiments were long. Significant time was saved by implementing improvements to the standard 3D reconstruction procedure. 3D data were collected for 9 samples. The high resolution and contrast of the images from Helios Nano 360 provided more accurate phase segmentation.

Amira<sup>TM</sup> (FEI) software was used for reconstructing 3D anodes from the SEM images. The auto-segmentation feature of the program allowed identification of three phases based on their grey scale differences. However, artifacts in the imaging were apparent because of the implementation of the FIB/SEM technique to non-conductive phases and porosity in the SOFC anode. Standard routines available in Amira<sup>TM</sup> (FEI) to address some of the image artifacts saved time in the manual segmentation of the anode phases. Nevertheless, the time needed for manual segmentation was still significant. Development of specific subroutines for automatically correcting for preferential milling or phase boundary separation could reduce the overall time for phase segmentation.



(c)





(b)



(d)



Figure 3.13: (a) SEM image of as-reduced sample for XEDS analysis (b) – (f) Elemental maps for Ni, Pd, Mg, Al and Zr in as-reduced sample. [Naima *Hilli, unpublished work]* 















(e)

Figure 3.14: (a) – (d) Elemental maps for Ni, Pd, Al and Mg in sample 925  $^{\circ}C / 2$  k h (e) Line profile of Ni (yellow) and Pd (blue) across anode and ACC layers in sample 925  $^{\circ}C / 2$  kh.

The chemical composition analysis of the anode confirmed that solid-state diffusion of Pd from the ACC to the anode had occurred during sintering of the cell, before operation. The metal phase of the anode was a solid solution of Ni and Pd for all samples. The presence of Ni and Pd in the PAB layer proved the volatility of the metallic elements during operation. The ceramic phases in the anode (YSZ) and the ACC layer (YSZ and Al-Mg spinel) were stable at all test temperatures.

# **Chapter 4: Quantification of the anode microstructure**

### 4.1 Overview

Multi-phase SOFC anodes have complex microstructure. Characterization of their microstructural changes in 3D after various stages of operation is essential for understanding the relationships between anode microstructure and performance, and for establishing a microstructural basis for the long-term prediction of performance.

In this research, the multi-phase SOFC anode microstructure is initially quantified by parameters such as *phase volume*, *particle diameter*, *surface area*, and *tortuosity*, which are specific to individual phases. These parameters are calculated independently for each phase; the other phases or the anode interfaces do not influence their calculations. Tracking the changes in these parameters with time of cell operation helps to quantify phenomena like particle coarsening, solid-state diffusion, phase volatization etc. that are part of the overall microstructure evolution. Changes in these basic parameters provide a basis for predictions of the microstructure evolution over long periods of operation.

The operational performance of SOFCs is related to derive microstructural parameters such as *percolated phase volume* and *triple phase boundary (TPB)*. The derived microstructural parameters are calculated by considering the spatial relationships of all the phases with each other and their connectivity with the electrolyte and the ACC. The percolated phase volume is necessary for transport of reactants to, and product from, the electrochemical reaction sites i.e. TPBs. By comparing percolated phase volumes and the TPB length between the as-reduced cell and the tested cells, prediction of long-term SOFC performance could be made.

The YSZ phase is microstructurally and thermodynamically stable under normal SOFC operating conditions [9]. At the operating temperatures of interest in the present work (approximately 800 - 925 °C), the YSZ phase exhibits little morphological change. In contrast, it is well known that Ni is mobile under cell operating conditions, leading to redistribution of Ni in SOFC anodes during use. As discussed in detail in §4.2.2, we observed gradients in the phase fractions of Ni and porosity across the anode thickness.

An essential consideration in any microstructural study is whether the sample being analyzed represents the entire material of interest. In 3D reconstructions, this means determining a representative sample volume (RSV) — in the present work, of the anodes of the tested cells. The evolution of microstructural gradients during SOFC operation required development of a novel method for calculating RSV in heterogeneous microstructures, described in §4.3.

Percolated phase volume contributes to mass and species transport. TPBs are classified as either electrochemically active or inactive based on their associativity with the percolated volumes. The TPB length was calculated (§4.4) using the widely adopted stereological method. The TPB calculated using this approach is step-wise in nature. In an additional novel method developed in this work, the surface encompassing the phase volume was smoothed. TPB length was calculated by finding the intersection points of the smooth surfaces of three phases. The TPBs calculated by this method are curvilinear in nature.

The effect of phase redistribution on particle size distribution is studied in §4.5. Detailed insights are developed for the shape and distribution of the particle diameters. The growth of Ni particles is quantified at the anode interfaces. The basic and derived microstructural parameters for the as-reduced cell and the cell tested at 800 °C, 860 °C and 925 °C were compared. The results for the microstructure parameters were extrapolated to predict the long-term microstructural changes and the SOFC performance. As the focus of the research was limited to the anode, the long-term SOFC performance was predicted based on the anode microstructure changes only. The effects of the microstructural changes in other SOFC layers were not considered.

### 4.2 Microstructural analysis and quantification

#### 4.2.1 Volume fraction and particle diameter

The phase volumes for Ni, YSZ and porosity were calculated by counting the number of voxels for each phase in each reconstructed anode. Because all the voxels analyzed in any particular specimen had the same volume (Table 3.2), and every voxel was assigned to one of the three phases, the fraction of voxels assigned to each phase was equal to the volume fraction of that phase (Equation 4.1), and the three volume fractions summed to 1. (Table 4.1).

The overall volume fractions for Ni (~0.3), pores (~0.3) and YSZ (~0.4) in the analyzed volumes exhibited some scatter among the as-reduced and tested specimens (Table 4.1). No systematic variations with testing time or temperature are discernible, e.g. with regard to possible loss of Ni during testing. The volume fractions for Ni and pores in the samples 860 °C / 4 kh and 925 °C / 2 kh differed significantly from those in the other samples. Two more anodes were reconstructed for these cells to verify the accuracy of the results. For these additional reconstructions, the data were collected from other areas of the same cells.

The other microstructure parameter, *phase surface area*, is the area of surface encompassing the phase volume. The surface area could be calculated by counting faces of voxels interfacing with other phases or with the boundaries of the reconstructed volume. But the stepwise surfaces would over-estimate the surface area. In an alternate approach, the stepwise surface of a phase was smoothened so that it preserved the shape of the phase volume. The smoothed surface was discretized by triangle mesh elements. The phase surface area was calculated by summing the area of each triangular mesh elements. The calculated surface area was used in equation 4.2 to calculate the phase particle diameter.

An effective average particle diameter was calculated using the surface area and the volume for a phase (Table 4.1). At all three testing temperatures, the particle diameters for the Ni and for the porosity were usually higher after testing, whereas the particle diameter for YSZ was relatively unchanged. These results are consistent with the other reports [9]. The coarsening of the Ni and porosity, but not of the YSZ, is attributed to transport of Ni within the anode during operation, and to relative morphological stability of YSZ under these operating conditions. The changes in Ni particle diameter and pore size were more pronounced at 925 °C than at 800 °C, consistent with thermally activated transport (whether by vapor- or solid-state mechanisms).

$$Volume \ Fraction_{Phase} = \frac{Volume_{Phase}}{Total \ Volume}$$
(4.1)

$$Particle \ Diameter_{Phase} = \frac{6*Volume_{Phase}}{Surface \ Area_{Phase}}$$
(4.2)

	Volume Fraction		Particle Diameter (µm)			
	Ni	Pores	YSZ	Ni	Pores	YSZ
As-Reduced	0.31	0.3	0.39	0.89	0.83	1.11
800 °C / 2 kh	0.35	0.22	0.43	1.14	0.73	0.94
800 °C / 4 kh	0.30	0.28	0.42	0.86	0.92	1.16
800 °C / 8 kh	0.28	0.33	0.39	1.22	0.99	0.90
860 °C / 4 kh	0.20	0.40	0.40	0.95	1.17	0.87
860 °C / 8 kh	0.32	0.30	0.38	1.23	0.97	0.84
860 °C / 16 kh	0.32	0.28	0.40	1.34	0.98	0.96
925 °C / 2 kh	0.23	0.42	0.35	1.33	1.30	0.97
925 °C / 4 kh	0.30	0.30	0.40	1.23	0.96	0.97

*Table 4.1: Volume fractions and particle diameters for the as-reduced specimen and the specimens tested at 800 °C, 860 °C and 925 °C.* 

### 4.2.2 Volume fraction across the anode thickness

The anodes studied here were bounded by the electrolyte on one side and the ACC on the other side. The volume selected for the analysis spanned essentially the entire anode thickness, without extending into the electrolyte or the ACC (Fig. 3.12).

Gradients in volume fractions for all three phases were further analyzed in x-, yand z- directions. The reconstructed anode volumes were sectioned virtually in three directions. The spacing between the sections was the length of a voxel in the direction under consideration. Thus the sections in the z-direction were made with the spacing between the sections equal to the voxel z dimension (Table 3.2). The variation in the volume fractions in x-, y- and z-directions for Ni, YSZ and porosity were then plotted per equations (4.3), (4.4) and (4.5):

Phase Volume Fraction<sub>x</sub> = 
$$\frac{Phase \ area \ in \ Slice \ yz}{Slice \ Area_{yz}}$$
 (4.3)

$$Phase Volume Fraction_{y} = \frac{Phase area in Slice xz}{Slice Area_{xz}}$$
(4.4)

Phase Volume Fraction<sub>z</sub> = 
$$\frac{Phase area in Slice xy}{Slice Area_{xy}}$$
 (4.5)

The *z*-direction was taken to be parallel to the anode thickness, i.e. the direction normal to the anode/electrolyte interface and the anode/ACC interface (Fig. 3.12). The zero of the *z*-axis was taken to be at the anode-electrolyte interface. The *x*- and *y*- directions were parallel to the anode interfaces with the electrolyte and the ACC. Volume fraction variations in the *x*-direction were always similar to those in the *y*-direction. (Appendix A summarizes the volume fraction variations in all three directions. Below, only the results in the *y*- and *z*-directions are shown.)

Fig. 4.1 shows the volume fraction profiles for all three phases in the as-reduced specimen and 925 C / 4 kh. The volume fraction variations were smoother in the *z*-direction due to the smaller spacing between the slices (Table 3.2). For the as-reduced specimen, the average volume fractions were 0.31, 0.30 and 0.39 for Ni, pore and YSZ respectively in the *y*- direction, and 0.30, 0.30 and 0.40 in the *z*- direction, i.e. within experimental uncertainty in both directions. These values were also within experimental uncertainty of the volume fractions calculated for the entire volume (0.31, 0.30, and 0.39, Table 4.1).

Figures 4.1c and d show the analogous results for sample 925 °C / 4 kh. The profiles in the y-direction were similar to those in the as-reduced specimen. However in the zdirection (i.e. across the anode thickness) significant and opposite gradients appeared for Ni and pores. Compared to the as-reduced specimen, the volume fraction of Ni in the tested specimen increased from 0.25 to 0.41 at the anode/electrolyte interface and decreased from 0.28 to 0.19 at the anode/ACC interface. The trend was reversed for the porosity: the volume fraction of pores remained same (~0.21) at the anode/electrolyte interface and increased from 0.29 to 0.41 at the anode/ACC interface. Interestingly, the average volume fractions for Ni, pore and YSZ were 0.30, 0.30 and 0.40 respectively as in the as-reduced specimen and as in the *y*- direction. As expected, the volume fraction of YSZ was uniform even in the *z*-direction.



Figure 4.1: Volume fraction variations of Ni, YSZ, and pore in y- and zdirections for the as-reduced specimen ((a) and (b)) and for the 925 °C/4 kh specimen ((c) and (d)). In (b) and (d), the values of the horizontal axis extend from near the anode/electrolyte interface on the left to the anode/ACC interface on the right. Solid lines: experimental data. Dashed lines: linear least-square fits to the experimental data.

The profiles of volume fraction for all three phases in *y*- and *z*-directions for the cells tested at 800 °C, 860 °C and 925 °C showed similar trends to those in Fig. 4.1 (Appendix A).

Figures 4.2 and 4.3 illustrate the changes in the phase profiles across the anode with time of operation at constant temperature. At 800 °C, compared to the as-reduced specimen, the volume fraction of Ni at the anode/electrolyte interface increased in the first 2 kh and remained high for 8 kh, e.g. from 0.28 to about 0.38 after 8 kh testing (Fig. 4.2 (a)). However, at the anode/ACC interface the volume fraction for Ni decreased gradually from 0.28 to 0.19 during the same period. The slopes of the Ni profiles across the anode became steeper with time of operation: from  $-0.006 \,\mu\text{m}^{-1}$  to  $-0.024 \,\mu\text{m}^{-1}$  to  $-0.029 \,\mu\text{m}^{-1}$  to  $-0.034 \,\mu\text{m}^{-1}$  after 0, 2, 4, and 8 kh of testing.

The profiles of the porosity were opposite to those of Ni. During the same test duration, the volume fraction of pores remained 0.20 at the anode/electrolyte interface but increased from 0.31 to 0.44 at the anode/ACC interface (Fig. 4.2 (b)). Similar to Ni, the slopes of the porosity across the anode became steeper with time of operation: from 0.008  $\mu$ m<sup>-1</sup> to 0.020  $\mu$ m<sup>-1</sup> to 0.021  $\mu$ m<sup>-1</sup> to 0.039  $\mu$ m<sup>-1</sup> after 0, 2, 4, and 8 kh of testing.

At 860 °C, the profiles for Ni and pores showed similar trends as at 800 °C (Fig. 4.3 (a) and (b)). During the 16 kh test (the longest test conducted for this work), the volume fraction of Ni increased from 0.28 to 0.44 at the anode/electrolyte interface and decreased from 0.28 to 0.17 at the anode/ACC interface. The volume fraction for pores decreased from 0.28 to 0.16 at the anode/electrolyte interface and increased from 0.29 to 0.43 at the anode/ACC interface. The slopes of linear curve fits for Ni and pores were  $-0.048 \ \mu m^{-1}$  and 0.046  $\mu m^{-1}$  respectively for 860 °C / 16 kh. These slopes were the steepest of all the

samples. The results for sample 860  $^{\circ}$ C / 16 kh indicated that the test duration has significant effect on the phase distribution in the anodes.







Figure 4.2: Volume fraction gradients comparison for Ni (a) and porosity (b) at 800 °C ((a) and (b)) during 8000 h of testing. 'm' is the slope of the linear curve fit ( $\mu$ m<sup>-1</sup>). The zero of the abscissa represents the anode/electrolyte interface. Solid lines: experimental data. Dashed lines: linear least-square fits to the experimental data.



(a)



(b)



(c)



Figure 4.3: Volume fraction gradients for Ni and porosity at 860 °C ((a) and (b)) and 925 °C ((c) and (d)). 'm' is the slope of the linear curve fit ( $\mu$ m<sup>-1</sup>). The zero of the abscissa represents the anode/electrolyte interface. Solid lines: experimental data. Dashed lines: linear least-square fits to the experimental data.

	Slope of Volume Fraction Profile (µm <sup>-1</sup> )		
	Ni	Porosity	
As-Reduced	-0.006	0.008	
800 °C / 2 kh	-0.024	0.020	
800 °C / 4 kh	-0.029	0.021	
800 °C / 8 kh	-0.034	0.039	
860 °C / 4 kh	-0.071	0.080	
860 °C / 8 kh	-0.011	0.026	
860 °C / 16 kh	-0.048	0.046	
925 °C / 2 kh	-0.009	0.009	
925 °C / 4 kh	-0.047	0.041	

Table 4.2: Summary of slopes of Ni and porosity volume fraction profilesacross the anode thickness

The trend for volume fraction of Ni and pores remained the same at 925 °C (Fig. 4.3 (c), (d). The sample 925 °C / 4 kh had steep slopes for both Ni -0.047  $\mu$ m<sup>-1</sup> and porosity 0.041  $\mu$ m<sup>-1</sup>. At 925 °C, steep gradients were developed in much shorter duration (~ 4 kh) than at 800 and 860 °C.

