

# Mapping Electrochemical Activity in Solid Oxide Fuel Cells

## X-ray nano computed tomography of heterogeneous microstructures

T. M. M. Heenan\*, D. J. L. Brett, P. R. Shearing

Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, London, UK, WC1E 7JE

\*Corresponding author: Heenan, T. M. M. ([Thomas.heenan.11@ucl.ac.uk](mailto:Thomas.heenan.11@ucl.ac.uk))

Solid oxide fuel cells (SOFCs) are electrochemical energy conversion devices which offer low-carbon electricity and heat [1]. In its simplest form, the SOFC can be described as two porous electrodes, the anode and cathode separated by a dense electrolyte. At sufficiently elevated temperatures (600 – 1000 °C) the electrolyte acts as an oxide ion conductor; O<sup>2-</sup> ions produced via the reduction of oxygen at the cathode are transported to the anode where hydrogen is oxidised forming water. A by-product of these REDOX reactions is the production of electricity via the flow of electrons from the anode to the cathode and heat from the exothermic reactions, which can be usefully recovered.

The electrolyte material must be ionically conducting, electronically insulating, dense to prevent gas crossover and stable in both reducing and oxidising environments. Commonly employed materials include the ceramics yttria stabilised zirconia (YSZ) and gadolinium doped ceria (GDC). Unlike the electrolyte which only promotes ionic mobility, the electrodes must promote three transport processes in the ionic, electronic and gaseous phases, which is achieved with use of either mixed ionic electronic conductors (MIECs) or composite cermet materials. Commonly employed anode materials include metal-ceramic cermets of Ni-YSZ or Ni-GDC whereas cathodes are typically perovskite-based compounds such as lanthanum strontium manganite (LSM) or lanthanum strontium cobalt ferrite (LSCF) and are also often combined with ceramics to form composites such as LSM-YSZ.

The locations within composite cermet materials where all three phases meet are defined as triple phase boundaries (TPBs) and percolated TPBs are thought to strongly influence the electrochemical performance at the cell level [2]. Sample composition, particle size distributions and phase percolation all contribute to the *active* TPB density [3]. In order to maximise TPB densities, and thus the performance of the cell, it is essential to understand component microstructures in three dimensions: this is achieved using microstructural analysis methods such as focused ion beam scanning electron microscopy (FIB-SEMs) and X-ray computed tomography (CT) at sub-micron resolution [4]. Three-phase segmentation of the 3D data-sets allows for the TPB locations to be mapped and a TPB density to be quantified.

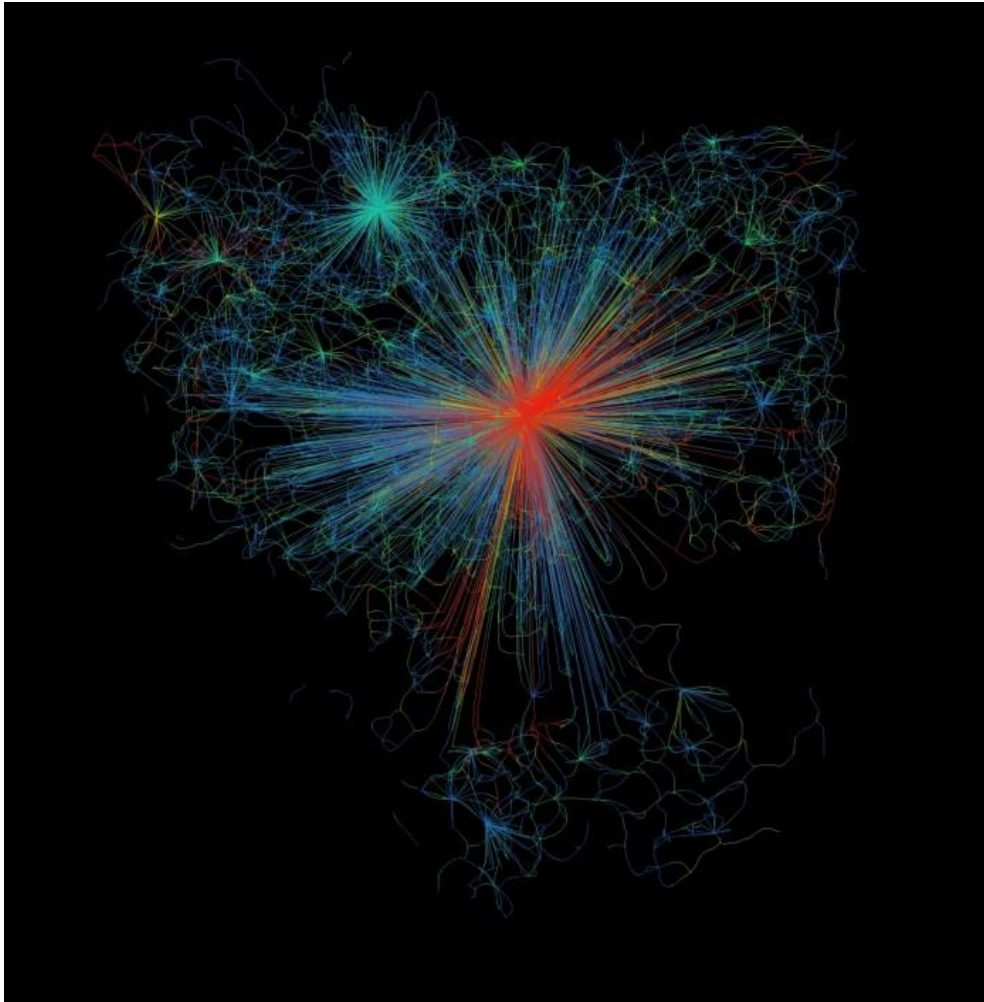
Unlike other fuel cells SOFCs do not require a pure hydrogen supply to the anode and a wide range of fuels including carbon monoxide and methane can be used for operation of a SOFC, although impurities such as sulphur and deposition of carbon remain an issue [5 - 7]. Moreover if oxygen enters the anode environment through poor sealing or gas crossover the Ni metal can undergo REDOX cycling, which is known to result in irreversible volume changes. Alas, even with a pure hydrogen feed SOFCs are still susceptible to degradation due to thermal gradients and thermal cycling making start-up and shut-down times prohibitively long.

