SOFC electrodes are typically porous composite materials bringing ionic, electronic and pore phases into intimate contact. These electrodes must fulfill a broad range of criteria from diffusion and electrocatalysis to mechanical support and redox tolerance. Historically design and optimisation have been largely empirical and characterisation of electrode microstructures at sub-micron length scales has been restricted to two-dimensional electron microscopy. In recent years, the development and application of focused ion beam and X-ray nano tomography tools has enabled characterisation of electrode microstructures in three dimensions providing unprecedented access to a wealth of microstructural information (see e. g [1,2]). As well as improving our understanding of existing electrode geometries, these tools have also been successfully applied to evaluate design and manufacturing strategies. With improved availability and functionality of high-resolution tomography tools, we can start to explore the effects of processing and operation on microstructure and performance. Using the unique benefits of non-destructive synchrotron X-ray nano-CT, we have explored microstructural evolution processes in-situ, using so-called “4D tomography”, facilitating an improved understanding of electrode aging and durability. These tomography platforms are however most powerful when used in conjunction with relevant simulation tools [3,4]. Here we present the results of finite element simulations, exploring coupled electrochemistry and transport and stress in composite SOFC electrodes, utilising experimentally derived microstructural frameworks.

Introduction

In common with all functional materials, the microstructure of a solid oxide fuel cell (SOFC) critically influences performance. The electrode microstructure determines the electrochemical performance of an SOFC over its full operating range. Considering the current–voltage behaviour of an SOFC electrode, operation in different regimes result in different voltage losses:
i. At low currents, losses are predominantly due to kinetic processes. In this regime optimal microstructures should maximise triple phase contact to enhance electrochemical performance.

ii. Conversely, at high current densities, SOFC operation is limited by mass transport of reactant species; negative mass transport effects are mitigated by developing a pore network optimised for reactant delivery.

Further, Ohmic effects, which are a contributory loss factor at all current densities, are dictated by the nature of conductivity of the ionic and electronic phases - this is determined by connectivity in accordance with fundamental percolation theory. Percolation is an inherently three dimensional problem: indeed 2D stereological interpretations can prove misleading or ambiguous [5].

Figure 1 is a schematic of a typical Ni/yttria stabilized zirconia (YSZ) composite electrode microstructure. The distribution of YSZ throughout the bulk electrode extends the electrochemically active zone normal to the electrode/electrolyte interface. For demonstration purposes, three types of triple phase boundaries (TPBs) have been identified: TPB1 can be considered theoretically active as there is a contiguous ionic, electronic and pore network to and from the point of interest. However, TPBs 2 and 3 are inactive because of a lack of connectivity in the electronic and ionic phases, respectively.

Figure 1. Schematic showing TPB distribution in an SOFC electrode. For an anode white corresponds to electrolyte material (YSZ) and black to the electronic conductor (Ni). Contiguity must be understood in three-dimensions to analyse activity of TPBs

While electrode microstructure impacts on SOFC performance across all regimes of operation, these effects are often conflicting and as such microstructural requirements are dependent on the perceived rate limiting step. The implications of electrode microstructure are not constrained to electrochemical performance; fuel cell microstructures should demonstrate mechanical integrity during thermal and load cycling and tolerance to redox cycling. Primdahl et al. have discussed attempts to simultaneously optimise the mechanical and electrochemical properties of anodes, noting that the conflicting requirements leave little room for compromise [6]. Further, attempts to design electrodes are compounded by the diverse range of processing and environmental parameters that can affect fuel cell microstructure.

The focus on microstructural optimisation as a means of improving performance is not constrained to academia; Versa Power have attributed their improved stack...
performance to be the result of proprietary cell microstructures [7]. However, there remains little consensus as to what constitutes a ‘good’ microstructure [8]. Furthermore, the breadth of processing parameters and environmental conditions that can affect microstructure is vast; therefore deconvoluting the contribution of different variables to microstructural evolution is challenging.

Previously, attempts to optimise electrode performance have been largely empirical, with microstructural optimisation inferred from improvements in electrochemical performance or through conventional microscopy methods, which provide limited site specific information in two dimensions. Parametric optimisation is challenging because of the difficulty in isolating individual processing or environmental effects on the basis of macroscopic performance data.

The development and adoption of micro-tomography techniques provides insight into fuel cell microstructures at unprecedented resolution. A recent review of techniques for the microstructural characterisation of SOFC electrodes is provided by Shearing et al. [9].