### 4.2.3 Role of cell configuration

All the samples except  $860 \degree C / 4$  kh were subscale cells. Due to the size of the cell, the variation in fuel composition, fuel utilization, pressure etc were minimum from inlet to outlet of the cell. The cell  $860\degree C / 4$  kh was a full-scale cell made from 6 full-size tubes. The tube 1 and tube 6 of the cell were inlet and outlet tubes respectively. With this

configuration tube 3 and 4 were mid-point in the fuel flow path. The sample  $860 \degree C / 4 \text{ kh}$  was prepared from the outlet tube i.e. tube 6.

The effect of the cell configuration on the volume fraction profile is evident in Fig. 4.4. The profiles for Ni and porosity for the full size cell were significantly steeper than those of the subscale size cells, with slopes of Ni and porosity profiles ( $-0.071 \ \mu m^{-1}$  and  $0.080 \ \mu m^{-1}$ ) nearly two times the maximum values in table 4.2.



Figure 4.4: Volume fraction variation of Ni and porosity in the outlet tube of the full size cell (860 °C / 4 kh). 'm' is the slope of the linear curve fit ( $\mu$ m<sup>-1</sup>). The zero of the abscissa represents the anode/electrolyte interface. Solid lines: experimental data. Dashed lines: linear least-square fits to the experimental data.

# 4.3 Tortuosity

Tortuosity is a measure of crookedness of the path within a phase. It is defined as the ratio of the curved phase length to the Euclidean distance. Tortuosity has an effect on gas-phase mass transport [21] but little effect on electronic or ionic conductivity, on the microstructural scale of the present cells. Therefore, tortuosity is a more relevant parameter for the porosity than for Ni and YSZ.

The literature contains several methods of calculating tortuosity. Zalc et al. [50] used flux-based Monte Carlo simulation to study molecular and Knudsen diffusion and concluded that for porosity greater than 10%, the simulation method is valid. Wilson et al. [20] and Izzo et al. [51] used the diffusion-based method, and the tortuosity was calculated by solving the Laplace equation.

Gostovic et al. [26] proposed a center-of-mass-based tortuosity (Fig. 4.5). In this method, the center of mass was calculated using Amira<sup>TM</sup> (FEI) for each phase in a section and then was tracked from section to section across the anode. The tortuosity was calculated by dividing the tracked length by the known Euclidean distance from the first slice to the last slice.



*Figure 4.5: Schematic illustration of the tortuosity calculation based on the center-of-mass method* [26].

	Tortuosity
	Pores
As-Reduced	2.60
800 °C / 2 kh	2.10
800 °C / 4 kh	1.50
800 °C / 8 kh	1.43
860 °C / 4 kh	1.41
860 °C / 8 kh	1.35
860 °C / 16 kh	1.56
925 °C / 2 kh	1.33
925 °C / 4 kh	1.47

Table 4.3: Tortuosity for the porosity in the direction of mass transport based on the center-of-mass method.

Table 4.3 gives the tortuosity for the porosity, calculated using the center-of-mass method [26]. The tortuosity decreased from 2.60 for the as-reduced specimen to 1.43 for the 800 °C / 8 kh, 1.56 for 860 °C / 16 kh, and to 1.47 for 925 °C / 4 kh. The reduction in tortuosity was gradual at 800 °C. At 925 °C, the tortuosity dropped from 2.60 to 1.33 in the first 2 kh, then remained unchanged from 2 kh to 4 kh. Although the tortuosity for the porous phase reached the same level for all three test temperatures (~1.4), that level was attained much faster at 860 °C (4 kh) and 925 °C (2 kh). The trend of decreasing tortuosity with time coincided with increase in size of the pores (Table 4.1 and Table 4.3).

Tortuosity calculated by the center-of-mass method combines the effect of shape, area of phase and number of phase regions in each section. In 3D, there are numerous gas channels in the anode for mass transport from the anode/ACC interface to the anode/electrolyte interface. In the center-of-mass method, the structure of gas channels is represented as a line connecting center of mass of sections in the direction of tortuosity calculation. If the structure of the gas channels in the anode were preserved during tortuosity calculation, it would give more insight into the mass transport through the anode.

The optimal way to preserve the structure of the gas channels would be to skeletonize the pore phase in the anode. The skeleton could be used to calculate tortuosity from any area on the anode/ACC interface to any area of the anode/electrolyte interface [52]. The percolated volume for each phase was skeletonized using Amira<sup>TM</sup> (FEI). A distance map was created for each voxel of the porosity. Based on the distance map, an iterative "thinning" process reduced the pathways through the porous structure to a skeleton representative of the original phase structure. The skeleton consisted of nodes and line segments connecting these nodes (Fig. 4.6). A node is defined as a location either at a boundary of the reconstructed volume, or at an interface with another phase where the path branches into multiple line segments.



Figure 4.6: (a) Overlay of skeleton on the pore phase. The pore phase here is from a sub-volume of the as-reduced specimen. (b) The skeleton of the pore phase from (a).
The Amira<sup>TM</sup> (FEI) program allowed the selection of only one pair of nodes at a time to calculate the shortest distance between them. Selecting the correct nodes from the complex skeleton structure (Fig. 4.7) for the distance measurement was labor intensive. Moreover, the shortest path calculated by Amira<sup>TM</sup> (FEI) was based on the fewest nodes in the path instead of the shortest distance. A Matlab (MathWorks Inc) program based on the *fast marching method* [53] was developed to automate the process of selecting the set of nodes on both the anode/ACC interface and the anode/electrolyte interface, and calculating the shortest distances between a pair of nodes, node 1 ( $x_1$ ,  $y_1$ ,  $z_1$ ), and node 2 ( $x_2$ ,  $y_2$ ,  $z_2$ ), from two interfaces following the skeleton structure. Fig. 4.8 depicts the algorithm for the shortest path calculation.

Four types of nodes were identified in the skeleton structure: start node, destination node, assigned node and unassigned node. As the names suggest, the start node was the node from which the calculation initiated, and the destination node is the node for which the tortuosity needs to be calculated. For the calculations here, the start node was always from the anode/ACC interface and the destination node was from the anode/electrolyte interface. The results were the same even if the selections were reversed. An unassigned node is a node whose connectivity with the start node and the destination node needs to be determined, and an assigned node is a node whose connectivity with the start node and the destination node is identified. At the start of an analysis, all nodes except the start node and the destination node were identified, they were re-categorized as assigned nodes. Fig. 4.9 shows the graphical representation of the shortest path calculations in 2D as an illustration. The Euclidean distances between a pair of nodes were calculated using equation 4.6. The tortuosity for each set of start and

destination nodes was calculated as a ratio of two values: the shortest distance between the pair of nodes following the skeleton; and the Euclidean distance.

Euclidean distance = 
$$\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}$$
 (4.6)



Figure 4.7: Skeleton representation of the porosity in the as-reduced specimen. The skeleton is represented by nodes (spheres) and segments (lines connecting spheres).

The skeleton paths for a few sets of nodes from two interfaces were close to straight lines, which gave tortuosity values slightly higher than 1. Other sets of nodes had curvilinear skeleton paths, giving tortuosity values much higher than 1. The tortuosity calculated using the skeletonization method yielded multiple tortuosity numbers, one for each pair of nodes from two interfaces. The tortuosity for each pair of nodes was summarized in the form of a tortuosity distribution map for the porous phase of the asreduced specimen (Fig. 4.10 (a)). The *x*-axis of the tortuosity distribution map has a set of nodes on the anode/electrolyte interface, and the *y*-axis of the map has a set of nodes on

the anode/ACC interface. The pore phase of the as-reduced specimen has a tortuosity range from 1.6 to 3.4. The tortuosity distribution map highlighted the pair of nodes with the highest and the lowest tortuosity (Fig. 4.10 (a)). Most pairs of nodes have tortuosity between 1.5 and 2.3 (Fig. 4.10 (b)).



*Figure 4.8: Algorithm for calculating the tortuosity based on the shortest distance between a pair of nodes* 



Figure 4.9: Schematic of the shortest path calculation in 2D. The algorithm calculates all the paths between the start node and the destination node and determines the shortest path (red) based on the distance.

Average values of tortuosity were calculated from tortuosity distribution maps for the pore phase of cells tested at 800 °C (Table 4.4). The standard deviations of the tortuosity distributions ranged from 0.25 - 0.50. The range of tortuosity (minimum tortuosity to maximum tortuosity) varied from specimen to specimen. Tortuosity calculated using the center-of-mass method (values from Table 4.3, included in Table 4.4) decreased with increasing time of operation. However the trend was reversed for tortuosity calculated using the skeletonization method (Table 4.4). For the as-reduced specimen, the average tortuosity was 1.82. It increased for the tested sample to the range of 2.60 - 2.80. The difference between the minimum tortuosity and maximum tortuosity increased as well. The increase in tortuosity for cells after operation may be due to widening the range of tortuosity.

In the skeleton method, the location of a node on the interface and its connectivity with a node from the other interface strongly influenced the tortuosity calculation. Straight skeleton paths yielded low values of tortuosity, while curved paths yielded higher tortuosity values. Unlike the center-of-mass method, skeleton paths are not restricted to progress in the forward direction only, and in all samples progressed forward and backward depending on the skeleton structure and the set of selected nodes (Fig. 4.11). The skeleton method therefore gave higher tortuosity values and did not show a distinct trend of tortuosity with time of operation.



Nodes on Anode - Electrolyte Interface

<sup>(</sup>a)



(b)

Figure 4.10: (a) The tortuosity distribution map for set of nodes from the anode/ACC interface and the anode/electrolyte interface for the pore phase of the as-reduced sample. (b) Histogram of the tortuosity for each pair of nodes calculated using the skeleton approach for the pore phase of the as-reduced sample.

	Skeleton method		Center-of-mass method	
	Tortuosity	Range		
As-Reduced	1.82 ± 0.25	(1.43 - 3.42)	2.60	
800 °C / 2 kh	$2.82 \pm 0.50$	(1.94 - 5.28)	2.10	
800 °C / 4 kh	2.67 ± 0.41	(1.80 - 5.10)	1.50	
800 °C / 8 kh	$2.56 \pm 0.40$	(1.72 - 3.97)	1.43	

Table 4.4: Tortuosity of the pore phase, calculated using the skeleton method and the center-of-mass method. The skeleton method gives a range of values of tortuosity due to analyzing multiple pairs of nodes from two interfaces. The center-of-mass method gives a single value for tortuosity.



Figure 4.11: Shortest path (highlighted in red) following a skeleton structure between a pair of nodes on the anode interfaces. The path is more curved as the skeleton structure directs it to the back face of the reconstructed anode before reaching the destination node (front top corner) on the anode/electrolyte interface.

## 4.4 Representative Sample Volume (RSV)

Even with advances in instrumentation and computational power, it is impractical to reconstruct the entire anode. Obtaining optimal SEM images requires slicing and imaging at relatively slow speeds, which is expensive and time-consuming. It is therefore common to reconstruct a portion of the entire anode volume.

In three-dimensional reconstruction of actual microstructures, the question of whether the volume of the reconstructed region is representative of the whole sectioned area is always critical. The size of the minimum volume needed to capture the characteristics of the entire anode could be different for homogeneous and heterogeneous microstructures. To compare the anode microstructure of the as-reduced specimen to the tested specimen and to draw meaningful conclusions, the reconstructed volumes should be larger than the minimum representative anode volume.

Previous reports on 3-D reconstruction of SOFC anodes have analyzed volumes of  $109 - 1121 \ \mu m^3$  [38, 54-56]. The 'cubic expansion method' was proposed to calculate the minimum sample volume based on changes in porosity only [57]. However, that technique might not be appropriate if a significant gradient exists in some microstructural parameter, as was observed for volume fractions of nickel and porosity in tested cells in this work (§4.2.2 - 4.2.3).

As an alternate method to calculate RSV, a corner of the reconstructed anode volume was selected as a vertex. The lengths of the reconstructed volume in the *x*- and *y*-directions were each divided into ten segments (Fig. 4.12 (a)). To ensure that the volume fraction gradient did not affect the RSV calculation, the thickness of the reconstructed volume in the *z*-direction (i.e., across the anode) was not subdivided. Dividing the reconstructed volume in this way generates 10 sub-volumes with volumes of 1%, 4%, 9%, to 100% of the reconstructed anode volume. Volume fractions of the three phases were calculated for each sub-volume (Fig. 4.12 (b)). The changes in volume fractions of the three phases were calculated for two consecutive sub-volumes using equation 4.7 (Fig. 4.12 (c)). RSV was determined when the changes in the volume fraction of all three phases for two consecutive sub-volumes sub-volume sub-volume

% Variation = Phase Volume  $Fraction_{RSV}$  – Phase Volume  $Fraction_{Next Small RSV}$ 

(4.7)

Table 4.5 summarizes values of RSV for the as-reduced cell and cells tested at 800 °C, 860 °C, and 925 °C. Values of RSV for all samples were smaller than the reconstructed anode volumes. So, the reconstructed volumes used for the microstructural analysis here were representative of the SOFC cell anode. Table 4.5 also shows that, as microstructural gradients developed during SOFC operations, larger RSVs were required for comparison to the gradient-free, as-reduced cell.

For the RSV calculation, the origin of the sub-volume was fixed at one corner of the reconstructed anode and the size of the sub-volume increased to find the RSV. To study the effect of the selection of the origin on the calculation of RSV, the origin was moved in both systematic and random manners such that the RSV remained within the reconstructed volume (Fig. 4.13). For the systematic variance analysis, the origin of the RSV moved first in the *x*-direction and then in the *y*-direction (Fig. 4.13 (a)) in constant increments. For the random variance analysis, the origin of RSV moved randomly in the *x*- and *y*-directions simultaneously (Fig. 4.13 (b)).

For the systematic variance analysis, RSV was moved 25 times i.e. 5 increments in the *x*-direction and 5 increments in the *y*-direction. For the random variance analysis, RSV was randomly moved 30 times. Volume fractions of the three phases were calculated for each move. Tables 4.6 and 4.7 show that the average volume fractions for the three phases were the same as the volume fractions of the RSV within small standard deviations. Moreover, average volume fractions were almost the same for systematic and random approaches. The results indicate that the origin has no effect on determining the RSVs for the microstructural analysis.



Figure 4.12: (a) Schematic illustration of the reconstructed volume divisions for the RSV analysis. (b) Volume fractions of the three phases in the anode for each sub-volume of 800 °C/2 kh (c) Volume fraction variance for two consecutive sub-volumes of 800 °C/2 kh to determine RSV. For 800 °C/2 kh, the RSV was 64% of the total reconstructed volume.

Sample	RSV (µm <sup>3</sup> )	Total Volume (µm³)
as-reduced	407.1	1130.6
800 °C / 2 kh	914.5	1407.6
800 °C / 4 kh	825.2	1558.0
800 °C / 8 kh	918.3	1130.0
860 °C /4 kh	353.7	994.3
860 °C /8 kh	517.0	1364.3
860 °C /16 kh	769.0	1599.2
925 °C / 2 kh	695.8	1445.0
925 °C / 4 kh	652.0	1253.7

 Table 4.5: Representative sample volume (RSV) and total reconstructed

 volume for the as-reduced specimen and the tested specimen.



Figure 4.13: RSV origin moving in systematic manner (a) and in random manner (b)

In summary, the statistical analysis of volume fractions using RSV as a base volume confirmed the reproducibility of the results and homogeneity of the anode microstructure in x- and y- directions. Furthermore, the results were not impacted by the selection of the RSV origin.

