



High-Temperature

Solid Oxide Fuel Cells for the 21st Century

Fundamentals, Design
and Applications

Kevin Kendall and Michaela Kendall



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Fundamentals, Design and Applications

Edited by

Kevin Kendall and Michaela Kendall



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Preface

The original edition of this book [1] 'High-temperature solid oxide fuel cells: Fundamentals, design and applications' (solid oxide fuel cells, SOFCs) was published in 2003 to celebrate a century of research, development and demonstration of these devices since Nernst's breakthrough in 1897 [2] when he first showed his new incandescent lamp based on zirconia formulations. But since the millennium, a number of very significant advances have been made, illustrating the accelerating pace for advance of SOFC technology. We believe that this justifies the publication of the present book, summarising the older results, then emphasising progress made in the last 15 years. The fact that approximately 4000 copies of the original volume were dispersed and downloaded has encouraged us to update the text.

Progress has been made in several areas which are covered in the new chapters:

- Materials invention covered in Chapters 1–7 explain how new electrolyte compositions, such as scandia-doped zirconia; new cathodes such as LSCF and new interconnects like ferritic stainless steel alloys have shown better performance.
- Stack inventions like m-SOFCs described in Chapters 8–10 have allowed smaller and more rapid starting devices to be proven.
- Application projects covered in Chapters 8–13 have taken new directions such that shipments and installations of SOFCs have risen exponentially, and the best example being the many thousands of SOFC CHP generators now installed in Japan.

Some areas such as thermodynamics have not changed much, but additional recent publications are now covered.

Sad events have also occurred, such as the death of the famous zirconia sensor researcher Hans-Heinrich Mobius who delivered Chapter 2 in the previous book. In addition, a number of the previous authors have retired, and so new younger experts are featured in this volume. We thank Subhash Singhal for instigating this book project and also thank all the SOFC authors who have made a contribution to this work.

Other SOFC books have appeared in the interim [3–8], but these have been essentially conference proceedings or have not given a broad coverage of the wider SOFC field. The present volume is unique in reviewing the big picture in all its complexity.

We thank Elsevier for their support and all the readers who have contributed to make this project successful.

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Introduction to SOFCs

1

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1.1 Introduction

Solid oxide fuel cells (SOFCs) are the most efficient devices yet invented for conversion of chemical fuels directly into electrical power. Originally the materials' compositions were found by Nernst [1–3] in Gottingen in the 1890s as described in Chapter 2, but considerable improvements in theory and experiment are still being made 120 years later. During the last decade, significant progress has been made to improve the materials, to construct better systems, to focus on simpler fuels and to seek premium applications. This chapter describes these improvements, after summarising the background and situation at 2000 covered in the last book [4]. Firstly, we describe the basic principles and then we review the areas of advance, following with brief descriptions of the history, materials, processing, stack designs, systems, fuels and applications.

1.2 SOFC principles

Figure 1.1 shows an SOFC scheme. It contains a solid oxide electrolyte made from ceramic such as yttria stabilised zirconia (YSZ) which behaves as a conductor of oxygen ions at temperatures from 500 to 1500 °C. This ceramic material allows oxygen atoms to be reduced on its porous cathode surface by electrons brought in through the metal interconnect, thus being converted into oxygen ions, which are then transported through the ceramic oxide electrolyte to a fuel-rich porous anode zone where the oxygen can react, say with hydrogen, giving up electrons to an external circuit as shown in Figure 1.1. Only five components are needed to put such a cell together: electrolyte, anode, cathode and two interconnect wires, although other layers are often added as described later in the chapter.

Of course, hydrogen is ideal for SOFC. But hydrogen is not the preferred fuel because it would more likely be used in a polymer electrolyte membrane fuel cell (PEMFC) which gives extra power at room temperature. Hydrocarbon gases such as methane, or propane derived from pipelines or liquid stores, or biofuels like methanol and formic acid are more attractive for SOFCs for several reasons:

- (1) They can potentially be reacted directly on the anode, impossible with PEMFCs at room temperature with existing catalysts.
- (2) Hydrocarbons react well with steam or air to provide hydrogen and carbon monoxide which then combine with oxygen ions at the anode/electrolyte interface.
- (3) The thermodynamic efficiency of such internal reforming processes can be impressive.

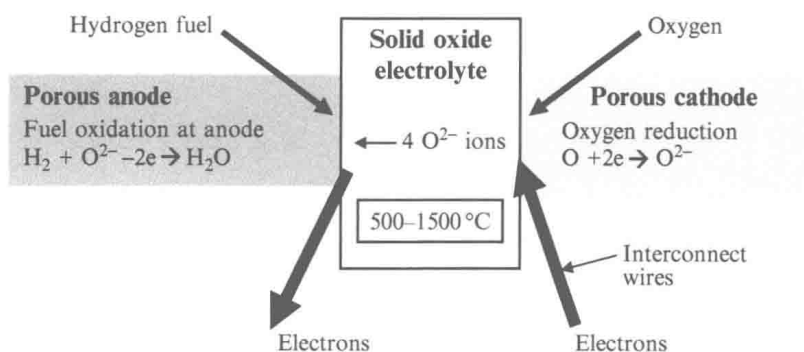


Figure 1.1 Schematic of solid oxide fuel cell (SOFC).

- (4) Hydrocarbon fuels give good energy storage density compared to hydrogen, especially when liquid, for example, propane/butane pressurised at room temperature or methane below its critical point of $-83\text{ }^{\circ}\text{C}$.