This issue's cover of Materials Today displays the Ni phase within a heterogeneous Ni-YSZ anode sample. X-ray tomography samples of ca. 50 µm in diameter were prepared from a bulk sample and an internal tomogram was collected from the Ni-YSZ sample: this was achieved using a lab-based X-ray nano-CT instrument (Zeiss Ultra 810, Carl Zeiss., CA, USA) with an isotropic voxel resolution of 32 nm. To obtain a tomogram many 2D radiograph projections are collected at discrete angular increments through rotation of the sample, these projections are then reconstructed using a filtered back-projection algorithm into a 3D volume of grey scale voxels [2].

Once reconstructed the data was segmented according to grey-scale into three phases: Ni, YSZ and pore. A centroid path [8] was then mapped for the Ni phase using Avizo Fire software (FEI, France) by applying a medial axis-based method using distance-ordered homotopic thinning (DOHT) where a skeletonization is achieved through a combination of morphological thinning and distance mapping techniques. The figure shows a centreline tree displaying the geometrical centre of the Nickel phase. Here the red and blue paths display the longest and shortest segment lengths respectively. Phase percolation is maximised for the longest segment lengths and the highest number of segments connected to each node: the effective electrical conductivity of this composite material is directly correlated to the complexity of the Ni phase microstructure [9].

Percolation of all three phases is required to ensure electrochemical activity of the TPB, and hence most literature distinguishes percolated from non-percolated TPB values. Inspecting the figure, the central node connecting many segments displays a large heterogeneous Ni particle while in contrast the empty region in the bottom left of the figure displays no paths as no Ni occupied this region.

Characterisation of these material heterogeneities in 3D will ultimately lead to an improved understanding of the relationship between performance and microstructure, and the non-destructive nature of X-ray nano CT also allows characterisation of microstructural degradation mechanisms. This improved understanding will contribute to design and manufacture of next generation materials and devices.



**Figure** Nickel phase centreline tree mapped for a Ni-YSZ SOFC anode sample using a medial axis-based method using a distance-ordered homotopic thinning method in Avizo Fire software: red and blue segment paths display the highest and lowest connectivity in the Ni phase respectively.

## **Acknowledgement**

The authors would like to acknowledge the EPSRC (EP/M014045/1), the Centre for Doctoral training and the Royal Academy for Engineering for financial support, access to the Ultra 810 instrument was supported by the EPSRC and UCL (EP/K005030/1).

## **Further reading**

- [1] Singhal, Subhash C., and Kevin Kendall, eds. High-temperature solid oxide fuel cells: fundamentals, design and applications. Elsevier, 2003.
- [2] Shearing, P. R., et al. "Microstructural analysis of a solid oxide fuel cell anode using focused ion beam techniques coupled with electrochemical simulation." *Journal of Power Sources* 195.15 (2010): 4804-4810.
- [3] Kenney, Ben, et al. "Computation of TPB length, surface area and pore size from numerical reconstruction of composite solid oxide fuel cell electrodes." *Journal of Power Sources* 189.2 (2009): 1051-1059.
- [4] Shearing, P. R., D. J. L. Brett, and N. P. Brandon. "Towards intelligent engineering of SOFC electrodes: a review of advanced microstructural characterisation techniques." *International Materials Reviews* (2013).
- [5] Badwal, S. P. S. "Stability of solid oxide fuel cell components." *Solid State Ionics* 143.1 (2001): 39-46.
- [6] Gorte, Raymond J., et al. "Anodes for direct oxidation of dry hydrocarbons in a solid-oxide fuel cell." *Advanced Materials* 12.19 (2000): 1465-1469.
- [7] Faes, A., et al. "Nickel–zirconia anode degradation and triple phase boundary quantification from microstructural analysis." *Fuel cells* 9.6 (2009): 841-851.
- [8] Taiwo, Oluwadamilola O., et al. "Comparison of three-dimensional analysis and stereological techniques for quantifying lithium-ion battery electrode microstructures." *Journal of microscopy* (2016).
- [9] Rhazaoui, K., et al. "Towards the 3D Modelling of the Effective Conductivity of Solid Oxide Fuel Cell Electrodes–Validation against experimental measurements and prediction of electrochemical performance." *Electrochimica Acta* 168 (2015): 139-147.