	Aver	age volume fra	action	Sta	andard Deviati	on
Sample	Ni	YSZ	Pore	Ni	YSZ	Pore
as-reduced	0.29	0.43	0.28	0.005	0.001	0.005
800 °C / 2 kh	0.36	0.43	0.21	0.004	0.004	0.006
800 °C / 4 kh	0.31	0.42	0.27	0.009	0.001	0.008
800 °C / 8 kh	0.28	0.38	0.34	0.003	0.002	0.004
860 °C / 4 kh	0.23	0.40	0.38	0.008	0.012	0.017
860 °C / 8 kh	0.32	0.37	0.31	0.014	0.010	0.009
860 °C / 16 kh	0.32	0.41	0.27	0.006	0.005	0.005
925 °C / 2 kh	0.24	0.35	0.41	0.016	0.006	0.014
925 °C / 4 kh	0.28	0.41	0.31	0.005	0.003	0.006

Table 4.6: Average Volume Fraction with standard deviation for Ni, YSZ and pores for systematically selected RSV in the reconstructed volume (N=25)

Sample	Aver	age volume fra	action	Sta	andard Deviati	ion
	Ni	YSZ	Pore	Ni	YSZ	Pore
as-reduced	0.29	0.41	0.30	0.007	0.001	0.001
800 °C / 2 kh	0.36	0.42	0.22	0.006	0.006	0.008
800 °C / 4 kh	0.32	0.42	0.26	0.007	0.002	0.006
800 °C / 8 kh	0.28	0.38	0.34	0.003	0.002	0.004
860 °C / 4 kh	0.22	0.40	0.38	0.011	0.011	0.019
860 °C / 8 kh	0.31	0.38	0.31	0.012	0.011	0.010
860 °C / 16 kh	0.33	0.41	0.27	0.006	0.004	0.006
925 °C / 2 kh	0.25	0.34	0.41	0.013	0.005	0.011
925 °C / 4 kh	0.28	0.41	0.31	0.007	0.004	0.007

Table 4.7: Average Volume fraction with standard deviation for Ni, YSZ

and pores for randomly selected RSV in the reconstructed volume (N=30)

# 4.5 3D phase connectivity

### 4.5.1 Percolated Volume of each Phase

The anodic half-cell reactions for various fuels are:

$$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$$
 (4.8 (a))

$$CO + O^{2-} \rightarrow CO_2 + 2e^{-} \tag{4.8 (b)}$$

$$CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^-$$
 (4.8 (c))

For these reactions to take place, conducting media must coincide at the so-called triple-phase boundary (TPB). The fuel needs to transport to, and the products of the chemical reaction must transport away from, the reaction sites. The ionic conductor needs to conduct oxide ions to the reaction sites, and the electronic conductor needs to conduct electrons away from the reaction sites. In a SOFC anode, the pores transport the fuel and the steam, YSZ conducts  $O^{2-}$  ions and Ni acts as an electronic conductor, and also as a catalyst for the chemical reaction (Fig 4.14).



Figure 4.14: Paths for transport of electrons, ions and gases in SOFC (Source: https://www.iwe.kit.edu/diplomarbeiten\_1804.php)

The oxygen ions are produced at the cathode and transport through the electrolyte (e.g. YSZ) to the anode reaction sites. Only YSZ that extends from a TPB in the anode to the electrolyte and then to a TPB in the cathode can contribute to cell operation. Similarly, in the LG cells studied here, the source of the fuel is at the PAB. The fuel transports through the PAB and ACC (both of which are porous) to the anode reaction sites. For cell operation, porosity must be continuous from PAB to ACC and finally to the anode reaction sites at TPBs. Interconnects between SOFCs are connected to the ACC layers of single cells in a stack. For effective removal of electrons generated at the anode reaction sites, the Ni phase

in the anode needs to be contiguous with interconnects via a continuous metal phase (Ni) in the ACC.

In a SOFC anode, a *percolated volume* of porosity allows effective mass transport; a percolated volume of Ni offers effective catalysis, and electron transport; and a percolated volume of YSZ offers effective ionic transport to the anode reaction sites. An isolated phase volume, which does not take part in the effective species transport, is called *non-percolated volume*.

The focus of this study is limited to the anode. For the purposes of this research, "percolated" means extending to the relevant boundary for transport of the species for which each phase is needed, i.e. the connectivity of Ni and porosity extend to the anode/ACC interface, and the connectivity of YSZ extends to the anode/electrolyte interface.

Fig. 4.15 schematically shows percolated and non-percolated volumes in a 2D anode. Volume A extends from the anode/electrolyte interface to the anode/ACC interface, which makes it a percolated volume for any phase. Volume B extends to the anode/electrolyte interface which makes it percolated for the YSZ phase. Volume C extends to the anode/ACC interface which make it percolated for the Ni phase and the porous phase. Volumes D and F are non-percolated volumes as they extend only to the non-useful anode interface for the respective phases. Volume G is the non-percolated for any phase as it does not extend to any anode interface.





Figure 4.15: Definition of percolated volumes (light green) and nonpercolated volumes (dark orange). Percolated volumes span across the anode (Volume A), connected to the anode-electrolyte interface for YSZ (Volume B) or connected to the anode-ACC interface for Ni and pores (Volume C).

To separate the percolated and the non-percolated volumes for each phase, the reconstructed anode data was exported from Amira<sup>TM</sup> (FEI) to MatLab<sup>TM</sup>. A MatLab<sup>TM</sup> routine was developed for the separation of the phase volumes based on their percolation bases (Fig. 4.16). All the voxels in the volumes went through an iterative process to verify their connectivity with the appropriate anode interfaces. For faster execution of the program, the connectivity of each voxel with the anode interface was determined by a forward sweep and a backward sweep. The forward sweep started at the respective interface for the each phase of the anode, (i.e. for Ni and porosity, the anode/ACC interface) and progressed towards the other interface. In each step, the voxels of one layer were identified as percolated if they were connected to the voxels of the same phase of the provious layer. Once the forward sweep reached the other interface, (i.e. for Ni and porosity, the anode/electrolyte interface), the backward sweep started and progressed

towards the original interface. The forward and backward sweeps assigned most of the voxels, if not all, to the correct percolated phase. Depending on the shape of the phase volume, some voxels could not be identified as percolated by the forward and the backward sweeps. In the next step, 'Voxel by Voxel' (VBV) operation was performed to identify those voxels that were not identified by the forward and the backward sweeps. VBV was an iterative process that continued to identify the percolated voxels until all the voxels were assigned correctly. The iterative algorithm was much faster in the case of the forward and the backward and the backward sweeps followed by the VBV operation than by just the VBV operation only.

All the voxels in the original reconstructed anodes were initially labeled 1, 2 and 3 for porosity, YSZ and Ni respectively. If the voxel was found to be percolated, their label was changed to 4, 5 or 6 for percolated porosity, YSZ and Ni respectively. The labels for the voxels of the non-percolated volumes remained the same as before.

The new data file with assigned percolated and non-percolated volumes was imported in Amira<sup>TM</sup> for visualization and analysis. Amira<sup>TM</sup> treated the data as 6 different materials based on the voxels' label assignments. Fig. 4.17 shows the percolated and non-percolated volumes for three phases in the as-reduced specimen.



Figure 4.16: Flow chart for an algorithm to distinguish percolated volumes from non-percolated volumes.



Figure 4.17: Separated percolated and non-percolated volumes for the asreduced specimen. The percolated volumes are labeled as Ni (royal blue), YSZ (red) and P (pore, white) and the non-percolated volumes are labeled as Ni' (beige), YSZ' (blue-gray) and P' (light blue).

In the as-reduced specimen, most of the phase volume was percolated (Fig. 4.18 (a)). The regions of the phases on the boundaries of the reconstructed volumes did not appear to be connected to their respective interfaces in the boundary plane. However, the three-dimensional distribution of the phases connected them to respective interfaces. In contrast, the non-percolated volumes were small and isolated (Fig. 4.18 (b)). As expected, the non-percolated volumes of Ni (Ni'), and porosity (P') were close to the anode/electrolyte interface. The non-percolated volumes of YSZ (YSZ') were close to the anode/ACC interface.







(b)

Figure 4.18: (a) Percolated volumes of Ni (blue), YSZ (red) and porosity (transparent) in the as-reduced specimen (b) Non-percolated volumes of Ni (yellow), YSZ (dark blue) and porosity (light blue).

It is essential to understand whether the percolated phase volume is one continuous volume or consists of multiple separate volumes. In the case of pores, a continuous percolated porous phase could offer efficient mass transport through multiple flow paths to and from the anode reaction sites. For the as-reduced specimen, the percolated volumes of each phase consisted of several isolated volumes (Fig. 4.19). Ni, porosity and YSZ had 29, 19, and 19 percolated volumes respectively. One of the percolated volumes for each phase was dominant and had the largest volume. The rest of the percolated volumes were very small (< 5  $\mu$ m<sup>3</sup>). The largest percolated volume of Ni was 324.4  $\mu$ m<sup>3</sup> out of 326.7  $\mu$ m<sup>3</sup> total Ni percolated volume. Similarly, the largest percolated porosity volume was 458.3  $\mu$ m<sup>3</sup> (out of 458.9  $\mu$ m<sup>3</sup> total) and the largest percolated YSZ volume was 458.3  $\mu$ m<sup>3</sup> (out of 458.9  $\mu$ m<sup>3</sup> total). In the reconstructed volume, those percolated volumes were separate. However, if the reconstructed volume is extended into the adjustant layers, electrolyte and ACC, the separated volume could be connected to the extention of the largest percolated volume of the anode in the adjustant layer.

The results were similar for the samples tested at 800 °C, 860 °C and 925 °C. So even though there was a depletion of Ni at the anode/ACC interface (Fig. 4.2 (a), 4.3 (a) and (c)), the Ni volume remained percolated during the operation of the SOFC.

By definition of the non-percolated volume, there is an increased probability of having non-percolated Ni and porosity close to the anode/electrolyte interface, and non-percolated YSZ close to the anode/ACC interface. Fig. 4.20 plots volume fraction variation of non-percolated volumes across the anode thickness for the as-reduced specimen. Here, z = 0 corresponds to the anode/electrolyte interface. Overall, the volume fractions of the non-percolated volumes for the three phases were small (0 – 0.03) for the as-reduced

specimen. The volume fractions for non-percolated Ni and porosity were 0.03 and 0.02 respectively at the anode/electrolyte interface. Beyond 1  $\mu$ m from the anode/electrolyte interface, the volume fractions of non-percolated volume for those two phases were close to zero for the rest of the anode thickness. The volume fraction of the non-percolated YSZ was close to zero for the entire anode thickness.



Figure 4.19: For the as-reduced specimen, the percolated volume of porosity, Ni and YSZ were made up of 19, 29 and 19 volumes respectively. One of the volumes of each phase was largest with volume close to total percolated volume for the phase.



*Figure 4.20: Non-percolated volume fraction variation across anode thickness for the as-reduced specimen.* 

	Percolated Volume (µm <sup>3</sup> )			Non-Percolated Volume (µm <sup>3</sup> )		
	Ni	Pores	YSZ	Ni	Pores	YSZ
As-Reduced	326.7	331.1	458.9	5.5	6.1	2.3
800 °C / 2 kh	474.4	284.8	576.9	8.2	9.8	0.9
800 °C / 4 kh	446.5	461.3	621.6	11.8	4.0	4.0
800 °C / 8 kh	285.2	358.2	412.4	21.3	5.3	5.6
860 °C / 4 kh	145.0	353.8	346.0	34.4	0.3	3.7
860 °C / 8 kh	409.7	399.0	496.3	7.6	1.0	3.1
860 °C / 16 kh	496.4	438.9	635.3	5.8	2.6	1.8
925 °C / 2 kh	286.4	577.2	473.6	35.8	1.1	4.9
925 °C / 4 kh	344.3	356.8	490.7	16.7	6.5	1.0

 Table 4.8: Percolated volume and non-percolated volume of Ni, porosity

 and YSZ for as-reduced specimen and tested specimen.

For all samples, non-percolated volumes of the three phases, Ni, porosity and YSZ were very small in comparison to the percolated volumes (Table 4.8). Though the percolated volumes of the three phases were made up of multiple volumes, one of the volumes of each phase had volume close to the total percolated volumes.

#### 4.5.2 Triple Phase Boundary (TPB)

Triple phase boundaries (TPB) — curvilinear boundaries in the electrodes where pore, electronic conductor and ionic conductor meet — are essential to the functioning of all fuel cells. For the SOFC anodes studied here, TPB is defined as a boundary where pore, nickel metal and zirconia meet.

Various methods have been reported for calculating TPB in 3D reconstructed anodes. In the Cartesian arrangement of voxels used in this study (and most other studies), each voxel edge (except those on the outer faces of the reconstructed volume) is shared by four voxels. An edge will form a section of TPB if at least one voxel each of pore, metal and ionic phase meet at their shared edge. One fourth of that TPB edge could be assigned to each of the neighboring voxels. The approach of Golbert et al. [58] divides the number of voxels adjacent to the TPB by 4 and multiplies the result by the voxel edge length to give TPB length. Suzue et al. [59] counted the cubic perimeter of all voxels adjacent to TPB and assumed that TPB is 20% of the calculated length.

Iwai et al. [22] has proposed the volume expansion method and the centroid method. In the volume expansion method, the volume of each phase in the reconstructed anode is expanded numerically. The intersection of the three expanded phases forms a tube-like volume. The center line length of the tube-like structure was reported as the TPB length. In the centroid method, the TPB edge is calculated by comparing the four neighboring voxels. The mid-points of the three consecutive TPBs were used to form triangles. The centroids of these triangles formed TPBs. Both of these methods aimed to reduce the over-estimation of TPB lengths due to its step-wise nature in 3D reconstructed anodes. Iwai et al. found positive correlation of the results from both of these results with the TPB length calculated by the stereological method (described in the next paragraph).

Smith et al. [60], Wilson et al. [54] and Vivet et al. [38] calculated TPB by the stereological method, which is also used for this project. The method is an extension of the traditional 2D stereological method to 3D. Instead of analyzing the 2D images in only one direction, the sections of reconstructions are analyzed in x-, y- and z-directions. The following method to calculate TPB is based on the procedure published by Vivet et al. [38].

To determine whether an edge is a TPB, 4 co-planar voxels in the *x*-*y* plane, labeled  $V_B$  (the base voxel),  $V_X$ ,  $V_Y$  and  $V_{X+Y}$  (Fig. 4.21), are compared. If at least two of the three neighboring voxels are assigned to phases other than that of the base voxel, the top-right edge of voxel V<sub>B</sub> is TPB. This comparison is iterated in the *x*- and *y*- directions to calculate

TPB in a particular plane (slice). This process is repeated for all the slices of the reconstructed anode.



Figure 4.21: 4 co-planar voxels to calculate TPB for voxel VB.

Fig. 4.22 shows preliminary results of TPB identification in one of the slices of the as-reduced specimen. In a 2D image, TPB appears as points where the boundary intersects the plane of the image.

The algorithm for calculating TPB points in 2D was repeated for all the slices in the *x*-, *y*-, and *z*-directions (Fig. 4.23). The TPB points calculated in each slice were multiplied by the voxel edge length in the direction perpendicular to the slices, to convert TPB points to TPB lengths for the particular slice. The sum of the TPB lengths of each slice equals the total TPB length for the reconstructed anode.

In typical SOFC electrodes, triple-phase boundaries are curvilinear microstructural features within the electrode volume. To compare the results of TPB lengths from sample to sample, TPB lengths are normalized to the volume, referred as 'TPB density'. Therefore, TPB density has units of length per unit volume or  $\mu$ m<sup>-2</sup>.





The TPB calculated using this approach follows the edge of each voxel. The voxels for all the reconstructed anodes are rectangular blocks, so the reconstructed TPB consists of line segments connected at right angles to each other to approximate the actual curvilinear TPB.

