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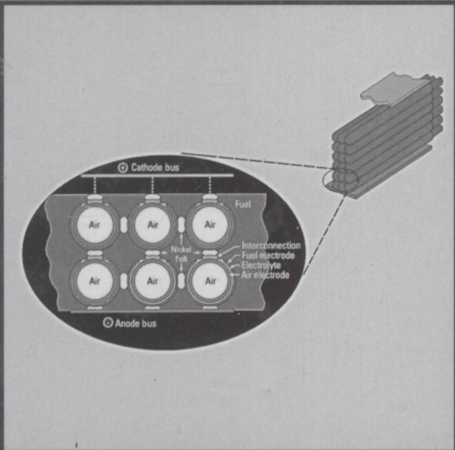

Solid oxide fuel cell technology

Principles, performance and operations

Kevin Huang and John B. Goodenough

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Solid oxide fuel cell technology

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Preface

Conventional fossil fuels will continue to be the primary energy resource to power human society for at least the next 50 years. How to convert fossil fuels into useful forms of energy in the most efficient manner with a minimal environmental impact will be the theme of future energy development and policy making. High-temperature solid oxide fuel cells (SOFCs) emerge as the leader in terms of conversion efficiency, fuel flexibility, and environmental impact among all types of power generation systems. They are in an excellent position to offer clean and efficient power generation. The compactness, modularity, and durability of high-temperature SOFCs find particular applications in stationary, distributed power generation, a niche market in which conventional heat engines find it difficult to compete. It is these unique advantages of SOFCs that have attracted lasting interest in research and commercialization worldwide over the last few decades.

Despite the promise of SOFCs, product cost and system reliability are the two foremost obstacles presently prohibiting the modern SOFC technology from being commercialized. Both hurdles are essentially rooted in the high operating temperature, a unique characteristic of SOFCs that has both positive and negative impacts. The high operating temperature activates the fuel reforming and oxidation reactions and avoids the CO poisoning of the electrodes commonly encountered in low-temperature fuel cells. It also permits the excessive heat in the exhaust to be further recovered for primary heat utilization or for secondary electricity production. Unfortunately, a high operating temperature unequivocally requires exceptional properties of materials and modules.

Chemical and electrical incompatibilities between ceramics and metals, as well as delicate management of different rates of thermal expansion among different cell components, are just a few examples of the pressing issues that need to be addressed in the product development of SOFC technology. Although the SOFC technology has been intensely pursued worldwide over the last few decades, a systematic narrative of the technology with an in-depth fundamental and engineering analysis is still lacking. The present book is intended to fill the gap and provide an important and useful scientific and engineering tool for researchers and engineers in the field of SOFCs.

The book is the fruition of R&D and commercialization efforts on SOFC technology in which the authors have been heavily involved. Chapter 1 gives an overview of SOFC technology including its history, advantages, potential markets, basic functional components, and leading stack designs. Chapters 2, 3, 4, and 5 cover the theoretical background for the SOFC technology. The electromotive force (EMF) of a concentration cell operating on the same chemical reaction as that of the SOFC is connected to such thermodynamic quantities of the reaction as the changes of the Gibbs free energy, the enthalpy, and the entropy. Principles of solid state physics and chemistry are used to interpret the physical and chemical factors that influence the electronic and ionic transport properties of the several component materials used and to provide a guide for the design of new materials, including the catalytic behavior of the anode and cathode. Irreversible thermodynamics is applied to the transport equations for mixed ionic/electronic conduction in the electrolyte and interconnects in order to reveal how mixed conduction effects the profiles of the partial pressure of oxygen and the relationships among leakage, ionic, and external-load current densities in order to establish criteria for selecting an optimum electrolyte material. Chapters 6, 10, and 11 focus on the issues associated with SOFC operations, such as how to set the electrical current to achieve desirable stack compositions with the required fuel and oxygen utilizations, how to estimate the exhaust temperature based on the energy balance principle, how to avoid carbon formation during steam reforming of methane, and how to understand the mechanisms of electrode poisoning. Chapters 7, 8, and 9 analyze the performance of SOFCs in great detail and the factors that determine this performance. The losses in electrical performance and electrical efficiency by various mechanisms are particularly discussed. Finally, a thorough technical review on materials in SOFC is given in Chapter 12.

It is the authors' sincere hope that this book can be of great help to the development and commercialization of the SOFC technology.