In this paper, we describe techniques for the collection of microstructural data using cutting-edge tomography techniques and methods to combine these with numerical simulation. Finally we consider how these methods can be extended to characterise microstructural evolution under conditions representative of SOFC operation.

Collecting Microstructural Data

Ni-YSZ symmetrical cells have been prepared by screen printing commercially available NiO-YSZ ink (Cerampaste manufactured by Ceramtec) onto commercially available pre-sintered, tape cast YSZ pellets (Nextech Materials). The single layer screen printed anodes were then sintered at 1350°C. Reduction of NiO to Ni followed the manufacturers guidelines: cells were heated to 600°C in 97% N2, 3% steam, at 600°C, the concentration of H2 was increased to 97% over a period of 1 hour, after which the cells were held for 1 hour before cooling in N2.

X-ray Techniques

The implementation of X-ray optics has dramatically improved the resolution that can be achieved in laboratory and synchrotron computed tomography[10]. By focusing the X-ray beam before and after transmission through the sample, near order of magnitude improvement in resolution is observed (~50 nm) by nano-CT compared to conventional X-ray micro-CT (~1 mm).

Samples are rotated through 180-190° with hundreds or thousands of radiographs (projections) collected at discrete angular steps. The transmission micrographs can be reconstructed into 3D volumes using standard back-projection algorithms (see Banhart [11] for further details).

In order to minimize noise in the reconstructed data set, it is desirable to maintain the sample within the field of view (FOV) throughout the sample rotation. For 50-150 nm spatial resolution this required samples having lateral dimensions of between 15 and 65
mm, a focused ion beam (FIB) sample preparation technique has been developed [12] whereby small sections of material can be excavated and micro-welded onto tungsten needles.

The fixed energy (8.1kV) associated with the Cu target normally found in laboratory based nano-CT system does allow for some differential contrast between the Ni and YSZ phases in composite SOFC electrodes [12] because the absorption edge of nickel metal at 1.488 Å lies between the Kα (λ = 1.542 Å) and Kβ (λ = 1.392 Å), however, this has not been sufficiently uniform to isolate triple phase contacts. Further development work is currently underway to improve the contrast that can be achieved for these composite electrodes using laboratory nano-CT.

Isolating the three-dimensional distribution of Ni, YSZ and pore phases has been achieved using synchrotron tomography where XANES principals have been applied to manipulate X-ray energies to establish phase contrast (and phase identification) for these composite materials [1].

Figure 2 a) shows a virtual slice from a nano-CT scan conducted using the Xradia Transmission X-ray Microscope (beam-line 32-ID) at the Advanced Photon Source (APS), Chicago. The 2D section shows the electrode-electrolyte interface for the electrolyte supported Ni-YSZ anode. Good contrast between the electrode phases is demonstrated – furthermore in this projection, you can clearly see the supporting needle and micro-weld and the Au ball used for sample alignment.

In addition to the electrode layer, we have successfully characterised the electrode-electrolyte interface and part of the bulk electrolyte layer- it is noteworthy that defects are visible in the (commercially purchased) electrolyte structure – the authors speculate this is due to potential air entrainment during the tape casting process. A 3D rendering is shown in Figure 2b.

![Figure 2](image-url)  
**Figure 2.** a) An individual “virtual-slice” from the computed tomography sequence showing the Ni-YSZ anode – YSZ electrolyte interface; b) a 3D rendering of the tomography data. The horizontal field of view shown is approximately 20 microns.
Focused Ion Beam Techniques

The sample has also been characterised using FIB tomography. FIB serial sectioning techniques are increasingly widespread [2, 4, 13-18] and enable the user to combine nano-scale ion beam milling with electron microscopy, obtaining a sequence of 2D micrographs that can be effectively recombined in 3D space. We have previously demonstrated good agreement between materials characterised using FIB and nano-CT techniques [12].

Figure 3 shows a micrograph of the Ni-YSZ electrode alongside a schematic of the FIB method. The micrograph shows distinct contrast between the Ni, YSZ and pore phase which allows automatic segmentation of the tomography data set [4].

Data was collected as outlined in Shearing et al [4]. From the FIB tomography sequence, 100 slices have been segmented and analysed, using a voxel dimension of 20 x 20 x 15 nm corresponding to a sample size of 6.68 x 5.04 x 1.50 µm. Whilst larger reconstructions have been conducted (e.g. [2,14]) this volume is representative of the screen-printed electrode which has a thickness of 5 µm.