Only TPBs that contact percolated volumes of all three phases (Ni, YSZ and porosity) can contribute to the functioning of the cell and are therefore termed "active" TPBs. Any TPB that is adjacent to at least one non-percolated phase volume is inactive. The active TPBs do not need to extend to either the anode/electrolyte interface or the

anode/ACC interface to be effective. The active TPBs could lie entirely inside the anode as long as the three phases bordering them are percolated volumes, i.e. extend to the respective interfaces.



Figure 4.23: The schematic of 3D TPB calculation in x-, y-, and z-directions in a reconstructed anode.

Total TPB and active TPB densities for the as-reduced specimen were  $5.2 \,\mu\text{m}^{-2}$  and  $4.4 \,\mu\text{m}^{-2}$  respectively. (The inactive TPB density is the difference in total and active TPB densities.) Almost all the volumes of the three phases in the as-reduced specimen were percolated (Table 4.8), which yielded a small difference between total and active TPB densities (Table 4.9). This difference was small as well for all other tested samples except for 860 °C / 4 kh and 925 °C / 2 kh, which had larger volume fractions of non-percolated Ni, 0.04 and 0.03 respectively.

	Total TPI	$\Lambda_{\rm otive}$ TDP $(\rm um^{-2})$	
	Full 3DR Volume	RSVs (N=4)	Acuve IPB (µm)
As-Reduced	5.2	5.0 ± 0.2	4.4
800 °C / 2 kh	3.8	3.9 ± 0.2	3.0
800 °C / 4 kh	3.0	3.0 ± 0.1	2.6
800 °C / 8 kh	2.7	2.7 ± 0.0	2.1
860 °C / 4 kh	2.7	2.7 ± 0.1	1.8
860 °C / 8 kh	2.9	3.1 ± 0.2	2.6
860 °C / 16 kh	2.2	2.3 ± 0.1	2.0
925 °C / 2 kh	2.3	2.3 ± 0.1	1.7
925 °C / 4 kh	2.5	2.5 ± 0.0	1.9

Table 4.9: Total TPB density and active TPB density for the as-reduced cell and cells tested at 800 °C, 860 °C and 925 °C. Total TPB density of the RSVs is the average TPB density of four subvolumes, equal in size to the RSV of the corresponding specimen, followed by the standard deviation.

At 800 °C, the active TPB density decreased significantly, from 4.4  $\mu$ m<sup>-2</sup> to 3.0  $\mu$ m<sup>-2</sup>, in the first 2 kh of operation. Thereafter the decrease in active TPB was gradual: to 2.6  $\mu$ m<sup>-2</sup> from 2 to 4 kh and to 2.1  $\mu$ m<sup>-2</sup> from 4 to 8 kh of operation. At 860 °C, the active TPB density was 1.9  $\mu$ m<sup>-2</sup> at 2 kh which was lower than 860 °C / 8 kh and 860 °C / 16 kh. This anomaly for 860 °C / 4 kh coincided with the other anomalous results from this sample, i.e. the values of the slopes of Ni and porosity profiles across the anode thickness, low volume fraction of Ni, etc. The active TPB density for 860 °C / 16 kh was comparable to 800 °C / 8 kh. However, the active TPB dropped significantly for 925 °C / 2 kh and leveled off for 925 °C / 4 kh.

To assess the experimental uncertainty in values of TPB density as measured by the stereological method, the values were recalculated from four subvolumes in each of the nine specimens studied in this work. The size of each subvolume was the RSV previously determined for each specimen (Table 4.5), and (as in Figure 4.12) each subvolume had the same thickness (between the anode-electrolyte interface and the anode-ACC interface) as that of the entire analyzed sample volume. To minimize overlap of the subvolumes, each was placed at a different vertex of the larger volume that had been reconstructed from each anode. Table 4.9 compares values of TPB density of the larger reconstructed volume to the average TPB density of the subvolumes.

Total TPB density of the entire anode volume fell within the range of the average TPB density  $\pm$  the standard deviation computed from the subvolumes (N = 4) for all nine cells. The standard deviations of TPB density ranged from  $\pm 0.0$  to  $\pm 0.2 \ \mu m^{-2}$ , and from  $\pm 0.1$  to 4.4% of the values obtained for the whole analyzed volume. The reconstructions of these nine specimens used four different voxel sizes (Table 3.2), but the standard deviations of the TPB density do not vary systematically with the voxel sizes. By these measures, the reproducibility of the values of TPB density computed using the stereological method was  $\pm 4.4\%$  or better.

TPBs identified in the stereological method always follow the x, y and/or z edge of the voxel. The stepwise nature of TPB is inherent in the method and approximate the curvilinear shape of TPB. Two consecutive segments of TPB could be in the same line or orthogonal to each other. The computed length of the TPB would be most accurate when the actual TPB is a straight line. The orthogonal segments in TPB length could underestimate or overestimate the TPB length (Fig. 4.24). If the true TPB is represented by curve 1, the stepwise TPB would overestimate the TPB length. In contrast, if the true TPB is represented by curve 2, the stepwise TPB would underestimate the TPB length. The accuracy of the TPB length could be improved by reducing the step sizes in TPB, i.e. reducing the voxel size. Once the 3D FIB/SEM experiment is completed, it is possible to increase the voxel size during 3D reconstruction process by resampling i.e. merging the voxels. But it would be impossible to reduce the voxel size from the original voxel size. Also, it is very expensive and time consuming to run the FIB/SEM experiment multiple times with different resolutions before hardware constraints are met.



Figure 4.24: The stepwise TPB could overestimate (a) or underestimate (b) the actual TPB. The true TPB is represented by curve 1(a) and curve 2 (b). The overestimation or underestimation of TPB length would depend on the shape of TPB curve and the size of the steps

By definition, TPB is formed by boundaries of three phases. A novel method for calculating TPB is proposed here to calculate TPB per this definition. The accuracy of TPB density calculated using the stereological method was checked by calculating TPB density by the intersecting surfaces.

It would be impractical to represent 3D contour surfaces such as the encompassing phase surfaces in SOFC anodes by equations. To represent the surfaces mathematically, the phase surfaces are meshed using a triangularization method. This allows the phase surfaces to be represented as a group of triangles and nodes forming the triangles. To illustrate this concept, in Figure 4.25 (a) a YSZ particle (light blue) and a Ni particle (golden) are represented as spheres. The third phase, porosity, is the space around the spherical particles. The solid particles were meshed using a surface triangular mesh (Fig. 4.25 (b)). Each triangle is the interface surface between two phases. The alternate red and yellow line segments in Fig. 4.25 (c) are the common edges of triangles forming YSZ and Ni surfaces, i.e. TPB.

Like the stereological method, the TPB obtained with this method is also formed by small line segments. But the angle between two consecutive line segments are not restricted to 90°, which allows the computed TPB potentially to be closer to the true shape of the TPB. As in the stereological method, the accuracy of TPB length would depend on the size of the triangle. However, the same FIB/SEM data could be used to obtain smoother triangular meshes to improve the accuracy until the hardware limitations on the computations were met.

It is worthwhile to note here that the same triangulation data were used to compute the interfacial area between two phases. Instead of common edge of triangles from the three phase surfaces, the common triangles in two phase surfaces are considered. The interface area is the total area of all the common triangles to two phases. Interface areas were used in the calculation of phase particle diameter (Equation 4.2).



Figure 4.25: (a) Simplified model of three phase structure: YSZ (light blue), Ni (golden) and porosity (transparent) (b) Triangular mesh representation of Ni and YSZ surface (c) Magnified view of TPB formed by common edge of YSZ and Ni triangular mesh elements.

Amira<sup>TM</sup> was used to form the surfaces encompassing the phases, and to mesh the surface with triangularization. The latest Amira<sup>TM</sup> version (5.5.6) allows visualization of the common line (i.e. TPB) formed by the intersecting surfaces, but it does not allow

calculation of the length of the common lines. To calculate the TPB length using the surface intersection method, a Matlab program was developed. First, the phase surfaces were meshed with triangular elements. The standard routine of Amira<sup>TM</sup> generate optimum amount of triangular mesh elements to preserve the shape of the phase volumes. The optimum number of triangles are referred as 100% quality mesh in this study. The triangle mesh was coarsened to get 75%, 50% and 25% of the optimum mesh elements to study the effect of mesh quality on TPB density calculation. The triangular meshed data were exported from Amira and used as the input for the Matlab program. Figure 4.26 presents the algorithm for calculating the TPB density using the surface intersection method.

Typically, the number of triangular mesh elements required for smoother surfaces is very large. For example, in the as-reduced specimen, Ni, YSZ and porous phase were formed by 3.2E+06, 3.7E+06 and 2.6E+06 triangles respectively. Such large data sets require higher computational power and long processing time. The processing data requirement could be reduced significantly by representing the phase surfaces by fewer mesh elements. Care must be taken to ensure that the accuracy of the TPB density is not compromised by reducing the number of triangular elements.



Figure 4.26: Algorithm for TPB density calculation by surface intersection.

Figure 4.27 summarizes the effect of triangular mesh quality on TPB density for the as-reduced specimen. Here, 100% mesh quality represents the optimum number of mesh triangles calculated by Amira<sup>TM</sup> to represent the phase surfaces. 75% mesh quality has 75% of the original total triangular mesh elements and so on. 100 % mesh quality has TPB density of 3.3  $\mu$ m<sup>-2</sup>. For the same sample, TPB density calculated using the stereological method was 5.2  $\mu$ m<sup>-2</sup> (Table 4.9). Wilson et al. [39] calculated TPB for a hypothetical structure of spherical particles using the stereological method to quantify the overestimation of TPB using stereological method. The author determined that the TPB

density calculated using the stereological method had to be divided by a correction factor of 1.455 to yield 'true' TPB density. Applying the same correction factor to the total TPB density of the as-reduced cell yielded 'true' TPB density  $3.6 \ \mu m^{-2}$ , which is much closer to, but still 9% higher than, the TPB density calculated by surface intersection. The TPB density by surface intersection method increases as the mesh quality decreases. The increase in TPB density is more in first 25% reduction in mesh quality and is gradual for further reduction in mesh quality.



Figure 4.27: Effect of triangular mesh quality on the TPB density using surface intersection method in the as-reduced specimen. 100 % mesh quality corresponds to highest number of triangular elements used for phase surface representation.

Even though TPB density calculated with 25% mesh quality was higher than the TPB density calculated with 100% mesh quality for the as-reduced specimen, the difference was relatively small. For the cells tested at 800°C, the TPB density was calculated using 25% mesh quality (Table 4.10). For these cells, the TPB densities calculated using the two methods were in excellent agreement, with differences smaller than 0.2  $\mu$ m<sup>-2</sup> (Table 4.9). This better agreement could result from having used a smaller voxel size for the 800 °C cells in the stereological method. The resolution of voxels in the *x*- and *y*-directions for samples tested at 800°C was 0.009  $\mu$ m, compared to 0.027  $\mu$ m for the as-reduced specimen, and the voxel volumes were 1.2E-05  $\mu$ m<sup>3</sup> versus 3.6E-05  $\mu$ m<sup>3</sup>.

	Total TPB Density
	(µm <sup>-2</sup> )
As-Reduced	3.75
800 °C / 2 kh	3.63
800 °C / 4 kh	3.03
800 °C / 8 kh	2.63

Table 4.10: Total TPB density for the as-reduced cell and cells tested at 800  $^{\circ}$  by the surface intersection method

The effect of high quality mesh on the finer resolution was checked by calculating the TPB density for 800 C / 8 kh. For 800 C / 8 kh, TPB density calculated using 100% mesh quality was 2.16  $\mu$ m<sup>-2</sup>. The difference between the results for 25% mesh quality and 100% quality mesh was similar for the as-reduced specimen (0.45  $\mu$ m<sup>-2</sup>) and the 800 C / 8 kh cell (0.47  $\mu$ m<sup>-2</sup>).

This analysis suggests that the stereological method and the surface intersection method can yield similar values of TPB density if the voxel size for the latter method is sufficiently fine. The consistency between the two methods in the trend of TPB density with testing time in the 800 °C cells suggests that either method can yield accurate relative variations between specimens, but that values of TPB density computed using different methods might not be comparable to each other without a comparison like that conducted here on the 800 °C specimens. For subsequent discussions in this section, TPB density by stereological method was used.

#### 4.5.3: TPB density profile across the anode thickness

The presence of three phases; Ni, pore and YSZ; is required to form TPB. As discussed in §4.2.2, Ni and pore phase redistributed during the cell operation. The volume fraction of Ni phase increased towards the anode/electrolyte interface and decreased towards the anode/ACC interface. As the presence of both phases is important to form TPB, it would be of interest to study the effect of the phase redistribution on TPB density across the anode thickness.

Fig. 4.28 (a) depicts the TPB density variation across the anode thickness for the as-reduced specimen. The volume fraction profiles for three phases were uniform for the as-reduced cell. So, the total TPB density and active TPB density were expected to have uniform profiles. However, it was interesting that the total TPB density and active TPB density profiles were uniform across the anode thickness for 925 °C / 4 kh (Fig. 4.28 (b)) as well. For the same sample, the slope of Ni and pore profiles were -0.047  $\mu$ m<sup>-1</sup> and 0.041  $\mu$ m<sup>-1</sup> respectively. The growth pattern for Ni and pore phases had opposite trends and might be negating the effect of growth which maintained the uniformity in TPB profiles. The TPB density profiles across the anode thickness for other samples were similar (Appendix C).






Figure 4.28: Total TPB density and active TPB density profile across the anode thickness for the as-reduced sample (a) and 925 C/4 kh (b)

For the as-reduced specimen, the differences between total TPB density and active TPB density at the anode/electrolyte interface and the anode/ACC interface were 0.4  $\mu$ m<sup>-3</sup> and 0.2  $\mu$ m<sup>-3</sup> respectively (Fig. 4.28 (a)). The larger differences between two TPB densities at the anode/electrolyte interface could be due to presence of relatively large volume fraction of non-percolated Ni and pore volumes close to the anode/electrolyte interface (Fig. 4.20).

# 4.6 Quantification of phase coarsening

### 4.6.1 Introduction

SOFC anode microstructure changes significantly with operation time and temperature. As reported in §4.2.1, the particle diameters of pores and Ni are smallest for the as-reduced cell. The diameters for these two phases increased with operation time and temperature. Equation 4.2 calculates the particle diameter using the entire phase volume and surface area. Even though it showed the trend of particle growth for Ni and porosity, it ignored the effect of phase redistribution discussed in §4.2.2 where gradients were formed for Ni and pores.

The YSZ phase is stable in typical SOFC operating conditions. In this research also, volume fractions of YSZ was uniform for the as-reduced cell and the tested cells (§4.2.2 and Appendix A). In contrast, Ni and pore phases redistributed in the anode during cell operation. In this section, the effects of phase distribution on the particle diameter of Ni and pore phases are studied. In the literature, Ni coarsening in SOFC is commonly discussed using particle size distribution (PSD) [32, 61, 62]. Traditionally, PSD was developed using 2D analysis of the images. An improved PSD approach was used here to

study the particle diameter and its distribution, offering more insight into the shape of the phase and quantifying the Ni coarsening.

The 3D reconstructed anode was virtually sectioned in the direction from the anode/electrolyte interface to the anode/ACC interface. The regions of the phase under consideration were identified. The process is illustrated with pores in the as-reduced sample. Fig. 4.29 shows one of the sections of the as-reduced specimen. The pores (red) were identified in the section. Area-based diameters were calculated for each pore in the section (equation 4.9). In the next step, the average diameter was calculated by averaging area-based diameters in the section. The process was repeated for each phase in each section. The results for Ni and pore phases are discussed in § 4.6.2 and § 4.6.3 respectively.

$$D_A = \sqrt{\frac{4A}{\pi}} \tag{4.9}$$



Figure 4.29: One of the sections of the as-reduced specimen. The three phases are Ni (green), YSZ (yellow), and porosity (red). In this example, 39 discrete regions were identified as pores for calculating average pore size for the section.