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1
Introduction to solid oxide fuel cells (SOFCs)

Abstract: Technology advancement to address the world's growing demand for clean and affordable energy will require simultaneous advances in materials science and technology in order to meet the performance demands of new power-generating systems. Fuel cells emerge as highly efficient, fuel flexible, and environmentally friendly electricity producing devices. These unique characteristics advantageously differentiate fuel cells from conventional heat engines for power generation and therefore have attracted worldwide attention – from research and development activities in institutes to commercialization efforts in industries – for the last few decades. In this chapter, the history, advantages, applications, and designs of solid oxide fuel cells (SOFCs) are briefly reviewed.

Key words: solid oxide fuel cell, advantages, applications, functionality, stack design.

1.1 A brief history of the solid oxide fuel cell (SOFC)[1, 2]

Fuel cells have been known to science for more than 150 years. As early as 1839, the Swiss scientist Christian Friedrich Schoenbein first asserted the possibility of a fuel cell that combined hydrogen with oxygen.[3] One month later, the English scientist William Robert Grove published the experimental observation of voltage in a concentration cell (called a 'gas cell' at the time) when combining hydrogen with oxygen in the presence of platinum.[4] A few years later, in 1845, he published the paper 'On the gas voltaic battery – voltaic action of phosphoros, sulphur and hydrocarbons',[5] which formally confirmed the technical feasibility of a fuel cell as a power-generating device. However, it was not until the end of the nineteenth century with the discovery by the German scientist Walther Nernst of the so-called 'Nernst mass'[6] of a ceramic material consisting of 85 mol% ZrO_2 and 15 mol% Y_2O_3 that the key solid electrolyte material for modern SOFCs was identified. Since then, many mixtures of ZrO_2 with the rare-earth and alkaline-earth oxides have been systematically studied, revealing a range of compositions with high oxide-ion conductivity. After electrochemistry was connected with thermodynamics, the basic principle that establishes the relationship between the chemical energy of a fuel and the voltage of a fuel cell was explained by H. von Helmholtz in 1882.[7] In 1894, W. Ostwald correctly pointed out that a fuel cell could produce electricity in a more efficient way than a conventional steam engine.[8] Such a realization undoubtedly became a stimulant for pursuing fuel cells as potential highly efficient power-generating devices in the twentieth century. If the nineteenth century was considered as an era of curiosity in fuel cells, the twentieth century was certainly the epoch for fuel cells to become the subject of intense research and development (R&D) and commercialization efforts.

The conceptual SOFC was probably first demonstrated in 1937 by the Swiss scientists Emil Bauer and Hans Preis using zirconia ceramics as the electrolyte, Fe_3O_4 as the cathode, and C as the anode.[9] Clearly, the problems of stability of the electrode materials and gas-phase diffusion were not recognized at the time. However, more concentrated and systematic studies on SOFCs started after the pioneering 1943 work by the German scientist Carl Wagner, who first recognized the existence of oxygen vacancies in mixed oxides such as doped ZrO_2, and attributed the observed electrical conductivity at high temperatures to the movement of these oxygen vacancies under a gradient of oxygen partial pressure.[10] In 1957, Kiukkola and Wagner published another landmark work describing thermodynamic investigations with concentration cells based on the solid electrolyte $Zr_{0.85}Ca_{0.15}O_{1.85}$.[11] It was this work that laid the theoretical foundation for the modern solid-state electrochemistry of the SOFC. A few years later, two scientists, Joseph Weissbart and Roswell Ruka, from the Westinghouse Electric Corporation, reported in 1961 the first solid-electrolyte-based device for measuring the oxygen concentration of a gas phase with a concentration cell,[12] which later led to their patent 'A solid electrolyte fuel cell' issued in 1962.[13] Based on these initial efforts, a group of Westinghouse engineers developed and successfully tested the first tubular 'bell-and-spigot' SOFC stack from 1962 to 1963. This development eventually became the foundation of today's cathode-supported, tubular seal-less SOFCs developed by Westinghouse/Siemens.