In the next section of this paper, we explore how experimentally derived microstructural data can be combined with numerical simulation tools.

Modelling Electrochemical Processes using a Volume of Fluid Methodology

Golbert et al [19] first reported a volume of fluid (VoF) technique for modelling coupled electrochemical and transport processes in synthetic microstructures generated from Monte Carlo techniques. This simulation has been subsequently combined with microstructural data from FIB experiments [4].

Firstly, voxellised FIB data is geometrically characterised for phase fraction and triple phase contact, the voxel data is then discretised into VoF elements which are groupings of voxels (as shown in Figure 4). Transport and electrochemistry in each VoF element is simulated.
The voxellised FIB data is discretised into VoF elements for electrochemical and transport simulation.

The VoF model assumes current generation at triple phase boundary points according to the Butler-Volmer equation – therefore, to simulate the electrochemical activity of the electrode, the model requires exchange current per unit TPB length as an input. With some notable exceptions [20-22], this data is not widely available in the literature, therefore we have adopted an iterative approach to match simulated electrode performance with that measured using impedance spectroscopy.

Electrical impedance spectra (EIS) for the electrolyte supported Ni-YSZ anode considered here was obtained using a symmetrical cell configuration [4]. Equivalent circuit analysis identified three processes at high, medium and low frequencies. We assume the high frequency process represents the resistance due to charge transfer – at low overpotentials, this corresponds to the gradient of the voltage-current density plot. This part of the EIS response is appropriate for comparison as our electrochemical model currently considers only electron transfer; we do not yet account for additional contributing processes such as adsorption and surface diffusion, which will be considered in future studies.

Using an iterative process to match the experimentally measured charge transfer resistance with the simulated V-I behaviour at low over-potential, we have isolated the exchange current per unit length for this Ni-YSZ electrode in 97% H₂, 3% steam at three temperatures:

The length-specific exchange current is estimated to be $9.4 \times 10^{-11}$, $2.14 \times 10^{-10}$ and $1.22 \times 10^{-9}$ A/μm at 800, 900 and 1000°C respectively. This provides good agreement with experimentally determined data from the literature [21].

Modelling Mechanical Processes using a Finite Element Methodology

The tomography data from the FIB experiments described previously has also been successfully combined with predictions of the stress by Finite Elements (FE). The tomography data set has been described using a high-fidelity mesh, which accurately represents the real-life electrode interfaces and which can be directly integrated with commercial stress simulation packages. The FE mesh is shown in Figure 5.
The finite element model was generated from the segmented tomography data using ScanFE software, [3] (ScanFE V3.1, Simpleware Ltd, UK). The model comprised 285,000 four-node tetrahedral elements (Abaqus type C3D4). The appropriate number of elements was determined from a mesh independence test, which showed that mesh independent stress results based on average stress were obtained at this element density. During meshing the Ni and YSZ phases were assigned to one of two material designations to allocate appropriate material properties. Node and element sets were automatically generated on the model cut planes and at the interface of the two phases.

Boundary conditions and load-cases in the form of a global temperature field were applied (as detailed below) using Abaqus CAE (v6.10, Simulia, UK) and finally a stress analysis was run using the Abaqus Implicit finite element solver. The analysis assumed that there was no separation of the Ni and YSZ phases and that the material behaviour was linear elastic.

In order to represent the reconstructed portion of the electrode as a section of a larger anode, the boundary conditions that were applied to the model constrained the cut planes to remain planar, while allowing bulk thermal expansion between opposite cut planes. This was achieved by restraining the degree of freedom of the nodes on one cut plane in the direction normal to the cut plane, then on the opposite cut plane the normal degree of freedom of the nodes on that plane were tied together. This has the effect of allowing bulk thermal expansion between opposing cut planes, while still imposing the condition that the cut planes remain planar. These mechanical boundary conditions are not considered to fully represent the behaviour of the cut planes of the sample in an actual fuel cell, but this will be investigated in due course through sub-modelling, where displacement boundary conditions are transposed from a larger, less detailed model.