# 4.6.2 Ni Phase coarsening

Fig. 4.30 (a) shows the average particle diameter of Ni across the anode thickness for the as-reduced specimen. Anode thickness = 0  $\mu$ m corresponds to the anode/electrolyte interface. Fig. 4.30 (a) shows that the average particle diameter was not constant across the anode for this specimen. But the linear curve fit indicated a fairly uniform average particle diameter across the anode thickness with only a small gradient. The trend is very similar to the volume fraction profile across the anode thickness for this specimen (Fig. 4.2 (a)).

For cells operated at 800 °C, the effect of Ni phase redistribution on the average particle diameter was apparent (Fig. 4.30(b)). Though the variation is noisy, a negative gradient is evident, as with the volume fraction variation (Fig. 4.2 (a)). The average Ni diameter increased from 0.7  $\mu$ m to 1.25  $\mu$ m at the anode/electrolyte interface. A similar trend existed at the anode/ACC interface, where the average Ni diameter increased from 0.65  $\mu$ m to 0.75 – 1.00  $\mu$ m in 8 kh of cell operation. Though the Ni particle diameter increased at both interfaces, the Ni particle growth was more pronounced at the anode/electrolyte interface. The slope of the Average Ni diameter decreased from -0.03  $\mu$ m/µm (as-reduced) to -0.08 µm/µm (860 °C / 8 kh) (Table 4.11).

Similar trends were observed at higher operation temperature, i.e. 860 °C and 925 °C. To simplify the graphical representation, Fig. 4.31 shows just the linear best-fit trend lines for the average Ni particle diameter. For both temperatures, there was a gradual increase in Ni particle diameter at the anode interfaces. At 860 °C, the Ni particle growth was similar to 800 °C up to 8 kh. However operating the cell for 16 kh increased the Ni particle diameter to 1.6  $\mu$ m at the anode/electrolyte interface. The effect of temperature on Ni particle growth was realized by comparing the Ni particle diameter at the anode/electrolyte interface for

three operation temperatures. For test duration of 4 kh, the Ni particle diameter increased to  $1.35 \ \mu m$  at  $925 \ C$ .







(b)

Figure 4.30: Average Ni particle diameter across the anode thickness for the as-reduced specimen (a) and cells tested at 800  $^{\circ}$ C (b). The dashed line represents the linear curve fits for the dataset across the anode thickness.

	Slope of average Ni diameter profile (μm / μm)			
as-reduced	-0.03			
800 °C / 2 kh	-0.04			
800 °C / 4 kh	-0.06			
800 °C / 8 kh	-0.08			

*Table 4.11: Slope of average Ni particle diameter profile for the as-reduced specimen and cells tested at 800 °C.* 



Figure 4.31: The slopes of Ni particle diameter profile at 860  $^{\circ}$ C (a) and 925  $^{\circ}$ C (b).

The average Ni particle diameter was further studied by analyzing the distribution of Ni diameter per slice. Understanding the Ni particle distribution would give more insight into the driving mechanism for Ni coarsening. Fig. 4.32 (a) plots, for each slice, the maximum diameter of the Ni particle profile in the as-reduced specimen. The minimum diameter was very small in every slice and was therefore excluded from the plot. As with the average Ni particle diameter, the maximum Ni particle diameter across the anode thickness was essentially uniform. However for the tested cells, significant gradients in maximum Ni diameter were evident (Fig. 4.32 (b), (c), (d)), with diameter decreasing from the electrolyte to the ACC. Only results for the maximum test duration at each operating temperature are shown; the observations for other times were similar.



Figure 4.32: The profile of maximum Ni particle diameter for the asreduced specimen (a); maximum and minimum particle diameters for tested samples 800 C / 8 kh (b) 860 C / 16 kh (c) 925 C / 4 kh (d).

There was a small increase in minimum diameter per section for tested samples compared to the as-reduced specimen, but the increase in maximum diameter was more significant. Studying the Ni particle distribution revealed that the trend line of average Ni particle diameter was mainly driven by the growth of maximum Ni particle diameter. The observation made here strongly supports the reports of Ni coarsening in the anode during cell operation [32, 44, 63]. During cell operation, the distribution of Ni particle diameter persists. But the maximum Ni particle diameter grew with cell operation. The growth of Ni particle diameter was greater near the anode/electrolyte interface than to the anode/ACC interface.

# 4.6.3 Porous phase coarsening

The pore phase also exhibited redistribution during cell operation (Fig. 4.2 (b), Fig. 4.3 (b) (d)). The diffusion of Ni towards the anode/electrolyte interface corresponded to porosity movement in the opposite direction, i.e. towards the anode/ACC interface.

Fig. 4.33 (a) plots the average pore diameter across the anode thickness for the asreduced cell. As with the Ni diameter, the average pore diameter is uniform across the anode thickness: ~0.52  $\mu$ m, slightly smaller than the average Ni diameter (~0.67  $\mu$ m).

At 800 °C, a positive gradient developed with cell operation. In the first 2 kh, the average pore diameter was the same as in the as-reduced specimen at the anode/electrolyte interface, but increased to 0.59  $\mu$ m at the anode/ACC interface. With further increase in cell operation time, the average pore diameter increased at both the anode interfaces. The growth was more pronounced at the anode/ACC interface than at the anode/electrolyte interface. The slopes for the linear fit for average pore diameter profiles were smaller than the average Ni diameter profiles (Table 4.12). Although the numerical values of average pore diameter and slope were different for the other samples after cell operation at 860 °C and 925 °C, the trends of pore diameter growth was similar across the anode thickness.



(a)



Figure 4.33: Average pore particle diameter across the anode thickness for the as-reduced specimen (a) and samples tested at 800  $^{\circ}$ C (b).

	Slope of average pore diameter profile (μm / μm)			
as-reduced	0.005			
800 °C / 2 kh	0.008			
800 °C / 4 kh	0.010			
800 °C / 8 kh	0.001			

Table 4.12: Slope of average pore diameter profile for the as-reducedspecimen and cells tested at 800  $\mathbb{C}$ 

For maximum pore diameter in the as-reduced specimen, a significant gradient of 1  $\mu$ m across the 6- $\mu$ m-thick anode was observed (Fig. 4.34 (a)), but this was still smaller than the gradients observed in the operated cells, with the maximum pore diameter increasing from the anode/electrolyte interface to the anode/ACC interface. There was not much change in maximum pore diameter at the anode/electrolyte interface for 800 °C / 8 kh and 860 °C / 16 kh. However for 925 °C / 4kh, it increased to 4.5  $\mu$ m at the same interface. As in the Ni phase, the growth of maximum pore diameter tracked with the growth of average pore diameter across the anode thickness.

# 4.6.4 Conclusion

Ni coarsening in SOFC anodes during cell operation was observed (§ 4.2), as has been reported in the literature [13, 36, 61]. The study of area-based diameter distributions gave more insight into other observed trends such as overall phase particle diameter change and phase volume fraction variation across the anode.



Figure 4.34: The profile of maximum pore particle diameter profile for asreduced sample (a); profiles of maximum and minimum pore diameter for tested samples 800 C / 8 kh (b) 860 C / 16 kh (c) 925 C / 4 kh.

The Ni particle diameter grew at both the anode interfaces, but the growth was more significant at the anode/electrolyte interface than the anode/ACC interface. This growth pattern developed a gradient across the anode. The opposite trends were observed for the pore diameter, as with the volume fraction variation (§4.2.2 and §4.2.3).

# 4.7 Long-term SOFC performance prediction

#### **4.7.1 Introduction**

The Department of energy's SECA program has established a maximum acceptable level of performance loss for SOFCs over 40 kh of cell operation. It is impractical for most lab-scale facilities to test SOFC for up to 40 kh, and iterative studies to refine cell structures and formulations are essentially ruled out. It would be valuable to be able to make reliable predictions of long-term performance loss based on modeling of microstructural changes.

One approach to predicting the long-term degradation of SOFCs has been to develop kinetic models of microstructural changes based on testing for shorter durations in realistic service conditions [16]. Another approach is based on computer simulations [9]. The structural parameters calculated from initial microstructures are input into the simulation to study the long-term evolution of the microstructure. Recently, the prediction of performance based on elevated-temperature ( $1100^{\circ}$ C) testing has been explored [42]. It is assumed that the elevated test temperatures degrade the SOFC in ways representative of SOFCs operated over long periods in normal conditions. An inverse correlation of the elevated temperature with operation time is yet to be proved.

In this study, a long-term prediction model is developed based on microstructure evolution observed in cells tested under normal operating conditions for up to two years (16 kh). The longest durations of SOFC operation here were 8 kh at 800 °C, 16 kh at 860 °C, and 4 kh at 925 °C. The maximum duration of cell testing reported in the literature to date is 4 kh [44].

# 4.7.2 Ni coarsening prediction

Ni coarsening, a well-known microstructural change in composite SOFC anodes [13, 16, 44], was observed (§4.2) in this study as well. Ni coarsening has been associated with degradation mechanisms such as loss of TPBs [34] and reduction in percolation of Ni phase [35]. The correlation of Ni coarsening to loss of electrochemical performance has been also studied [16].

The mass transport processes that lead to growth of Ni particles are thermally activated. Three possible mechanisms for Ni particle growth are evaporation-condensation, surface diffusion, and bulk diffusion. Evaporation-condensation could be significant when small amounts of H<sub>2</sub>O are present [32]. Ni surface diffusivity is of the order of  $10^{-10}$  m<sup>2</sup>s<sup>-1</sup> in comparison to the bulk diffusivity of the order of  $10^{-16}$  m<sup>2</sup>s<sup>-1</sup>[9]. The ratio of surface to bulk diffusivity of  $10^6$ , and a lack of evidence specifically supporting evaporation-condensation, suggests that surface diffusion may dominate the Ni coarsening mechanism [9].

Ni coarsening has been reported to follow Ostwald ripening kinetics [64](equation 4.10) or exponential growth [65](equation 4.11). Simwonis et al. [12] tried to fit their cell performance data to the Ostwald ripening kinetics, but the particle growth predicted by the model was too large compared to loss of cell performance measured. The authors concluded that the differences could be due to some neglected effects in the testing.

YSZ in the SOFC anode restricts Ni coarsening [12, 44]. This effect is not considered in simple Ni coarsening models such as Ostwald ripening and exponential growth. Typically, Ni particles grows much faster in the beginning and reach a plateau in size (§4.2.1). A special model is required to account for such behavior.

The Ostwald ripening model and exponential growth model were applied to the calculated Ni particle diameters (Table 4.1).

$$D^3 - D_0^3 = k_{s,Osw} \cdot t \tag{4.10}$$

$$D = D_0 \cdot \exp(k_{s,Expt} \cdot t) \tag{4.11}$$

with: *D*, diameter at time *t*; *D*<sub>0</sub>, initial diameter; *t*, time;  $k_{s,Osw}$ , rate constant for Ostwald ripening;  $k_{s,Expt}$ , rate constant for exponential growth. As expected, both the models did not fit well with the calculated Ni diameters (Fig. 4.35).

Other researchers have modeled the growth of Ni in Ni-YSZ cermets as relaxation kinetics with a single time constant (Eq. 4.12) [16, 44, 46].

$$D = D_0 + (D_{max} - D_0) \cdot \left(1 - exp\left(-\frac{t}{\tau_{r,dia}}\right)\right)$$
(4.12)

Here  $D_{max}$  is a hypothetical maximum value of Ni particle diameter approached asymptotically as *t* approaches infinity, and  $\tau_{r,dia}$  is a characteristic relaxation time for the grain growth mechanism. Figure 4.36 shows that this model fits the present data much better than the Ostwald ripening or exponential growth models (Fig. 4.35).



*Figure 4.35: Fitting the traditional growth models, Ostwald ripening (a) and exponential growth (b), to the measured Ni particle diameters at 800 °C. Neither model fit the measured values well.* 

The best fit curve to the calculated Ni particle diameter at  $800^{\circ}$  and  $860^{\circ}$  were developed using Excel program (Microsoft). The SOLVE command was used to minimize the chi-squared error estimation. The two unknowns in equations 4.12,  $D_{\text{max}}$  and  $\tau_{r,dia}$ , were allowed to float in the calculation. Table 4.13 summarizes the results of the curve fitting and the predicted values of D at 40 kh of operation  $(D_{40kh})$ . Figure 4.36 (a) and (b) show the best fits for operation temperatures 800 °C and 860 °C. The calculated values of  $\tau_{r,dia}$  were 1.52E+3 h and 7.09E+3 h for 800 °C and 860 °C respectively. The fitted values of D<sub>max</sub> were 1.23 µm for 800 °C and 1.39 µm for 860 °C. It is interesting to note here that value of  $D_{\text{max}}$  and  $D_{40\text{kh}}$  are same for both temperatures. In other words, no significant change in Ni diameter is predicted beyond 40 kh of cell operation. (Having data points at more testing times might refine this prediction.) Also as expected,  $D_{40kh}$  and  $D_{max}$  were larger for 860 °C than for 800 °C. Using the same model, other researchers calculated  $D_{\text{max}}$ between 0.73 and 0.85  $\mu$ m [16, 46]. It is important to note that the values of  $D_0$  in both of these prior studies were around 0.63  $\mu$ m and operating temperature were 800 °C [16] and 850°C [46].

Temperature	D <sub>max</sub>	τ <sub>r,Dia</sub>	Rate Constant k <sub>r,Dia</sub>	$\sum \chi^2$	D <sub>40 kh</sub>
(°C)	(µm)	(h)	(h <sup>-1</sup> )		(µm)
800	1.23	1.52E+03	6.6E-04	1.3E-12	1.23
860	1.39	7.09E+03	1.4E-04	9.2E-12	1.39

Table 4.13: Summary of the curve fitting parameters, Dmax and  $\tau_{r,Dia}$ , in the relaxation kinetic model. The model predicted the Ni particle diameters 1.23 µm and 1.39 µm at 800°C and 860°C respectively after 40 kh cell operation.

Note that the values of Ni particle diameter for samples  $800 \ C / 4$  kh and  $860 \ C / 4$  kh were excluded from the curve fitting. For sample  $800 \ C / 4$  kh, the Ni diameter was 0.86  $\mu$ m, smaller than Ni diameter for the as-reduced specimen (0.89  $\mu$ m). Such reduction in Ni diameter could not be explained and has not been reported in literature. The deviation of Ni particle could be due to known differences in test conditions, or to unrepresentative samplings of the test volumes. The Ni volume fraction for  $860 \ C / 4$  kh was 0.20, significantly different from the typical values (~0.30). Also sample  $860 \ C / 4$  kh was from the outlet tube of stack configuration (§4.2.3).

Similarly for sample  $925 \ C / 2$  kh, the Ni volume fraction was an atypical 0.23. For the same reason, the Ni particle diameter for  $925 \ C / 2$  kh was not included in the fitting. With the exclusion of  $925 \ C / 2$  kh, there were not enough data points to perform curve fitting to the relaxation kinetic models at  $925 \ C$ .

The calculated rate constants ( $k_r$ ) are 6.6E-4 h<sup>-1</sup> at 800 °C and 1.4E-4 h<sup>-1</sup> at 860 °C (Table 4.11). Interestingly the rate constant at higher temperature, 860 °C, was lower than at lower temperature, 800 °C. A similar trend was also reported in the literature. Faes et. al. [16] calculated a rate constant of  $6.62 \pm 0.97E - 3 h^{-1}$  at 800 °C, whereas at 850 °C, Tanasini and Faes [46] calculated a rate constant of  $2.25E-03 h^{-1}$ .

The longest previous test duration fit to the relaxation kinetic model was 1130 h [16, 44]. Because the coarsening kinetics observed in each study will depend on details of the starting anode microstructure and the test conditions used, the values of the fitting parameters may not be comparable to those of other studies. Values of the growth rate constant (k) calculated from tests of short duration could significantly over- or underestimate the Ni particle growth in 40 kh. Nevertheless, the fact that the relaxation model

applies to the present data up to as long as 16 kh and at temperatures ranging from 800 to 860 °C suggests that this model would provide a more realistic description of Ni coarsening kinetics up to 40 kh than any of the other models considered so far.



