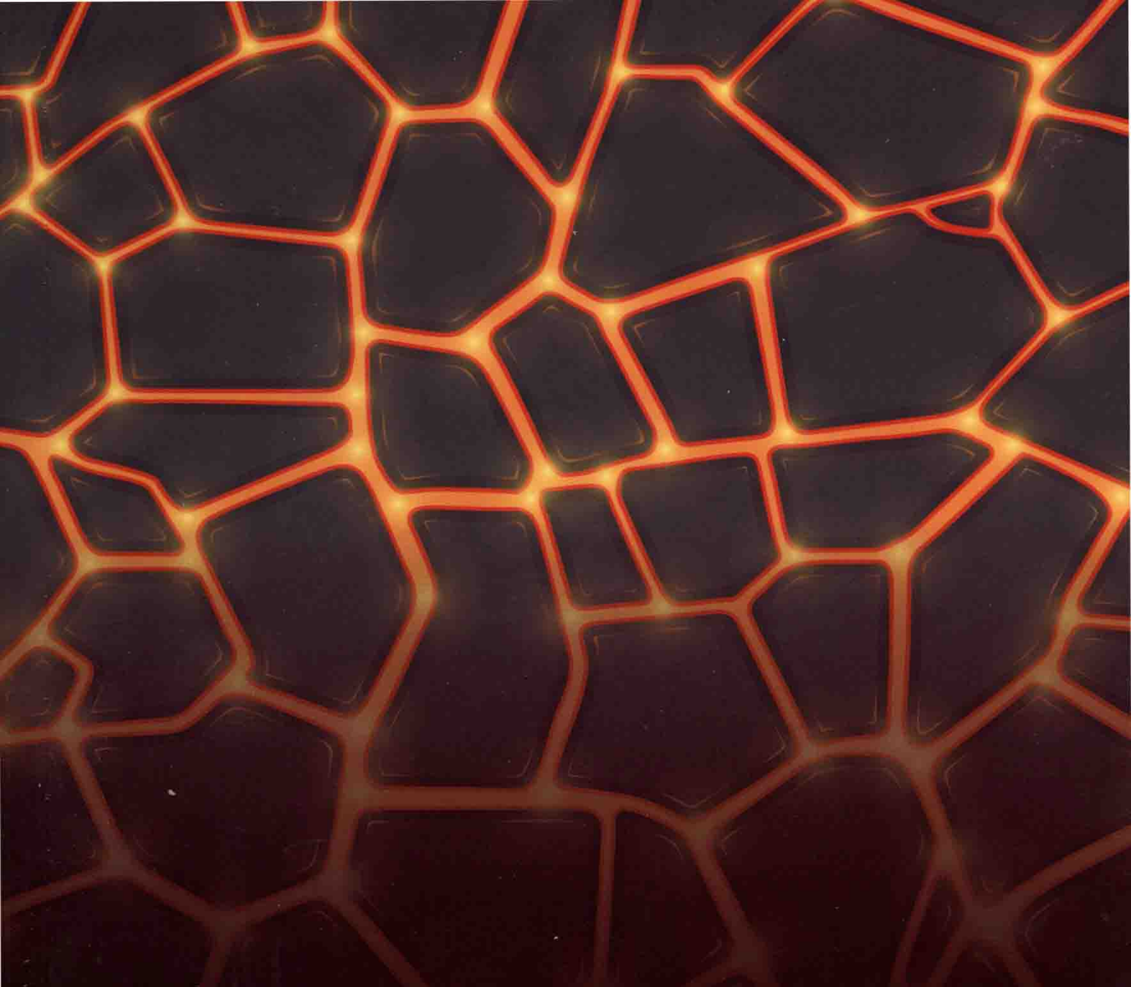

Solid Oxide Fuel Cell Lifetime and Reliability

Critical Challenges in Fuel Cells

Edited by
Nigel P. Brandon,
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Chapter 1

An Introduction to Solid Oxide Fuel Cell Materials, Technology and Applications

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Chapter Outline

This chapter aims to give the reader an overview of solid oxide fuel cell (SOFC) technology in terms of both the fundamental theory and real world applications. It concludes with an introduction to the various degradation mechanisms common to many fuel cell systems today, which are discussed in detail in the following chapters of this book.

