

## Solid Oxide Fuel Cells and Electron Backscatter Diffraction (EBSD)

### Introduction

Fuel cells are a major part of the discussion in addressing the world's energy needs. Fuel cells are highly efficient power sources with long term stability and low emissions. A fuel cell running on hydrogen can be compact and lightweight, have no major moving parts and produce very low emissions. For these reasons, they are particularly attractive for application in remote locations. A fuel cell is an electrochemical conversion device composed of an anode and a cathode separated by an electrolyte. Electricity is produced when fuel is introduced at the anode and an oxidant is present at the cathode. The fuel and the oxidant react within the electrolyte. While there are a wide variety of fuel cell types, we will focus on solid oxide fuel cells or SOFCs, where the electrolyte is a solid oxide. Advantages of SOFCs are their high efficiency, long term stability, fuel flexibility, low emissions, and relatively low cost. The largest disadvantage is the high operating temperature [1]. While the basic components of a SOFC are relatively simple, the functional requirements for the materials used in the different components are extremely demanding [2].

### Electrolyte

The following set of properties must be considered when selecting an electrolyte material.

- High ionic conductivity
- Negligible electronic conductivity
- Stability in both the oxidizing and reducing atmospheres
- Chemical reactivity with the anode and cathode materials
- Impermeability to prevent mixing of the fuel and oxidant gas feeds
- Operating temperature

The most common SOFC electrolyte material is yttria ( $Y_2O_3$ ) stabilized zirconia ( $ZrO_2$ ) or YSZ. It generally requires an operating temperature above  $850^\circ C$ . This high operating temperature places severe demands on the materials used in constructing the fuel cell. The operating temperature is principally governed by the nature of the electrolyte, i.e. its ionic conductivity, and the thickness of the electrolyte layer. There are therefore two possible approaches to lowering the operating temperature. The first is to reduce the thickness of the electrolyte layer and the second is to search for alternative electrolyte materials with higher oxygen ion conductivities [2].

The layer thickness can be reduced using thin film deposition techniques, which is an area of ongoing research, particularly for mobile electronics applications. Several different materials are under investigation including gadolinia doped ceria, as well as zirconia and ceria doped with other oxides. Lanthanum gallate based structures [2], strontium titanate [3] and Perovskite type oxides [4] are under consideration as well.

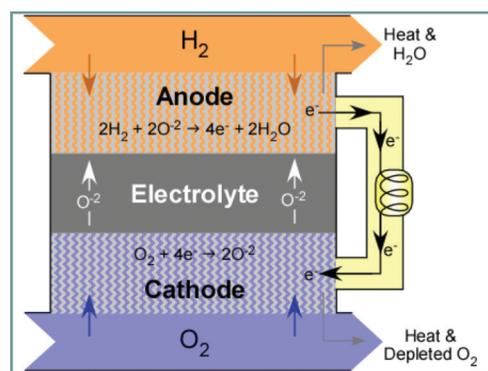


Figure 1. Schematic of solid oxide fuel cell.

These materials have different strengths and weaknesses in terms of ion conductivity and durability in the oxidizing and reducing atmospheres present in the system and are thus a focus of ongoing research. Another area of research is in the optimization of the material microstructure through controlled processing to improve performance, such as ion conductivity.

### Anode

The anode is a porous layer on the electrolyte where oxygen ions diffusing through the electrolyte oxidize the hydrogen fuel, producing water and electricity. The anode material must meet the following set of requirements.

- Oxidation promotion of hydrogen fuel
- Electrically conductive
- Stable in a reducing atmosphere
- Porous
- Similarity with electrolyte thermal expansion
- Chemical reactivity with the electrolyte
- Ion conductive

As the fuel arriving at the anode is a reducing agent, the anode can be made of metal. However, the material must not oxidize during operation, thus limiting the candidate metals to nickel, cobalt and the noble metals. Nickel is most often used because of its low cost compared to the others. In order to enable flow of the fuel to the electrolyte, the anode must remain porous at the elevated operating temperature. Another requirement is to sufficiently minimize the mismatch in thermal expansion between the anode and electrolyte to maintain adhesion at the interface. These two requirements are achieved by dispersing the nickel within the solid electrolyte material to form a cermet. [2]

The anode material choice may vary particularly as the electrolyte material is varied. Other materials under consideration include nickel/ceria cermet for ceria-gadolinia based SOFCs, the use of various dopants and electrically conducting oxides such as  $\text{LaCrO}_3$  [2] and  $\text{SrTiO}_2$  [5].