The anode reactions then become more complicated with a range of possible products shown in the following chemical equations:



The key benefits which make the SOFC more attractive than PEMFCs are twofold:

- (1) Direct use of liquid fuels which have much superior energy storage capacity (e.g. a factor 6) when compared with compressed hydrogen gas.
- (2) Availability of high-quality heat which can be used to give advance in practical applications as described in the following chapters.

Examples of applications demanding this heat are domestic homes which need both power and heat, auxiliary power units (APUs) on vehicles and stationary power generation. In each of these cases, the electrons are extracted from the fuel in the fuel cell at a temperature around $600\text{--}1000\text{ }^{\circ}\text{C}$, as shown in Figure 1.1. A domestic system would then use the heat to produce hot water as currently achieved with simple heat exchangers. In a vehicle, the heat could be used to warm the cab as illustrated in Figure 1.2. A stationary power generation system may use the waste heat to drive a heat engine such as a stirling or gas turbine motor.

It is essential to realise that the heat is inevitably generated in the SOFC by reaction exotherm, ohmic losses, electrode overpotentials, etc., as described in Chapter 3. These losses are present in any fuel cell arrangement and cannot be eliminated completely. Indeed, the heat is necessary to maintain the operating temperature of the cells, replacing the heat lost by thermal conduction and radiation to the



Figure 1.2 Truck with APU running on CNG.

surrounding environment. The benefit of the SOFC over competing fuel cells is the high temperature of the exhaust heat, making its utilisation simple and economic. Thus both electricity and heat are desirable products from the SOFC. The ratio of power to heat can realistically be adjusted from 20% to about 70% depending on the system design, but for basic designs, range from 40% to 60%. These figures compare with about 20–27% for an automobile combustion engine, about 50–60% for the best combined cycle gas/steam turbine power plant and around 40–60% for a diesel combustion generator combined with a steam cycle.

From these basic principles, it is possible to recognise the issues that remain to be solved if SOFCs are to be successful in this century.

1.3 Problems to be resolved

The SOFC process described above is almost magical in its elegance and simplicity, and it is surprising that this process has not yet been commercialised to supplant the inefficient and polluting combustion heat engines which currently dominate our civilisation.

There are several technical reasons why SOFCs have not yet competed successfully with combustion devices, as shown in Figure 1.3, but cost and durability issues also need attention. In the first place, combustion has been accepted for several thousand years, and such established technologies are difficult to supplant. Secondly, combustion does not require any additional materials or interfaces; it can occur freely once

COMBUSTION	SOFC
Established technology	Disruptive technology
Independent of materials	Depends on five materials
Dirty fuels still combust	Clean fuels are necessary for SOFC

Figure 1.3 Difficulties of challenging combustion with SOFC.

ignition of the fuel has occurred. Containment and expansion of the hot gas product is the only requirement for power production. Contrast this situation with the SOFC which needs five materials and four interfaces, each of which can block the power output when contaminated with a single molecular layer of silica. Thirdly, combustion can occur with almost any oxidisable substance so that cheap available complex fuels, for example, petroleum or biomass, may be used. Purity is crucial to fuel cells but has not yet been a barrier to combustion, except where emissions legislation has been imposed.

Consider these three challenging areas in more detail. The historic dominance of combustion is difficult to overcome because the concepts are ingrained in our psyches. From the steam turbine of Hero two millennia ago, to the Watt steam engine two centuries back, to the Diesel engine of 1897, it has been evident that heat engines can utilise the additional hot gas pressure created by combustion to produce power of enormous utility. It is much less obvious that electrochemical potential of fuels can be used in a similar way. Electrochemistry, which can reasonably be dated to Volta's invention of the battery in 1800, has made enormous strides in two centuries but still falls short in competition. A recent example is the push towards battery electric cars which many observers feel should take over soon from combustion engine automobiles. Despite a number of advantages of efficiency and reduced emission, these machines cannot yet beat the consumer preference for combustion vehicles based on price, range, infrastructure and fuel recharge times [5]. Perhaps the main reason for this is the complex nature of automobile technology. A recent paper shows that the use of composite materials in cars is just as important as moving to an electric drive [6]. However, the longer-term effect of emission regulations together with the simplicity and efficiency of electrical drives should eventually lead to fuel cells taking over from combustion devices [7].

The materials problems of SOFCs are profound and dominate this book. Although YSZ has been known for 120 years to provide a suitable electrolyte (Chapter 4), the present anode composition did not appear until the 1960s and the lanthanum strontium cobalt ferrite (LSCF) cathode has only just been optimised in this century as described in Chapters 5 and 6. Moreover, the use of ferritic stainless steel interconnections and the coatings required to inhibit corrosion are of relatively recent origin as defined in Chapter 7. The way in which these materials are best assembled to produce working stacks has been changing continuously since 1990 as illustrated in Chapters 8–10. The nature of the interfaces, especially the catalytic surfaces, has also been critically recognised as detailed in Chapters 11–14.

The effect of fuel purity (Chapter 14) is hugely important because our present infrastructure is based largely on refined petroleum which typically contains hundreds of molecules, including sulphur compounds which corrode SOFC anodes based on nickel in a very short time. Diesel engines and other combustion systems can withstand extraordinary variations in fuel composition, which today differs significantly from town to town and country to country. But fuel cells make use of catalysts which can easily be poisoned by low-level impurities, and there is great difficulty attached to running SOFCs on applications now dominated by diesel technology. Ships, trucks and buses fall into this category. A typical programme to