A BRIEF HISTORY OF SOLID OXIDE FUEL CELLS

Fuel cells are a family of electrochemical devices, which generate electricity by promoting a redox reaction across an ionically conductive membrane. Although fuel cells were first reported in 1839 by Sir William Grove, it was not until 1961, when NASA began Project Gemini, that they found their first practical application [1]. Fuel cells are typically named in terms of two key

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characteristics: the mobile ion and the electrolyte material, with the operating temperature also being used to subclassify in some cases.

SOFCs are named after their ion conducting, ceramic oxide electrolyte and their history is tied to some of the great names in science and engineering. Faraday's early investigations of conduction in ceramics in the 1830s [2], led him to classify conductors into two categories, although the exact mechanism for these two modes of conduction was unknown. It was not until much later, in the 1890s, when Walther Nernst observed the significantly increased conductivity of mixed oxides over their pure constituents that the first technological implication of ion conduction in solids was conceived. Although ultimately not a commercial success, due in part to its high cost, the "Nernst Glower" was nearly twice as efficient as the carbon filament lamps of the day [3]. The device consisted of a ceramic oxide rod made of yttria-doped zirconia (often referred to as the "Nernst Mass") which, after preheating to around 1000°C, would begin to conduct under load; this in turn led to the temperature increasing further, causing the rod to glow. The 1930s saw the conceptual development of ion conduction through lattice defects by Schottky [4] and Frenkel [5], which led to the submission of the first SOFC patent through Siemens and Halske [6].

The first cell beginning to resemble a modern configuration was proposed by Baur and Preis [7], who used the "Nernst Mass" for the electrolyte in combination with metal oxide electrodes. Although the system was a failure due to high Ohmic losses, it spurred a new wave of investigation into conducting mixed oxides. Over the following 30 years, Kiukkola and Wagner [8] and many others [9,10] undertook a systematic investigation into ion-conducting electrode materials in order to find structures that had both the mechanical and electrochemical properties required for a durable fuel cell.

By 1970 the adoption of electroceramics for a broad range of other industrially relevant applications, such as sensors (e.g., lambda sensors that are widely used today to measure the air/fuel ratio in engine exhaust gases) and oxygen separation membranes, led to key advances in materials processing and the materials supply chain. Other related advances, for example in the semiconductor industry, resulted in processes emerging such as electrochemical vapor deposition [11]. This allowed for much thinner layers of high-purity material to be deposited, which not only had the potential to reduce Ohmic losses, but also opened the possibility of using materials previously deemed too costly.

Following the first and second oil crises of the 1970s, which cumulatively led to a 10-fold increase in the price of oil [12], governments from fuel importing nations began to invest more heavily in the research and development of alternative energy technologies [13]. Since the early 1990s, a sequence of SOFC companies predominantly from the United States, Western Europe, and Japan have emerged aiming at bringing a range of SOFC configurations to market.

These companies are developing technologies largely focussed on the distributed generation market.

- Residential combined heat and power (c. 1 kW_e)
  - e.g., Solid Power, Ceres Power
- Commercial grid-independent generators (c. 100 kW_e)
  - e.g., Bloom Energy
- Industrial SOFC gas turbine hybrids (c. 1 MW_e)
  - e.g., LG Fuel Cell Systems

Common to all of these applications is the necessity for the devices to operate for extended periods (5–10 years) without requiring significant maintenance or replacement. It is also critical for the cells, stacks, and systems to be able to withstand the inevitable shut down events, which poses a particular problem for SOFCs due to their high operating temperature and brittle ceramic components.

State of the art SOFC devices can already achieve electrical efficiencies of above 50% and combined heat and power systems exist with total efficiencies in excess of 90%. These two metrics are very impressive on their own, but in combination with the lack of NO_x/SO_x or particulates in the exhaust stream and the low noise/vibration of these systems, the appeal of SOFC devices is clear. However, SOFCs will not be able to fully deliver on their potential until the degradation issues key to lifetime are resolved, which is the subject of this book.