As with the electrolyte material, research is also being conducted in microstructure optimization. Conductivity depends on microstructure, in particular the size and particle size distribution of the solid electrolyte and nickel particles and the connectivity of the nickel particles in the cermet.

## Cathode

The cathode is a porous layer on the electrolyte where oxygen is reduced to form oxygen ions, which are diffused through the electrolyte. Cathodes have a specific set of requirements:

- Promotion of oxygen reduction
- Electronically conductive
- Stable in an oxidizing atmosphere
- Porous
- Similarity with electrolyte thermal expansion
- Chemically unreactive with the electrolyte
- Ion conductive

Maintaining these requirements at the elevated operating temperatures limits the cathode material choice to noble metals or electronically conductive oxides. Due to the high cost of noble metals, electronically conductive oxides are exclusively used. Strontium-doped lanthanum manganite (LSM) being the most common. LSM has a coefficient of thermal expansion that is similar to that of YSZ.

Similar to the anode, the cathode material choice may vary particularly as the electrolyte material is varied. Other materials under consideration include  $\text{LaCoO}_3$  [2] and lanthanum strontium cobalt ferrite [1]. Also, various methods of improving performance such as electrical conductivity through microstructure optimization are being investigated.

## Interconnect

The interconnect provides an electrical contact between the cathode and anode. Typically, the interconnect sits between each individual cell to combine the electrical output of all cells in the stack. It must therefore have high electrical conductivity in both the oxidizing atmosphere at the cathode and reducing atmosphere at the anode and be stable in both atmospheres as the operating temperature is elevated. The interconnect must therefore meet the follow set of criteria.

- Chemically unreactive with the anode, cathode or electrolyte
- Highly electrically conductive
- Similarity with the thermal expansion of the anode, cathode and electrolyte
- Stable in both oxidizing and reducing atmospheres
- Impermeable

These requirements severely restrict the choice of materials, especially at the high operating temperatures of YSZ-based SOFCs. Most zirconia-based SOFCs use lanthanum chromite,  $\text{LaCrO}_3$ . As lower temperature SOFCs are being developed, other materials are being considered such as  $\text{SrTiO}_2$  [5] and Crofer 22 APU [6]. Crofer 22 is a high temperature stainless steel with a low coefficient of thermal expansion, thermal stability at high temperature, good thermal conductivity of the oxide layer and high electrical conductivity.

## Characterization

EDAX's Scanning Electron Microscope (SEM) based tools are well suited for research and development of SOFCs. Energy Dispersive Spectroscopy (EDS) is capable of quantifying chemical composition at submicron length scales. Electron Backscatter Diffraction (EBSD) provides crystallographic information at scales of tens of nanometers.

Examples of EDS studies include the chemical composition and spatial distribution of composition within the constituent fuel cell materials. Because of the microscopic capability of EDS on the SEM, it is possible to look at compositional gradients

across the reaction zones at the interfaces between the different fuel cell components. For example, Figure 2 shows a peak in the spatial distribution of chromium at the interface between a Crofer interconnect and its oxide scale.

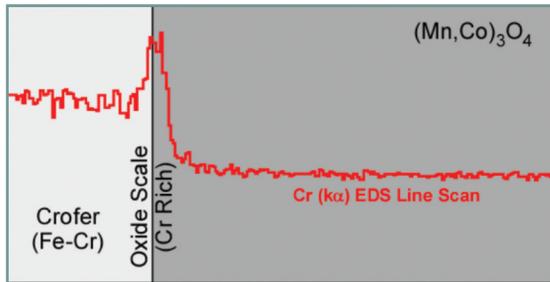


Figure 7. Schematic of a chromium EDS line scan of a post-tested SOFC showing minimal chromium migration from the stainless steel interconnect into the  $Mn_{1.5}Co_{1.5}O_4$  barrier coating. [7]

EDS is also well suited for determining the chemical composition of specific features observed in the microstructure. However, some phases form polymorphs, which have the same chemical composition but different crystallographic structure. In these cases, coupling EDS with EBSD using EDAX's unique ChI-Scan software allows such phases to be unambiguously identified. An example is shown in Figure 3. In this figure, the EBSD has been used to differentiate the cubic and monoclinic phases of YSZ. Coupling the EBSD results with simultaneously collected EDS data shows that the cubic zirconia is yttrium-rich relative to the monoclinic zirconia.

Because EBSD data can be collected rapidly and automatically using modern Orientation Imaging Microscopy (OIM™) systems, it is possible to map the spatial distribution of crystallographic orientation within the microstructure. Figure 4 shows an example for YSZ. The map is colored according to the accompany scale. The grains colored red have [001] axes normal to the section plane, the blue are [111] type and the green are [101] type. In this case, there is no preferred orientation. Such information allows the researcher to correlate properties with the orientation aspects of the microstructure.