As the YSZ phase is wetted by the Ni phase, a strain continuity condition was imposed at the interface between the Ni and YSZ phases. The solid phases were free to expand into the pore phase. A global temperature field $T_0$ of 298 K was applied as an initial, zero stress condition, which was subsequently increased to a temperature $T_1$ of 1073 K in a single analysis step.
The mechanical properties of the materials required for the thermo-mechanical stress analysis are summarised in Table 1. E is the Young’s modulus (in GPa), \( \nu \) is the dimensionless Poisson’s ratio and \( \alpha \) is the coefficient of thermal expansion (1/K).

**Table 1. Material properties**

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Temp (K)</th>
<th>E (GPa)</th>
<th>( \nu )</th>
<th>( \alpha ) (( \times 10^{-6} ))</th>
<th>Yield (MPa)</th>
<th>UTS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Ni [23]</td>
<td>1073</td>
<td>207</td>
<td>0.31</td>
<td>13.5</td>
<td>59</td>
<td>317</td>
</tr>
<tr>
<td>YSZ [24]</td>
<td>1073</td>
<td>157</td>
<td>0.313</td>
<td>10.5</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

The differential thermal expansion of the Ni and YSZ phases generates stresses within the composite structure that peak at the interfaces of the solid phases. Figure 6 shows the maximum principal stress field generated when the global temperature increases from \( T_0 \) to \( T_1 \). In the Ni phase the peak maximum principal stress of over 200 MPa is a significant proportion of the failure strength of 317 MPa, and well above the yield strength of 57 MPa at 1073 K, illustrating that the elastic analysis used is oversimplified leading to an over-estimation of the peak stresses.

![Figure 6](image)

**Figure 6.** A 3D reconstruction of the Ni-YSZ electrode (left) with Maximum principal stress distribution throughout the Ni and YSZ phases in 3D and a cross-section through A-A (right).

The analysis shows that the highest stresses appear at the interfaces between the Ni and YSZ phases. The stresses predicted by this analysis approach the failure strength of the Ni phase and exceed the yield strength by some margin, implying that stress relief
through plastic deformation is likely to occur at the phase boundaries as the sample is heated from room to operating temperature. By assuming perfectly elastic material behaviour and a zero stress state at room temperature, the analysis predicts that either plastic deformation would occur within the Ni phase near the phase boundary, or interface cracking might occur. Unfortunately the strength of the Ni-YSZ interface is currently not known. Assuming the failure characteristics of YSZ are the same in compression and tension, the characteristic strength of YSZ at these volumes is therefore exceeded, so that were plastic deformation not to occur some fracturing of the ceramic matrix would be expected.

Further work is underway to simulate the mechanical performance of the Ni-YSS electrode: YSZ electrolyte interface which has been successfully characterised using synchrotron nano-CT.

Characterising Microstructural Evolution using High Resolution X-ray Tomography

The non-destructive nature of X-ray tomography enables researchers to characterise microstructural evolution processes. Whilst similar experiments are possible using destructive techniques such as FIB tomography, inherent sample to sample variations in microstructure mean that any microstructural comparisons before and after environmental change must be made on a statistical basis.

Using synchrotron X-ray nano-CT we have successfully demonstrated the potential for characterising microstructural change that occurs on a single sample in-situ and ex-situ of the X-ray microscope stage.

![Figure 7. a) A schematic representation of a lens-based nano-CT system on beam-line 32 ID at APS; b) Implementation of a prototype micro-tube furnace.](image)

As the nano-CT system does not operate under vacuum, it is possible to implement a variety of different environments in situ, broadly representative of SOFC operating conditions. A schematic diagram of the experimental setup of the lens based nano-CT system at APS is shown in Fig. 7 alongside our in situ furnace for studies at temperature and under different gas environments. This provides an opportunity to study transient microstructural changes. In the future, these ‘four-dimensional’ tomography techniques may be used to explore micro-structural changes associated with cell processing, redox cycling and long term degradation.
Conclusions

Understanding the influence of electrode microstructure is key to improving SOFC technology. Tomography techniques using X-rays and focused ion beams are becoming increasingly widespread in SOFC research owing to their ability to provide detailed microstructural information.

Furthermore the ability to combine microstructural data with relevant simulations provides a powerful tool for establishing microstructure-performance relationships and for isolation of microscopic contributions to macroscopic electrode behaviour. In the future the ability to non-destructively characterise microstructural evolution processes will provide an improved understanding of the dynamics of electrode aging and degradation empowering researchers to design high performance electrodes.

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