SOLID OXIDE FUEL CELL FUNDAMENTALS

The Nernst potential, E_{Nernst}, of an SOFC is a function only of the physical properties and chemical composition of its two incoming gas streams (fuel and oxidant). It can be determined using the Nernst equation, which is the sum of the standard cell potential E^0 and a term that describes the activity at the specific conditions in question,

$$E_{\mathrm{Nernst}} = E^0 + \frac{RT}{2F}\ln\left(\frac{P_{\mathrm{H_2}}P_{\mathrm{O_2}}^{1/2}}{P_{\mathrm{H_2O}}}\right) \tag{1.1}$$

where R is the universal gas constant, T is the temperature, F is the Faraday constant, and P_x is the normalized partial pressure of species x. The standard cell potential term, E^0, is calculated as the difference between the equilibrium potentials of the two reduction/oxidation (redox) reactions under standard conditions:

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightleftharpoons \mathrm{H_2} \quad (E^0 = 0\,\mathrm{V}) \tag{1.2}$$

$$\frac{1}{2}\mathrm{O_2} + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightleftharpoons \mathrm{H_2O} \quad (E^0 = 1.23\,\mathrm{V}) \tag{1.3}$$

For the hydrogen–oxygen redox couple under standard conditions, the cell potential is 1.23 V. As a current is drawn, the system moves away from equilibrium and the potential between the two electrodes decreases. The Nernst potential describes an idealized reaction, which is a useful reference when quantifying the four main categories of losses (overpotentials) in SOFCs: activation losses, Ohmic losses, concentration losses, and crossover losses.

Activation Losses

Activation losses can be considered as the potential required to drive the reaction forward at the required rate, noting that the high operating temperature of SOFCs significantly improves the reaction kinetics. The Butler–Volmer equation quantifies the effect of the charge transfer processes at each electrode on the total current density, j,

$$j = j_0 \left[\exp\left(\frac{\alpha_a n F \eta}{RT} \right) - \exp\left(\frac{\alpha_c n F \eta}{RT} \right) \right] \tag{1.4}$$

where n is the number of electrons involved in each electrode reaction, η is the activation overpotential, and α_a and α_c are the anodic and cathodic charge transfer coefficients, respectively. The activation overpotential is described by the relation,

$$\eta = E_{\text{electrode}} - E_{\text{Nernst}} \tag{1.5}$$

which is the difference between real and equilibrium potentials, specified at each electrode. The magnitude of this overpotential increases at each electrode with the current, thus reducing the overall potential of the cell.

Ohmic Losses

These are caused by the resistance to flow of electrical current through the cell. Typically the ionic transport, as opposed to electronic, is the most significant contribution to this overpotential. The intrinsic conductivities of the various materials, the cell and stack geometry, and the convolution of the conduction paths in the porous electrodes, all need to be considered.

Concentration Losses

The electrochemical reactions typically only occur in a region close to the electrode–electrolyte interface, which means the gases must first travel through much of the porous electrodes. At high current densities, this can become the rate limiting step for the system.

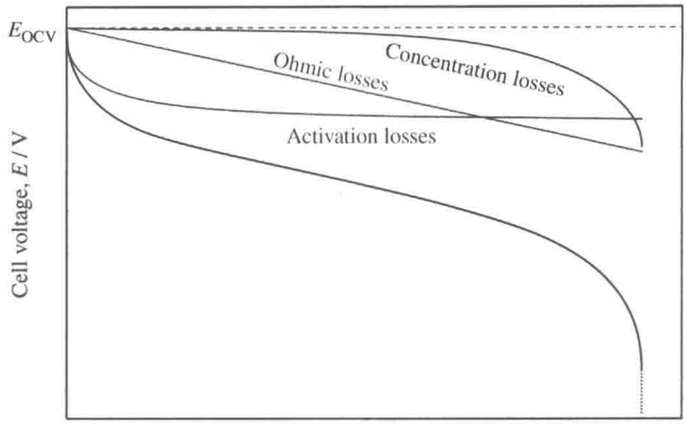

FIGURE 1.1 Plot of current density against cell voltage, illustrating the breakdown of cell performance by loss type.