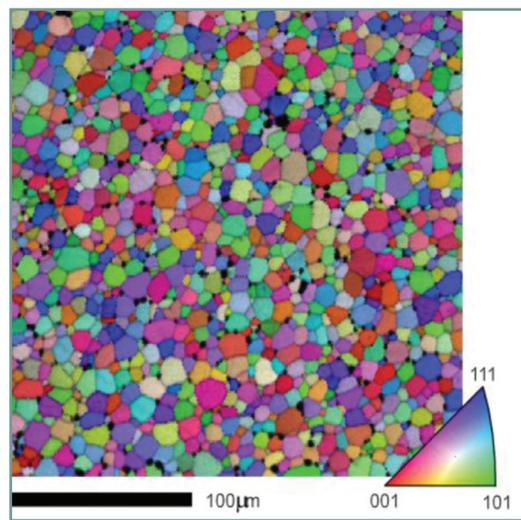


Figure 4. EBSD orientation map of YSZ.

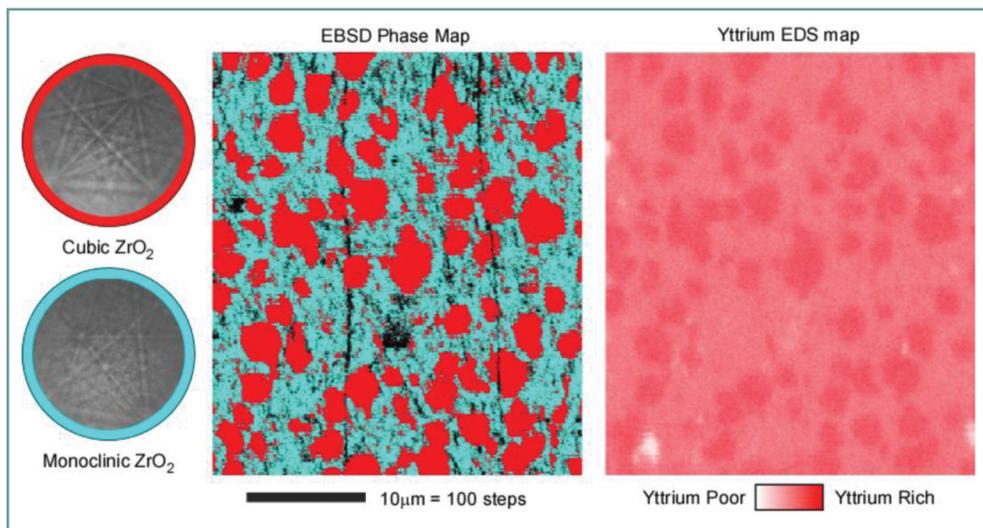


Figure 3. EBSD phase map and an EDS elemental map for yttrium obtained simultaneously, showing the correlation between phase and yttrium content. [8]

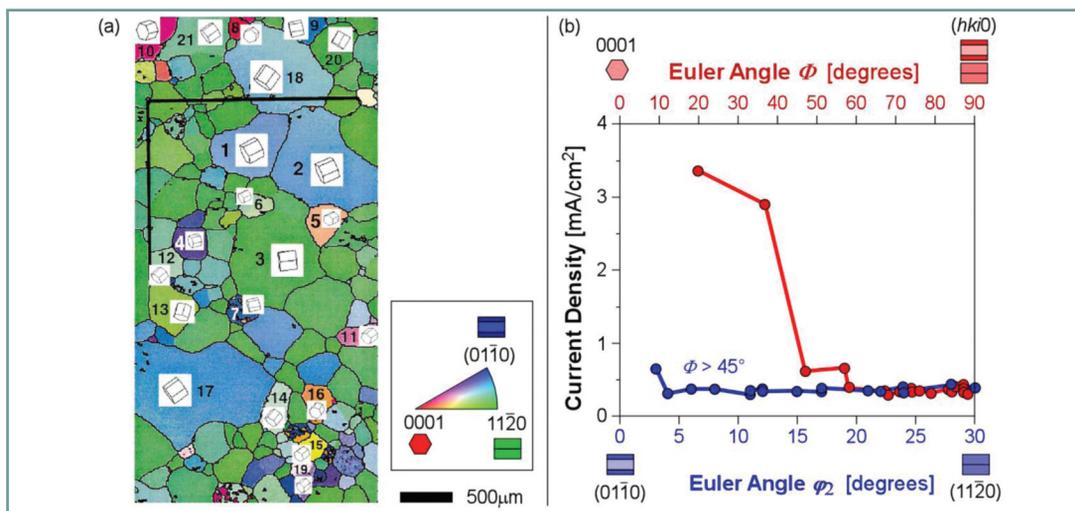


Figure 5. (a) Orientation map with specific grains labeled. (b) Chart showing the variation in current density as a function of orientation from the microelectrochemical measurements on the labeled grains in (a). [9]