Figure 4.36: Growth of Ni particle at  $800 \ C$  (a) and  $860 \ C$  (b). The relaxation kinetic model fit well with the measured Ni particle diameters.

#### 4.7.3 TPB change prediction

Ni coarsening reduces the surface area of the Ni phase, which should tend to reduce the TPB density of the anode. TPB density is considered to be a measure of the performance of the cell. Ni coarsening tends to reduce the percolation of the phase [35], which lowers active TPB density further compared to total TPB density.

Similar to Ni coarsening (§4.6.4), the changes in total and active TPB density were significant in the first 2 kh of operation and were more gradual afterwards (Table 4.9). Use of the relaxation kinetic model for modeling Ni coarsening made a similar model the first choice to model TPB density changes. Faes et. al. [16] found agreement between the experimental results and this model for TPB as well. The reversed trend of TPB density change required a modification to equation 4.13:

$$TPB(t) = TPB_{min} + (TPB_0 - TPB_{min})exp\left(-\frac{t}{\tau_{r,TPB}}\right)$$
(4.13)

with: TPB(*t*), TPB density at time *t*; TPB<sub>min</sub>, a hypothetical minimum value of TPB density approached asymptotically as *t* approaches infinity; TPB<sub>0</sub>, TPB density at *t*=0;  $\tau_{r,TPB}$ , a characteristic relaxation time.

The best fit curves to the measured TPB density at 800 °C and 860 °C were developed using a similar method to those discussed for modeling Ni coarsening in §4.6.2. Table 4.14 summarizes the results and gives predicted values of TPB density after 40 kh of operation (TPB<sub>40kh</sub>). Figure 4.37 (a) and (b) show the best fits for operation temperatures 800 °C and 860 °C. Calculated  $\tau_{r,TPB}$  was 2.23E+03 h for 800 °C and 7.28E+03 h for 860 °C. The fitted values of *TPB*<sub>min</sub> for two temperatures were 2.03 µm<sup>-2</sup> for 800 °C and 1.70µm<sup>-2</sup> for 860 °C. As in the Ni coarsening model, the value of TPB<sub>min</sub> and TPB<sub>40 kh</sub> are the same for both temperatures. Also as expected, the value of TPB<sub>40 kh</sub> (and also TPB<sub>max</sub>) was smaller for 860 °C than 800 °C.

For many physical phenomena for which relaxation kinetics is applicable — e.g. anelastic mechanical vibrations, capacitor charging and discharging, hopping of ions in alternating electric fields — a common characteristic is a mechanism of change whose driving force (and thus its speed) diminishes as the process proceeds. Qualitatively, this should also be true for Ostwald ripening: as the radius of curvature of a coarsening particle increases, the driving force for its continued growth decreases. Unlike relaxation kinetics, Ostwald ripening also involves the shrinking of small particles, a process whose driving force increases as the process proceeds. The question then is whether the presence of the essentially fixed and rigid YSZ framework within which the Ni coarsening takes place somehow neutralizes the accelerating rate of loss of small particles. If this were the case, it might explain why relaxation kinetics is more successful than Ostwald ripening at describing Ni coarsening in Ni-YSZ cermet SOFC anodes.

Temperature	TPB <sub>min</sub>	τ <sub>r,TPB</sub>	Rate Constant k <sub>r,TPB</sub>	$\sum \chi^2$	TPB <sub>40 kh</sub>
(°C)	(µm⁻²)	(h)	(h <sup>-1</sup> )		(µm <sup>-2</sup> )
800	2.03	2.23E+03	4.5E-04	1.7E-11	2.03
860	1.70	7.28E+03	1.4E-04	1.0E-10	1.71

Table 4.14: Summary of the curve fitting parameters, TPBmin and  $\tau_r$ , TPB, in the relaxation kinetic model. The model predicted TPB density 2.03  $\mu$ m-2 at 800 °C and 1.71  $\mu$ m-2 at 860 °C after 40 kh cell operation.

Fae et. al. [16] attempted to model the TPB density to represent electrochemical behavior of the SOFC based on the Butler-Volmer equation to calculate the SOFC degradation rate (equation 4.14). For all stacks under consideration, the cell degradation rate ( $\Delta u/\Delta t$ ) predicted by the model was significantly less than experimental measurement [16]. This observation signifies the presence of additional degradation mechanisms such as delamination of layers, cathode degradation, mechanical structural loss etc.

$$\frac{\Delta u}{\Delta t} = \frac{RT}{\alpha F t} ln \left( \frac{l_{TPB,0}}{l_{tpb}} \right)$$
(4.14)

# 4.7.4 Tortuosity Changes

The growth on Ni particle and reduction in tortuosity are often reported in the same study. However, a direct relationship of change in tortuosity to the SOFC performance is questionable, explained as follows.

Transport properties M of fluids are related to tortuosity by equation 4.15 [66]. The inverse relationship between these two parameters indicates that with reduced tortuosity after prolonged cell operation, the mass flow rate through the anode should increase. If transport of fuel to TPB is governing the cell performance, the cell performance should improve over time. This contradicts the experimental results of this study and those reported in literature.

$$M = \frac{\phi P \beta}{\tau} \tag{4.15}$$

Here *M*, ratio of effective to intrinsic transport property;  $\phi$ , phase fraction; *P*, percolation factor;  $\beta$ , constriction factor and  $\tau$ , tortuosity.



Figure 4.37: Reduction in active TPB density at  $800 \ C$  (a) and  $860 \ C$  (b). The relaxation kinetic model fit well with the measured Ni particle diameters.

It would be possible to develop the relaxation model for tortuosity also, but neither the present results nor the literature suggest that it is related to cell performance. Tortuosity alone should not be used for predicting long-term performance of SOFC. Perhaps an allinclusive model linking microstructure to cell performance could incorporate decreasing tortuosity as a higher-order effect that improves cell performance, overshadowed by more primary effects that reduces cell performance. For this study, focusing on the long-term changes of Ni particle diameter and TPB density would be more appropriate for understanding long-term SOFC performance.

# 4.7.5 Conclusion

Ni grain size grew significantly during cell operation at  $800 \,\text{°C}$ ,  $860 \,\text{°C}$ , and  $925 \,\text{°C}$ . Surface diffusion could be driving mechanism for Ni coarsening due to much higher surface diffusivity of Ni at  $1100 \,\text{°C}$  in comparison to the bulk diffusivity [9]. The relaxation kinetic model fits well to the calculated Ni particle diameters at  $800 \,\text{°C}$  and  $860 \,\text{°C}$ . The model predicted the Ni particle growth of 38.2% at  $800 \,\text{°C}$  and 57.3% at  $860 \,\text{°C}$  after 40 kh of operations. As expected the Ni particle diameter at higher temperature was larger.

Ni coarsening drives reduction in both TPB density of the Ni phase. TPB density changes with operation could also be modeled using single-time-constant relaxation kinetics. The model predicted the reduction in TPB density to 2.03  $\mu$ m<sup>-2</sup> (800 °C) and 1.71  $\mu$ m<sup>-2</sup> (860 °C) in 40 kh of cell operation.

Measurement of SOFC degradation includes the combined effect of changes in electrode microstructure, degradation in layer interfaces and changes in electrolytes. The focus of this study is limited to the anode layer. Even though Ni coarsening is not significant beyond 8 kh at 800°C and 16 kh at 860°C, overall SOFC degradation could continue due to changes outside the anode.

The tortuosity of the pore changed with test duration. However the effects of changes in tortuosity on the cell performance in unknown, and qualitatively would favor improved performance with time, contrary to long-term experience. Therefore the long-term changes in tortuosity with time were not analyzed here. For future work, the model could be developed combining the changes of tortuosity with other microstructural parameter to predict a more refined model of long-term SOFC performance.

# **4.8 Cumulative Insight**

In the literature, the effect of one operational parameter, typically time, is studied. This is the known first research to study the effect of two operational parameters, time and temperature, in a systematic manner. Surface diffusion of Ni is temperature-driven phenomenon. Including the temperature as a variable in the study, insight was gained into microstructural changes in SOFCs over significant ranges of both operating time and temperature. Furthermore, the maximum test duration in microstructural studies of SOFCs reported prior to this work was 4 kh. To predict the microstructure after 40 kh of operation (the current target lifetime for SOFCs), 4 kh test duration is very short. Access to longer testing times is crucial for understanding long-term microstructure changes.

# 4.8.1 Ni diameter growth

Two types of microstructural changes, volume fraction variation across the anode thickness and Ni particle growth, were discussed throughout the research. Volume fraction profiles across the anode thickness showed strong trends with operation time at each temperature. The volume fraction profiles became steeper with time. Ni depleted at the anode/ACC interface and diffused to the anode/electrolyte interface. Because the YSZ volume fractions were stable for all cells during operation, the diffusion of Ni to the anode/ACC interface led to the formation of gradients in porosity opposite to those seen for Ni.

Electrical conductivity of Ni ( $10^4$  S/cm) is six orders of magnitude higher than the ionic conductivity of YSZ (14×10<sup>-03</sup> S/cm) [38]. This suggests that electrochemical reaction sites close to the anode/electrolyte interface would exhibit less ohmic loss than those far from the electrolyte and contribute more to cell performance than sites far from the electrolyte [36]. This would also contribute to variations in temperature, fuel composition, and partial pressure of fuel/steam across the anode thickness. All these variations could favor Ni diffusion towards the anode/electrolyte interface. Overall Ni volume fractions were uniform for most of the samples (Table 4.1), so loss of Ni to outside due to evaporation-condensation can be neglected. However, the possibility of Ni evaporation-condensation within the anode cannot be neglected here. It is possible that the presence of H<sub>2</sub>O in anode forms Ni(OH)<sub>2</sub> which evaporates due to order of magnitude higher partial pressure in comparison to Ni. Condition might be favorable to transport Ni vapor towards the anode/electrolyte interface and precipitate on Ni close to the anode/electrolyte interface. The study of Ni growth orientation would provide more insight into the possible Ni growth mechanism at the anode/electrolyte interface. Surface diffusion of Ni is widely accepted as a mechanism for Ni growth [9, 13, 45]. In absence of Ni growth orientation, it would be safe to assume that the Ni coarsening in the anode was due to surface diffusion of Ni.

Average values of Ni particle diameter were calculated from Ni volume fraction (Equation 4.2). In this regard, these two microstructural parameters, phase volume and diameter, are related. If Ni phase re-distribution in the anode was due to evaporation-condensation, higher volume fraction of Ni at the anode/electrolyte interface was driving the Ni diameter growth. However if Ni diffuses to the anode/electrolyte interface by surface diffusion, as is widely accepted in the literature, the particle diameter would be the governing microstructure parameter. In that case, the volume fraction profiles observed across the anode thickness were due to the growth of Ni diameter across the anode thickness.

# 4.8.2 Relationship of Ni diameter growth and total TPB density

With cell operation, total TPB density of the anode decreased (\$4.5.2). The relationship between Ni diameter and TPB density could be further studied by plotting these microstructural parameters against each other. During isothermal long-term operation at 800, 860 °C and 925 °C, Ni particle diameter increased while total TPB density decreased (Fig. 4.38 (a) - (c)). The reduction in TPB density varied linearly (with similar slopes) with increase in Ni particle diameter at 800 °C, 860 °C and 925 °C (The results for 800 °C / 4 kh and 860 °C / 4 kh are excluded from the plots in figure (a) and (b) respectively, for reasons that are presented in \$4.7.2.). Figure 4.38 (d) combines the results in a single plot, which shows that there is a linear relationship between Ni diameter and TPB density independent of temperature. A cell tested at low temperature for long duration would reach similar TPB density as a cell tested at high temperature for short time, if the Ni coarsening is similar in both cases.



*Figure 4.38: Reduction in Total TPB with increase in Ni particle diameter at 800*  $\mathbb{C}$  (*a*), 860  $\mathbb{C}$  (*b*) *and 925*  $\mathbb{C}$  (*c*) *at all three temperatures together* (*d*).

# **4.8.3** Effect of percolated phase microstructure changes on electronic and mass transports

The difference between active TPB density and inactive TPB density is directly due to presence of non-percolated volume. During the research, the percolated volumes of all three phased remained very high percentages of the total volume even after cell operation, which resulted in most of the total TPB density being electrochemically active in the anode. However, depletion of Ni at the anode/ACC interface could have reduced the Ni and pore phase connections points to the adjacent ACC. This could be further illustrated by the schematic in Fig. 4.39. The volume of the phase in figure 4.39 (a) is percolated for Ni or pore phase as the phase is attached to the anode/ACC interface. The phase volume is connected to the ACC at three locations. This would allow multiple paths for electrons from TPB sites (in anode) to interconnects (in ACC) and mass flow to and from ACC. However if the microstructure changed slightly to figure 4.39 (b), it maintained high percolated volume, but the phase connection points to ACC layers are reduced to two. Loss of Ni connection points to the ACC would require longer transport path for electrons. The resistance of a wire with uniform diameter is proportional to the length of the wire and inversely proportional its diameter. Increase in Ni diameter would reduce the electrical resistance, but longer path of electron transport would increase the electrical resistance. Changes in percolated pore phase would be affected in different manner. Loss of connection points with the ACC would develop 'dead ends' in the flow network. The active TPB density associated with dead ends might not be as effective, as the mass flow through the dead end is not continuous.

Tortuosity calculated using the skeleton method needs to follow the skeleton of the porosity to reach from the anode/ACC interface to the anode/electrolyte interface. Therefore, it inherently excludes the dead ends in tortuosity calculation. The active TPB density could be further divided into two groups based on their associativity with the flow network: through "flow active" TPB and "dead end flow active" TPB. The skeleton structure of the phase with different diameters at different location could be used to divide active TPB density. It would be interesting to study the trends in "flow active" TPB with cell operation, and the resulting relationship with cell degradation.



Figure 4.39: (a) Percolated Ni or pore phase has 3 contact points with ACC (b) Percolated Ni or pore phase volume is nearly same as before but the contact point with ACC is reduced to 2. TPB points are indicated by '.'.

# 4.8.4 Flow though the porous phase

Mass transport through the porosity in anode would be affected by microstructural changes such as development of dead ends, decrease in tortuosity, particle diameter growth and changes in the particle side distribution (PSD). The development of dead-end flow paths would reduce the effective mass transport in those areas (§4.8.3). On the other side, decrease in tortuosity of porous phase would improve the overall mass transport (Equation 4.15). The change in pore diameter and its distribution (PSD) with cell operation would change the mass transport of fuel and H<sub>2</sub>O to/from the anode reaction cites. At SOFC operating temperature, the mean free path of the gas component is about  $0.2 - 0.5 \,\mu\text{m}$  [67]. The probability of Knudsen diffusion, in which mass transport is limited by the collisions of the gas molecules with the pore walls, increases if the pore diameter in the flow path is smaller than the mean free path of fuel and H<sub>2</sub>O.

The populations of diameter in the range of interest for flow rate,  $0.2 - 0.5 \mu m$ , could be conveniently analyzed by plotting the pore diameter as cumulative % population (Fig. 4.40). For the convenience of comparing the plots in the diameter range  $0.2 - 0.5 \mu m$ , the pore diameter on the abscissa is limited to 2  $\mu m$ . For the as-reduced specimen, 70% of the pore diameters were smaller than 0.5  $\mu m$ . For the cells after operation, the percentage of pore diameters smaller than 0.5  $\mu m$  decreased, i.e. the curves for the tested cells shifted to the right.