Crossover Losses

This category covers two fairly distinct sources of loss. First, electrolytes, either through porosity or cracking, may be gas permeable, which means that some of the fuel is either exhausted or locally combusted. Second, internal electrical currents may occur in the electrolyte if it is not a perfect electronic insulator. These two losses are responsible for the difference between the theoretical Nernst potential and measured open circuit voltage (OCV).

The relative significance of each of these types of loss is dependent on the load applied. The graph in Fig. 1.1 plots the cell voltage as a function of current density and is labeled with the contributions of the first three sources of loss described above.

The redox reaction in an SOFC is split into two half-cell reactions (see Eqs. (1.2) and (1.3)), with one occurring at each electrode and completed by the transport of mobile ions and electrons around separate paths.

SOLID OXIDE FUEL CELL DESIGN

The electrochemically active components of conventional SOFCs comprise two porous electrodes, an anode and a cathode, separated by a dense electrolyte. Each of these components must exhibit certain characteristics for the system to function effectively; for example, in a typical SOFC the electrolyte must be gas tight and conductive to ions, but not to electrons. The performance of the anode and cathode is strongly influenced by both their material composition and their porous microstructure [14]. Both electrodes support electrochemical reactions and must also allow for conduction through their bulk and diffusion through their pores. A schematic of a planar cell assembly with interconnects can be seen in Fig. 1.2. Interconnects are used to collect the current and guide the gas flows, but are also required for stacking multiple cells in series.

Early fuel cells were predominantly tubular in design, in part because these systems were much easier to seal, and some developers continue to pursue this design; however, most commercially available systems today are in the planar configuration due to manufacturing considerations, optimal volumetric power density, and the ease of cell stacking. Stacking allows the system to have a higher voltage (series stack) or current (parallel stack) than a single cell. The schematic in Fig. 1.2 shows a series configuration of planar cells.

Several other cell geometries have also been developed, a selection of which are shown in Fig. 1.3, including the no longer pursued bell-and-spigot type, which is a means of serial stacking a tubular design with repeat frustum units [15]; the tubular design, which is a tubular cell with diameters in the range of 1−30 mm [16]; and the flat-tubular geometry, which combines the sealing and mechanical advantages of a tube, whilst maintaining the "stackability" of planar cells [17].

In addition to the geometry of the whole assembly, the relative thickness of each layer of the cell must be optimized. Typically, one of the four layers in the systems will be used as a support onto which the remaining layers can be deposited, as shown in Fig. 1.4. The supporting layer will inevitably be thicker than the others and so must be carefully optimized to minimize the

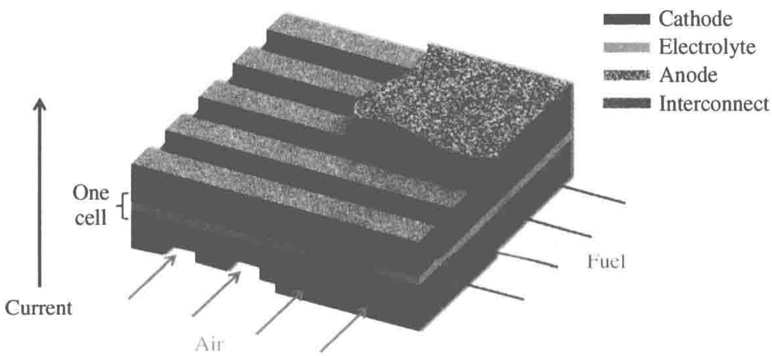

FIGURE 1.2 SOFC schematic of a single cell between two interconnects, showing the passage of fuel and air streams relative to the electrodes.

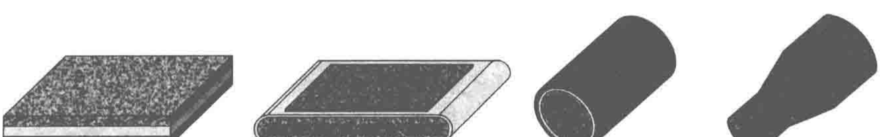

FIGURE 1.3 Schematic representation of SOFC cell geometries, including (l−r) planar, flat tubular, tubular, bell-and-spigot.