One example is the link between oxidation rate and orientation. Coupling microelectrochemical experiments with EBSD, Davenport and König [9] have shown that oxidation is a function of orientation. Photoresist microelectrodes were applied to specific grains in a polycrystalline titanium sample after scanning the measurement area using EBSD. The electrochemical and EBSD results are summarized in Figure 5 for a potential of 10V. There is clearly a large difference between the results with basal planes parallel to the surface versus normal to the surface. The authors were further able to correlate the quality of the EBSD patterns with oxidation layer thickness. Since the oxidation rate is anisotropic, the properties of the fuel cell materials can be fine tuned by optimizing the microstructure through process control. The goal would be to create a preferred orientation so as to increase the fraction of grains with oxidation resistant planes parallel to the surface or normal to the surface depending on the specific application.

Ions seek to follow the lowest energy path through the crystal structure. Thus, ion conductivity is generally an anisotropic material property. In addition, as the bonds are different in ceramics, the grain boundaries are not as dense as in metals. Thus, the diffusion of ions is typically faster along and across grain boundaries than within the grains [10].

A few authors have studied the impact of grain boundaries on ion conductivity [3,5]. However, this is an area that needs further examination. For example, Shih et al. [3] have used EBSD to study the role of the population of Σ3 type boundaries

in ion conductivity of SrTiO<sub>3</sub>. Σ3 boundaries are special boundaries with a high fraction of coincidence at the boundary between two crystal lattices. Figure 6 shows the distribution of special boundaries in the YSZ sample shown in Figure 4(a) as measured by OIM™. In this case, the fraction of special boundaries is small; the majority of grain boundaries are random high angle boundaries. It should be noted that OIM™ is capable of measuring the preferred orientation or crystallographic texture as well. In this case, the crystallographic texture is essentially random as shown in Figure 6(b).

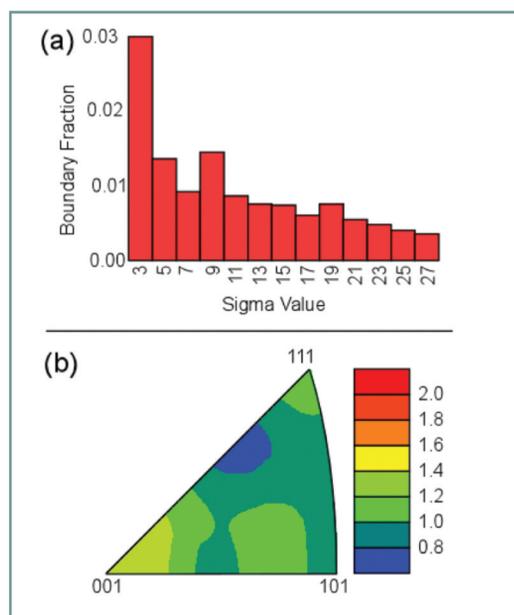


Figure 6. (a) Distribution of special grain boundaries and (b) an inverse pole figure texture plot for the YSZ EBSD data show in Figure 4.

Understanding how charged ions or electrical current are conducted through the microstructure enables the materials engineer to tailor the microstructure to achieve the optimal performance for a particular application. For example, consider the following three conditions.

a) For a property that is shape anisotropic, i.e. the property is greater in the grain elongation direction than in the transverse direction, the optimal microstructure would be that shown in Figure 7(a). This microstructure is also optimal for a material property which is stronger along the grain boundaries than through the grains. For example, if diffusion of ionic species is faster along grain boundaries than through the grains, then this microstructure would improve diffusion in the vertical direction. In fact, a more optimized microstructure in this case would be composed of very thin rods extending through the entire thickness of the layer.

b) For a material property where the strongest anisotropy is crystallographic, i.e. stronger in one crystallographic direction than another, it would be better to align this crystallographic direction with the direction in the bulk, as shown in Figure 7(b).

c) In the case where certain types of boundaries are more suited to the material property than others, it would be beneficial to align the good boundary types in the direction of desired performance enhancement as shown in Figure 7(c).