At 800 °C (Fig. 4.40a), the curves for the as-reduced specimen, 800 °C / 2 kh and 800°C / 8 kh overlapped up to diameter ~0.3 µm. Beyond 0.3 µm diameter, the curves for 800 °C / 2 kh and 800°C / 8 kh shifted to the right i.e. the population of the small-diameter pores decreased. The curve for 800°C / 8 kh departed from 800 °C / 2 kh further beyond ~0.9 µm diameter. (The 800 °C / 4 kh specimen, which gave anomalous microstructural results in other measures (§4.7.2), showed a more pronounced loss of small pores than did the 2 kh and 8 kh specimens.)

A similar trend occurred in cells tested at 860 °C and 925 °C (Figs. 4.40 (b) and 4.40(c)). The pore size distributions for specimens 860 °C / 8 kh, 860 °C / 16 kh and 925 °C / 2 kh had no overlap with the as-reduced sample, and the % population with pore diameter lower than 0.5 µm dropped to 50% or less. The curve for specimens 860 °C / 4 kh and 925 °C / 4 kh followed the as-reduced sample up to 0.3 µm and separated to lower percentages beyond 0.3 µm.









Figure 4.40: Cumulative population plots of diameter at 800  $^{\circ}$ C (a), 860  $^{\circ}$ C (b) and 925  $^{\circ}$ C (c).

The shift of the cumulative plots to the right in an indication of pore diameter growth. Possibility of Knudsen diffusion decreased as the percentage population of pores with diameter lower than gas mean free path drops. These geometrical changes in the flow path during operation would improve mass transport in the anode, as would the reduction in tortuosity reported in §4.3.

Microstructure changes of pore phase such as reduction in tortuosity, increase in particle diameter and shift of PSD to larger diameter would improve the mass transport. However, the development of dead end would reduce the effective mass transport. Even though the particle diameter of the pore phase increased with time, the flow through the pore phase is governed by the 'bottleneck' (the smallest diameter) in the flow path. The flow dynamics should be studied in detail to understand the effect of these microstructure parameters changes on mass transport and its relationship to cell performance.

# **Chapter 5: Conclusions and Future Work**

# **5.1 Conclusions**

In this research, the effects of operation temperature and time on the microstructures of SOFC anodes were studied. Sequential sectioning was carried out with a dual-beam FIB/SEM on multiphase, composite SOFC anodes that had been operated under practical conditions at 800°C, 860°C and 925 °C for 2 – 16 kh, Images of these sections were analyzed and reassembled to reconstruct 3D portions of the anode from the electrolyte/anode interface to the anode/ACC interface. Amira<sup>TM</sup> was used to segment the three phases of the anode — metal (Ni), ceramic (YSZ), and porosity. A total of nine anodes — one as-reduced, and eight after operation — were reconstructed. Modifications to the standard sectioning technique consisting of exposed anode on two orthogonal sides of mount, mounting the specimen on 45° mount, and epoxy filled pores enabled faster image acquisition and analysis, and enabled reconstruction of larger volumes (1000 – 1600  $\mu$ m<sup>3</sup>) than have been reported by other groups 109 - 1121  $\mu$ m<sup>3</sup> [40, 54, 56].

Bulk microstructural parameters such as phase volume fractions, surface area and phase particle diameters were quantified to study the anode microstructure evolution with time and temperature. The volume fractions of the three phases were similar in all samples except 925 C / 2 kh and 860 C / 4 kh. For both the nickel and porosity, the particle diameter increased with time at all three temperatures: 800 C, 860 C and 925 C. Due to low mobility of YSZ below 925 C, the YSZ particle diameter remained unchanged.

A systematic study was performed to verify that the reconstructed anode volume represented the microstructure of the entire anode. The RSV for the as-reduced specimen was significantly smaller than that for the cells after operation. For future studies, a minimum reconstructed volume of  $1000 \ \mu m^3$  would be sufficient to study anodes with feature sizes similar to those in this study. Nevertheless, researchers should verify the RSV for the microstructure being studied.

3D reconstructed volumes allow the study of microstructures in any cross-sections and in selected sub-volumes. The volume fractions for three phases were uniform across the anode thickness for the as-reduced cell. However, for tested cells, the volume fraction for Ni increased at the anode/electrolyte interface, and the volume fraction of porosity increased at the anode/ACC interface. The gradients in volume fraction became steeper with longer cell operation. The YSZ volume fraction profile remained uniform for the cells after operation.

3D reconstruction is a powerful tool to study microstructural properties such as phase percolation, tortuosity and TPB that can only be depicted accurately in three dimensions. Most of the Ni and pore volumes that experienced phase redistribution during operation remained percolated after operation. Because of the high percentage of phase percolation, the difference in total TPB density and active TPB density was small for all the samples.

The total and active TPB density profiles were uniform across the anode thickness for most of the specimens (Appendix C). The study in this section helped elucidate the uniformity in TPB profiles. For TPB to form, it requires all three phase to present. The growth pattern for Ni and porous phases had opposite trends and negate the effect of growth which maintained the uniformity in TPB profiles. The slight gradient in TPB profiles were due to difference in growth rate for Ni and pore. Active TPB density is often directly related to the cell performance. In this study, first the stereological method was used to calculate total and active TPB densities, and the active TPB density was maximum for the as-reduced specimen. The active TPB density dropped drastically in first 2k h of cell operation. Thereafter the reduction in active TPB density was gradual. For the as-reduced specimen, the stereological method tends to overestimate the TPB density due to stepwise nature of the computation. The TPB density measured by this method was 23.8% higher than that determined by the surface intersection method. The accuracy of the TPB density depends on the mesh quality. However, the even at 25% mesh quality, the accuracy of TPB by surface intersection method was much better than the stereological method.

The trends for tortuosity were similar to those for TPB density. It is often reported as one of the microstructural properties which changes with time. However the effect of the tortuosity changes correlate negatively to cell performance. This indicates that the electrochemical reaction at TPB sites is not restricted by the mass transport of the species. Even though tortuosity of the Ni and pore phases changes with time and it is crucial for mass transport, its importance in predicting long-term performance is yet to be established.

Long-term microstructural evolution of the Ni particle diameter and TPB density was most closely represented by a relaxation kinetic model with a single relaxation time. The model predicted that the Ni particle diameter will grow to 1.2  $\mu$ m and 1.4  $\mu$ m in 40 kh of cell operation. During the same time, the reduction in TPB density will reduce to 2.0  $\mu$ m<sup>-2</sup> at 800 °C and 1.7  $\mu$ m<sup>-2</sup> at 860 °C.

The scope of this research was limited to the microstructural changes in the anode. During cell operation, additional microstructure changes happen in other active layers and their interfaces. All those changes have a cumulative effect on the cell performance. Therefore, the rate of microstructural changes in the anode alone might not necessarily correlate to the rate of degradation of SOFC performance.

# **5.2 Future work**

# 5.2.1 3D Characterization of composite anode using dual-beam FIB/SEM and EDX/EBSD

A new development in 3D reconstruction is combining the dual-beam FIB/SEM technique with energy dispersive x-ray spectroscopy (EDXS) and electron backscattered diffraction (EBSD). The instrumentation for combined FIB/SEM and EDXS/EBSD is available commercially (Oxfard Instruments, <u>www.oxfard-instruments.com</u>). Shearing [68] demonstrated the use of 3D EDXS/EBSD technique in characterizing SOFC electrode material. While FIB/SEM provides morphological information, EDXS/EBSD provides chemical composition and crystallographic orientation in 3D microstructure.

In this technique, FIB sequentially removes slices of the material. EBSD data are captured using a low-light CCD camera from the freshly cut surface. The software generates an orientation map and a grain boundary map for each slice. The process is automated until the desired volume of data is collected. The orientation and grain boundary maps are combined using 3D viewer software. The resultant reconstruction volume contains information related to morphology, grain boundaries, phase distribution and chemical composition in 3D.

The additional information from these techniques would provide detailed understanding of Ni coarsening. It would be possible to view the preferred orientation of
Ni particle growth. It would also provide insight into the Ni coarsening mechanism i.e. diffusion vs. evaporation / condensation. The chemical composition information from EDXS would provide information related to diffusion of elements from other layers such as ACC into the anode and its effect on the cell performance. 3D grain boundary information could provide better understanding of ionic, electronic conduction path and electrochemical importance of the grain boundary.

#### 5.2.2 Microstructural evolution using Phase-Field Modeling

It is common to use a hypothetical anode microstructure as a starting point for simulating microstructural evolution during cell operation [41]. With the information available from 3D reconstruction, the actual microstructure of an as-reduced sample could be used as input microstructure in a simulation to study the microstructural changes with time, under various assumed kinetic models. The results from the simulation could be compared with the calculated results in this research to determine which kinetic model best predicts the observed microstructure of the anode up to 16 kh, and then use that model to predict the microstructure after 40 kh of cell operation. The phase field modeling (PFM) technique could be used for the microstructural evolution simulation [9, 41]. Multiple models for grain growth — surface diffusion, bulk diffusion, and evaporation-condensation — could be studied to understand Ni coarsening in the anode.

PFM describes the microstructure with continuous time-dependent phase-field variables, called order parameters. The SOFC anode microstructure has 3 phases, which requires three order parameters to describe the anode microstructure. An order parameter has uniform value for each phase and changes continuously at the interface of two phases. A smooth sinusoidal variation of the order-parameter would be used at the interface of two phases in this project. The thickness for the interface would be chosen so as to give a compromise between computational time and agreement with observed results. The orderparameter is restricted to have values between 0 and 1. Fig 5.1 shows the phase-field representation of a SOFC anode [41].



*Figure 5.1: Phase-field representation of the SOFC anode [41]* 

The microstructure change of a SOFC anode is calculated by solving the Cahn-Hilliard equation. The microstructure would evolve to achieve minimum free energy.

$$\frac{\partial \eta_i}{\partial t} = \nabla \cdot \left( M \nabla \frac{\delta \varphi}{\delta \eta_i} \right), i = 1 \text{ to } n \tag{5.1}$$

Where  $\eta_1$ , order parameter for phase 1 and so on (up to 3 for SOFC anodes);  $\varphi$ , total free energy of the microstructure; *M*, kinetic rate coefficient; *t*, time.

The free energy for the anode microstructure could be expressed in terms of order parameters in many forms. One such total free energy expression is

$$\varphi = \int \left[ f(\eta_i) + \sum_{i=1}^n \frac{\alpha_i}{2} (\nabla \eta_i)^2 \right] dV$$
(5.2)

Where f, bulk free energy and expressed as a function of order parameters; n, number of order parameters.

The Cahn-Hilliard equation would be solved in conjunction with the free energy equation and the bulk free energy. The order parameters would be updated using the following expression

$$\eta_i(t + \Delta t) = \eta_i(t) + \Delta t \frac{\partial \eta_i}{\partial t}$$
(5.3)

## Appendix – A

Volume fraction profiles for Ni, pore and YSZ in x-, y- and z- directions. Each figure has three plots. The first plot is volume fraction profiles in z- direction (anode thickness).



Figure A1.1: Volume fraction profiles for Ni, pore and YSZ in x-, y- and zdirections for 800  $\mathbb{C}$  / 2 kh. The abscissa is anode thickness (µm)/distance (µm) and ordinate is volume fraction.



Figure A1.2: Volume fraction profiles for Ni, pore and YSZ in x-, y- and zdirections for 800  $\mathbb{C}$  / 4 kh. The abscissa is anode thickness (µm)/distance (µm) and ordinate is volume fraction.



Figure A1.3: Volume fraction profiles for Ni, pore and YSZ in x-, y- and zdirections for 800 C/8 kh. The abscissa is anode thickness ( $\mu$ m)/distance ( $\mu$ m) and ordinate is volume fraction.



Figure A1.4: Volume fraction profiles for Ni, pore and YSZ in x-, y- and zdirections for 860  $^{\circ}C$  / 4 kh. The abscissa is anode thickness ( $\mu$ m)/distance ( $\mu$ m) and ordinate is volume fraction.



Figure A1.5: Volume fraction profiles for Ni, pore and YSZ in x-, y- and zdirections for 860 C/8 kh. The abscissa is anode thickness ( $\mu$ m)/distance ( $\mu$ m) and ordinate is volume fraction.



Figure A1.6: Volume fraction profiles for Ni, pore and YSZ in x-, y- and zdirections for 860 C/16 kh. The abscissa is anode thickness ( $\mu$ m)/distance ( $\mu$ m) and ordinate is volume fraction.



Figure A1.7: Volume fraction profiles for Ni, pore and YSZ in x-, y- and zdirections for 925 C/2 kh. The abscissa is anode thickness ( $\mu$ m)/distance ( $\mu$ m) and ordinate is volume fraction.



Figure A1.8: Volume fraction profiles for Ni, pore and YSZ in x-, y- and zdirections for 925 C/4 kh. The abscissa is anode thickness ( $\mu$ m)/distance ( $\mu$ m) and ordinate is volume fraction.

### Appendix – B

Plots for volume fraction variation for two consecutive sub-volumes to calculate RSV. In the plots, the abscissa is % volume of total volume and the ordinate is % variation of volume fractions in two consecutive sub-volumes. RSV was calculated when % variation in volume fractions of two consecutive sub-volumes is less than  $\pm 1.0\%$ .



Figure A2.1: As-reduced sample - RSV volume = 36% of total volume (407.1  $\mu m^3$ )



Figure A2.2: 800 °C / 2 kh - RSV volume = 64% of total volume (914.5  $\mu$ m<sup>3</sup>)



Figure A2.3: 800 °C / 4 kh - RSV volume = 49% of total volume (825.2  $\mu m^3$ )



Figure A2.4: 800 °C / 8 kh - RSV volume = 81% of total volume (918.3  $\mu m^3$ )



Figure A2.5: 860 °C / 4 kh - RSV volume = 36% of total volume (353.7  $\mu$ m<sup>3</sup>)



Figure A2.6: 860 °C / 8 kh - RSV volume = 36% of total volume (517.0  $\mu$ m<sup>3</sup>)



Figure A2.7: 860 °C / 16 kh - RSV volume = 49% of total volume (769.0  $\mu m^3$ )



Figure A2. 8: 925 °C / 2 kh - RSV volume = 49% of total volume (695.8  $\mu m^3$ )



Figure A2.9: 925 C/4 kh - RSV volume = 49% of total volume (652.0  $\mu m^3$ )

# Appendix – C

Plots are for total TPB density and active TPB density across the anode thickness.



*Figure A3.1: Total TPB density and active TPB density across the anode thickness for the as-reduce sample.* 

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Figure A3.2: Total TPB density and active TPB density across the anode thickness for 800 C/2 kh.



Figure A3.3: Total TPB density and active TPB density across the anode thickness for 800 C/4 kh.



Figure A3.4: Total TPB density and active TPB density across the anode thickness for 800 C/8 kh.



Figure A3.5: Total TPB density and active TPB density across the anode thickness for 860 C/4 kh.



Figure A3.6: Total TPB density and active TPB density across the anode thickness for 860 C/8 kh.



Figure A3.7: Total TPB density and active TPB density across the anode thickness for 860  $\degree$  / 16 kh.



Figure A3.8: Total TPB density and active TPB density across the anode thickness for 925 C/2 kh.



Figure A3.9: Total TPB density and active TPB density across the anode thickness for 925 C/4 kh.

#### References

[1] *Monthly Energy Review*, Review, vol. Monthly Energy Review, Monthly Energy Review, April 2013.

[2] K. H. a. J. Goodenough, *Solid oxide fuel cell technology*: CRC Press LLC, 2009.

[3] A. B. Stambouli, and E. Traversa, "Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy," *Renewable & Sustainable Energy Reviews*, vol. 6, no. 5, pp. 433-455, Oct, 2002.

[4] S. Vora. "U.S. Department of Energy's SECA Program:

2011 Progress and Plans."

[5] B. White, *DOE Solid Oxide Fuel Cell Program Status*, SECA Workshop, November 2012.

[6] F. J. Gardner, M. J. Day, N. P. Brandon *et al.*, "SOFC technology development at Rolls-Royce," *Journal of Power Sources*, vol. 86, no. 1-2, pp. 122-129, Mar, 2000.