In practice, not all microstructures can be achieved and properties may differ both crystallographically within grains and with grain boundary type, so that some hybrid structure would provide the best overall performance. Additionally, in almost all cases, the objective is to maximize one property without creating deleterious effects on other properties. Thus, a balanced approach must be considered. The capability of EBSD to characterize both grain orientation and grain boundary

misorientation makes it an ideal tool for characterizing the microstructures to ensure the objectives of the microstructure engineering are being achieved. With automated EBSD systems, it is possible to characterize these aspects of microstructure with statistical reliability.

### Conclusions

EBSD is a tool well suited for the characterization needs of solid oxide fuel cell research and development. In particular, the characterization of both orientation and grain boundaries in polycrystalline microstructures. In addition, coupling EBSD with EDS expands the ability of both techniques to meet a wide variety of materials characterization needs at the microscopic scale.

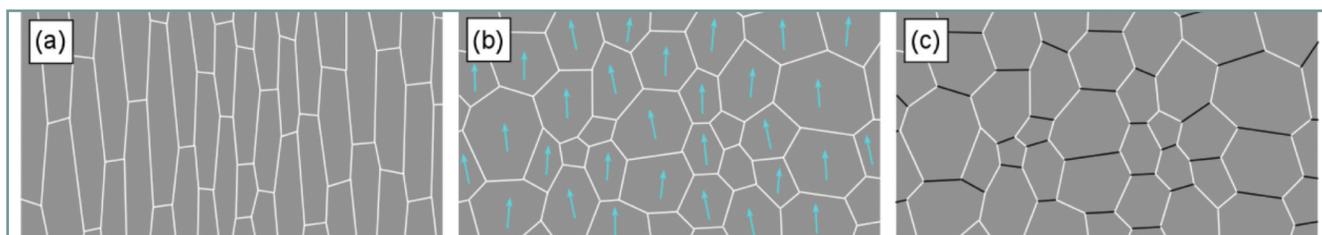


Figure 7. Idealized microstructures for a desired material property where (a) the property is stronger in the grain elongation direction or along grain boundaries as opposed to through grain interiors, (b) the property is stronger in a specific crystallographic direction or (c) the property is stronger for certain grain boundary types (white) and weaker for others (black).

## Bibliography

- [1] Wikipedia – Solid Oxide Fuel Cells
- [2] R. M. Ormerod (2003) "Solid oxide fuel cells." *Chemical Society Reviews* **32**, 17-28.
- [3] S.-J. Shih, C. Bishop & D. J. H. Cockayne (2009). "Distribution of 3 misorientations in polycrystalline strontium titanate." *Journal of the European Ceramic Society* **29**: 3023-3029.
- [4] N. Sammes & Y. Du () Intermediate-Temperature SOFC Electrolytes in *Fuel Cell Technologies: State and Perspectives Proceedings of the NATO Advanced Research Workshop on Fuel Cell Technologies: State and Perspectives Kyiv, Ukraine 6–10 June 2004*, eds. N. Sammes, A. Smirnova & O. Vasylyev, Springer: Netherlands, 19-34.
- [5] F. Horikiri, L. Q. Han, A. Kaimai, T. Otake, K. Yashiro, T. Kawada & J. Mizusaki (2006). "The influence of grain boundary on the conductivity of donor doped SrTiO<sub>3</sub> " *Solid State Ionics* **177**: 2555-2559.
- [6] [thyssenkruppvdm.de/\\_pdf/Crofer22APU\\_e.pdf](http://thyssenkruppvdm.de/_pdf/Crofer22APU_e.pdf)
- [7] S.P. Simner, M.D. Anderson, G-G Xia, Z. Yang & J.W. Stevenson (2005). "Long-Term SOFC Stability With Coated Ferritic Stainless Steel Interconnect" *Ceramic Engineering and Science Proceedings* **26**: 83-90
- [8] P. M. Delaforce, J. A. Yeomans, N. C. Filkin, G. J. Wright, & R. C. Thomson (2007). "Effect of NiO on the Phase Stability and Microstructure of Yttria-Stabilized Zirconia" *Journal of the American Ceramic Society* **90**: 918–924.
- [9] B. Davepon, J. W. Schultze, U. König & C. Rosenkranz (2003). "Crystallographic orientation of single grains of polycrystalline titanium and their influence on electrochemical processes." *Surface and Coatings Technology* **169-170**: 85-90
- [10] C. B. Carter, M. G. Norton (2007) *Ceramic Materials*, Springer: New York, pp. 197-198