[7] J. P. Strakey, *Status of SECA program*, SECA workshop, November 2001.

[8] J. B. Goodenough, and Y. H. Huang, "Alternative anode materials for solid oxide fuel cells," *Journal of Power Sources*, vol. 173, no. 1, pp. 1-10, Nov, 2007.

[9] H. Y. Chen, H. C. Yu, J. S. Cronin *et al.*, "Simulation of coarsening in three-phase solid oxide fuel cell anodes," *Journal of Power Sources*, vol. 196, no. 3, pp. 1333-1337, Feb, 2011.

[10] W. Z. Zhu, and S. C. Deevi, "A review on the status of anode materials for solid oxide fuel cells," *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing*, vol. 362, no. 1-2, pp. 228-239, Dec, 2003.

[11] H. Yokokawa, H. Y. Tu, B. Iwanschitz *et al.*, "Fundamental mechanisms limiting solid oxide fuel cell durability," *Journal of Power Sources*, vol. 182, no. 2, pp. 400-412, Aug, 2008.

[12] D. Simwonis, F. Tietz, and D. Stover, "Nickel coarsening in annealed Ni/8YSZ anode substrates for solid oxide fuel cells - In memoriam to Professor H. Tagawa," *Solid State Ionics*, vol. 132, no. 3-4, pp. 241-251, Jul, 2000.

[13] R. Vassen, D. Simwonis, and D. Stover, "Modelling of the agglomeration of Niparticles in anodes of solid oxide fuel cells," *Journal of Materials Science*, vol. 36, no. 1, pp. 147-151, Jan, 2001.

[14] H. S. Song, W. H. Kim, S. H. Hyun *et al.*, "Influences of starting particulate materials on microstructural evolution and electrochemical activity of LSM-YSZ composite cathode for SOFC," *Journal of Electroceramics*, vol. 17, no. 2-4, pp. 759-764, Dec, 2006.

[15] A. Tewari, and A. M. Gokhale, "Estimation of three-dimensional grain size distribution from microstructural serial sections," *Materials Characterization*, vol. 46, no. 4, pp. 329-335, Apr, 2001.

[16] A. Faes, A. Hessler-Wyser, D. Presvytes *et al.*, "Nickel-Zirconia Anode Degradation and Triple Phase Boundary Quantification from Microstructural Analysis," *Fuel Cells*, vol. 9, no. 6, pp. 841-851, Dec, 2009.

[17] F. Zhao, Jiang, Y., Lin, G. Y. & Virkar A. V., Solid Oxide Fuel Cell VII (ed. Singhal, S. C.), pp. 501-510, 2001.

[18] J. R. Wilson, and S. A. Barnett, "Solid oxide fuel cell Ni-YSZ anodes: Effect of composition on microstructure and performance," *Electrochemical and Solid State Letters*, vol. 11, no. 10, pp. B181-B185, 2008.

[19] E. A. Holm, and P. M. Duxbury, "Three-dimensional materials science," *Scripta Materialia*, vol. 54, no. 6, pp. 1035-1040, Mar, 2006.

[20] J. R. Wilson, W. Kobsiriphat, R. Mendoza *et al.*, "Three-dimensional reconstruction of a solid-oxide fuel-cell anode," *Nature Materials*, vol. 5, no. 7, pp. 541-544, Jul, 2006.

[21] N. Vivet, S. Chupin, E. Estrade *et al.*, "Effect of Ni content in SOFC Ni-YSZ cermets: A three-dimensional study by FIB-SEM tomography," *Journal of Power Sources,* vol. 196, no. 23, pp. 9989-9997, Dec, 2011.

[22] H. Iwai, N. Shikazono, T. Matsui *et al.*, "Quantification of SOFC anode microstructure based on dual beam FIB-SEM technique," *Journal of Power Sources*, vol. 195, no. 4, pp. 955-961, Feb, 2010.

[23] M. Kishimoto, H. Iwai, M. Saito *et al.*, "Quantitative evaluation of solid oxide fuel cell porous anode microstructure based on focused ion beam and scanning electron microscope technique and prediction of anode overpotentials," *Journal of Power Sources*, vol. 196, no. 10, pp. 4555-4563, May, 2011.

[24] M. Kishimoto, K. Miyawaki, H. Iwai *et al.*, "Effect of Composition Ratio of Ni-YSZ Anode on Distribution of Effective Three Phase Boundary and Power Generation Performance," *Fuel Cells*, vol. 13, no. 4, pp. 476-486, Aug, 2013.

[25] D. Gostovic, J. R. Smith, D. P. Kundinger *et al.*, "Three-dimensional reconstruction of porous LSCF cathodes," *Electrochemical and Solid State Letters*, vol. 10, no. 12, pp. B214-B217, 2007.

[26] D. Gostovic, N. J. Vito, K. A. O'Hara *et al.*, "Microstructure and Connectivity Quantification of Complex Composite Solid Oxide Fuel Cell Electrode Three-Dimensional Networks," *Journal of the American Ceramic Society*, vol. 94, no. 2, pp. 620-627, Feb, 2011.

[27] Z. J. Jiao, N. Shikazono, and N. Kasagi, "Quantitative Characterization of SOFC Nickel-YSZ Anode Microstructure Degradation Based on Focused-Ion-Beam 3D-Reconstruction Technique," *Journal of the Electrochemical Society*, vol. 159, no. 3, pp. B285-B291, 2012.

[28] S. Zhang, "QUANTITATIVE CHARACTERIZATION AND MODELING OF THE MICROSTRUCTURE OF SOLID OXIDE FUEL CELL COMPOSITE ELECTRODES," Material Science and Engineering, Georgia Institute of Technology, 2010.

[29] P. S. Jorgensen, K. V. Hansen, R. Larsen *et al.*, "A framework for automatic segmentation in three dimensions of microstructural tomography data," *Ultramicroscopy*, vol. 110, no. 3, pp. 216-228, Feb, 2010.

[30] A. Hagen, R. Barfod, P. V. Hendriksen *et al.*, "Degradation of anode supported SOFCs as a function of temperature and current load," *Journal of the Electrochemical Society*, vol. 153, no. 6, pp. A1165-A1171, 2006.

[31] L. Holzer, B. Munch, B. Iwanschitz *et al.*, "Quantitative relationships between composition, particle size, triple phase boundary length and surface area in nickel-cermet anodes for Solid Oxide Fuel Cells," *Journal of Power Sources*, vol. 196, no. 17, pp. 7076-7089, Sep, 2011.

[32] L. Holzer, B. Iwanschitz, T. Hocker *et al.*, "Microstructure degradation of cermet anodes for solid oxide fuel cells: Quantification of nickel grain growth in dry and in humid atmospheres," *Journal of Power Sources*, vol. 196, no. 3, pp. 1279-1294, Feb, 2011.

[33] K. Du, F. Ernst, M. Garrels *et al.*, "Formation of nickel nanoparticles in nickelceramic anodes during operation of solid-oxide fuel cells," *International Journal of Materials Research*, vol. 99, no. 5, pp. 548-552, May, 2008.

[34] T. Iwata, "Characterization of Ni-YSZ anode degradation for substrate-type solid oxide fuel cells," *Journal of the Electrochemical Society*, vol. 143, no. 5, pp. 1521-1525, May, 1996.

[35] B. Iwanschitz, J. Sfeir, A. Mai *et al.*, "Degradation of SOFC Anodes upon Redox Cycling: A Comparison Between Ni/YSZ and Ni/CGO," *Journal of the Electrochemical Society*, vol. 157, no. 2, pp. B269-B278, 2010.

[36] P. R. Shearing, D. J. L. Brett, and N. P. Brandon, "Towards intelligent engineering of SOFC electrodes: a review of advanced microstructural characterisation techniques," *International Materials Reviews*, vol. 55, no. 6, pp. 347-363, Nov, 2010.

[37] B. Munch, and L. Holzer, "Contradicting Geometrical Concepts in Pore Size Analysis Attained with Electron Microscopy and Mercury Intrusion," *Journal of the American Ceramic Society*, vol. 91, no. 12, pp. 4059-4067, Dec, 2008.

[38] N. Vivet, S. Chupin, E. Estrade *et al.*, "3D Microstructural characterization of a solid oxide fuel cell anode reconstructed by focused ion beam tomography," *Journal of Power Sources*, vol. 196, no. 18, pp. 7541-7549, Sep, 2011.

[39] J. R. Wilson, J. S. Cronin, A. T. Duong *et al.*, "Effect of composition of (La0.8Sr0.2MnO3-Y2O3-stabilized ZrO2) cathodes: Correlating three-dimensional microstructure and polarization resistance," *Journal of Power Sources*, vol. 195, no. 7, pp. 1829-1840, Apr, 2010.

[40] P. S. Jorgensen, K. V. Hansen, R. Larsen *et al.*, "High accuracy interface characterization of three phase material systems in three dimensions," *Journal of Power Sources*, vol. 195, no. 24, pp. 8168-8176, Dec, 2010.

[41] J. H. Kim, W. K. Liu, and C. Lee, "Multi-scale solid oxide fuel cell materials modeling," *Computational Mechanics*, vol. 44, no. 5, pp. 683-703, Oct, 2009.

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[42] K. Yakal-Kremski, J. S. Cronin, Y. C. K. Chen-Wiegart *et al.*, "Studies of Solid
 Oxide Fuel Cell Electrode Evolution Using 3D Tomography," *Fuel Cells*, vol. 13, no. 4, pp. 449-454, Aug, 2013.

[43] M. Shah, P. W. Voorhees, and S. A. Barnett, "Time-dependent performance changes in LSCF-infiltrated SOFC cathodes: The role of nano-particle coarsening," *Solid State Ionics*, vol. 187, no. 1, pp. 64-67, Apr, 2011.

[44] G. J. Nelson, K. N. Grew, J. R. Izzo *et al.*, "Three-dimensional microstructural changes in the Ni-YSZ solid oxide fuel cell anode during operation," *Acta Materialia*, vol. 60, no. 8, pp. 3491-3500, May, 2012.

[45] S. Gao, J. Y. Li, and Z. J. Lin, "Theoretical model for surface diffusion driven Niparticle agglomeration in anode of solid oxide fuel cell," *Journal of Power Sources*, vol. 255, pp. 144-150, Jun, 2014.

[46] P. Tanasini, M. Cannarozzo, P. Costamagna *et al.*, "Experimental and Theoretical Investigation of Degradation Mechanisms by Particle Coarsening in SOFC Electrodes," *Fuel Cells*, vol. 9, no. 5, pp. 740-752, Oct, 2009.

[47] E. A. Wargo, T. Kotaka, Y. Tabuchi *et al.*, "Comparison of focused ion beam versus nano-scale X-ray computed tomography for resolving 3-D microstructures of porous fuel cell materials," *Journal of Power Sources*, vol. 241, pp. 608-618, Nov, 2013.

[48] M. D. Uchic, L. Holzer, B. J. Inkson *et al.*, "Three-dimensional microstructural characterization using focused ion beam tomography," *Mrs Bulletin*, vol. 32, no. 5, pp. 408-416, May, 2007.

[49] D. N. Joseph Goldstein, David Roy, Charles Lyman, Patrick Echlin, Eric Lifshin, Linda Sawyer, Joseph Michael, *Scaning Electron Microscopy and X-Ray Microanalysis*, Third ed.: Springer, 2007.

[50] J. M. Zalc, S. C. Reyes, and E. Iglesia, "The effects of diffusion mechanism and void structure on transport rates and tortuosity factors in complex porous structures," *Chemical Engineering Science*, vol. 59, no. 14, pp. 2947-2960, Jul, 2004.

[51] J. R. Izzo, A. S. Joshi, K. N. Grew *et al.*, "Nondestructive reconstruction and analysis of SOFC anodes using x-ray computed tomography at sub-50 nm resolution," *Journal of the Electrochemical Society*, vol. 155, no. 5, pp. B504-B508, 2008.

[52] D. Wiedenmann, L. Keller, L. Holzer *et al.*, "Three-Dimensional Pore Structure and Ion Conductivity of Porous Ceramic Diaphragms," *Aiche Journal*, vol. 59, no. 5, pp. 1446-1457, May, 2013.

[53] J. A. Sethian, "Fast marching methods," *Siam Review*, vol. 41, no. 2, pp. 199-235,Jun, 1999.

[54] J. R. Wilson, M. Gameiro, K. Mischaikow *et al.*, "Three-Dimensional Analysis of Solid Oxide Fuel Cell Ni-YSZ Anode Interconnectivity," *Microscopy and Microanalysis*, vol. 15, no. 1, pp. 71-77, Feb, 2009.

[55] P. S. Jorgensen, K. Yakal-Kremski, J. Wilson *et al.*, "On the accuracy of triple phase boundary lengths calculated from tomographic image data," *Journal of Power Sources*, vol. 261, pp. 198-205, Sep, 2014.

[56] J. S. Cronin, J. R. Wilson, and S. A. Barnett, "Impact of pore microstructure evolution on polarization resistance of Ni-Yttria-stabilized zirconia fuel cell anodes," *Journal of Power Sources*, vol. 196, no. 5, pp. 2640-2643, Mar, 2011.

[57] Y. Guan, W. J. Li, Y. H. Gong *et al.*, "Analysis of the three-dimensional microstructure of a solid-oxide fuel cell anode using nano X-ray tomography," *Journal of Power Sources*, vol. 196, no. 4, pp. 1915-1919, Feb, 2011.

[58] J. Golbert, C. S. Adjiman, and N. P. Brandon, "Microstructural Modeling of Solid Oxide Fuel Cell Anodes," *Industrial & Engineering Chemistry Research*, vol. 47, no. 20, pp. 7693-7699, Oct, 2008.

[59] Y. Suzue, N. Shikazono, and N. Kasagi, "Micro modeling of solid oxide fuel cell anode based on stochastic reconstruction," *Journal of Power Sources*, vol. 184, no. 1, pp. 52-59, Sep, 2008.

[60] J. R. Smith, A. Chen, D. Gostovic *et al.*, "Evaluation of the relationship between cathode microstructure and electrochemical behavior for SOFCs," *Solid State Ionics*, vol. 180, no. 1, pp. 90-98, Feb, 2009.

[61] D. Kennouche, Y. C. K. Chen-Wiegart, J. S. Cronin *et al.*, "Three-Dimensional Microstructural Evolution of Ni-Yttria-Stabilized Zirconia Solid Oxide Fuel Cell Anodes At Elevated Temperatures," *Journal of the Electrochemical Society*, vol. 160, no. 11, pp. F1293-F1304, 2013.

[62] L. Holzer, D. Wiedenmann, B. Munch *et al.*, "The influence of constrictivity on the effective transport properties of porous layers in electrolysis and fuel cells," *Journal of Materials Science*, vol. 48, no. 7, pp. 2934-2952, Apr, 2013.

[63] B. Iwanschitz, L. Holzer, A. Mai *et al.*, "Nickel agglomeration in solid oxide fuel cells: The influence of temperature," *Solid State Ionics*, vol. 211, pp. 69-73, Mar, 2012.

[64] M. N. Rahaman, *Sintering of Ceramics*, Boca Raton: CRC Press, 2008.

[65] K. B. G. Froment, *Chemical Reactor Analysis and Design*, 2nd ed., New York: Wiley, 1990.

[66] L. Holzer, B. Iwanschitz, T. Hocker *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," *Journal of Power Sources*, vol. 242, pp. 179-194, Nov, 2013.

[67] M. Andersson, J. L. Yuan, and B. Sunden, "SOFC modeling considering hydrogen and carbon monoxide as electrochemical reactants," *Journal of Power Sources*, vol. 232, pp. 42-54, Jun, 2013.

[68] P. Shearing, "Characterization of SOFC electrode microstructure in three dimensions," Imparial College, London, UK, 2009.

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