During the same period, advances in electrode materials for SOFCs have also taken place. The most noticeable progress was in the evolution of the cathode material. It started with the noble metals such as platinum and transitioned to doped In_2O_3[14] and finally settled on today's doped $LaMnO_3$. The evolution of cathode materials was clearly driven by the performance requirement, viz. the capability to activate effectively the oxygen-reduction process. The unique electrical and catalytic properties possessed by rare-earth, transition-metal perovskite oxides best satisfy the cathode requirement. However, the requirement for a thermal-expansion match between cathode and electrolyte has narrowed the practical cathode material to the doped $LaMnO_3$ for ZrO_2-electrolyte-based SOFCs. Another important material, developed by Meadowcroft in 1969, was the doped $LaCrO_3$ perovskite that is stable in both oxidizing and reducing atmospheres;[15] it immediately found use as an interconnect in SOFCs. A patent filed by Spacil in 1964 described a composite anode consisting of Ni metal with a ZrO_2-based electrolyte that has remained the standard choice of anode for SOFCs.[16]

Historically speaking, the period from the 1970s to the 1990s marks an important era in the technical development of SOFCs. In the 1970s, the electrochemical vapor deposition (EVD) process was invented in Westinghouse by an engineer of genius, Arnold Isenberg, who demonstrated the making of a perfectly dense ZrO_2 electrolyte thin film on the substrate of a porous, tubular substrate at relatively low temperatures. Based on this important invention, Westinghouse successfully manufactured and tested a series of SOFC generator systems in the range of 5–250 kWe from the 1970s to 1990s and clearly positioned itself as the world leader in modern SOFC technology. It was also during this period that various SOFC stack designs flourished, from tubular to planar in geometry, and alternative materials for the cathode, the anode, and the interconnect were also explored as the substrate.

A real advancement of anode-supported planar SOFCs took place after the pioneering work of de Souza *et al.* of Berkeley National Laboratory, published in 1997;[17] they essentially demonstrated that an electrolyte on a porous anode substrate can be co-fired at high temperatures into a dense thin film without invoking chemical reactions. The cathode was applied afterwards and sintered at much lower temperatures to minimize chemical reactions. As a result, the single-cell performance has been significantly improved, which in turn has allowed an anode-supported SOFC to operate at lower temperatures where commercially available oxidation-resistant alloys such as thermal-expansion-compatible ferritic steels can be utilized as interconnect materials for SOFC stacks. A majority of today's SOFC designs adopt the anode-supported planar geometry based on considerations of cost and performance. However, the reliability and stability appear to be the leading issues for commercialization at the present time.

Looking through the history of SOFCs, it is not difficult to find that the ZrO_2-based materials have remained the mainstream electrolytes since the discovery by Nernst over 100 years ago. As early as 1990, Goodenough *et al.*[18] had pointed out that high oxide-ion conduction can exist in the perovskites and hence in other structures than the classical fluorite structure, giving hopes for finding a new family of oxide-ion conductors in other crystal structures. This prediction was favorably vindicated by the noteworthy discovery of the high oxide-ion conductivity perovskite Sr- and Mg-doped $LaGaO_3$ (LSGM) by Ishihara *et al.*[19] in 1994, immediately confirmed by Feng and Goodenough[20] in the same year, followed by a systematic characterization of the system by Huang *et al.*[21, 22] The high oxide-ion conductivity and the crystallographic compatibility with cathode materials make LSGM even more attractive for low-temperature SOFCs. Mitsubishi Materials has recently demonstrated an excellent stack performance of an SOFC based on LSGM electrolyte operating at 800 °C.[23]

In summary, the major driver for sustaining the development of SOFC technology is the intrinsically high electrical efficiency compared with a conventional heat engine. After a century of scientific research and commercial engineering, development in the areas of materials, designs, and system integration has advanced dramatically. A thorough review of SOFC materials and fabrication techniques is given in Chapter 12. The feeling is that commercialization of the technology is on the horizon.

1.2 Advantages of the solid oxide fuel cell

The fuel cell is a device that directly converts the chemical energy in fossil fuels into electrical power in an electrochemical manner. Unlimited by the Carnot cycle, a fuel cell has an inherently higher electrical efficiency than conventional heat engines, particularly for the less than 1 MW class. Higher electrical efficiency infers a reduced CO_2 emission per unit electricity produced if hydrocarbons are used as fuels; this influence has become increasingly important as we endeavor to minimize the emission of greenhouse gases in future power generation. Another conceivable benefit is the minimal environmental impact from a fuel-cell generator compared with a conventional heat engine. Owing to its relatively low operating temperature, the formation and therefore the emission of nitrogen oxides (collectively known as NO_x) are negligible. Use of a desulfurizer subsystem in a fuel-cell generator ensures almost zero emission of sulfur oxides (collectively known as SO_x). In addition, fuel-cell power generators are much quieter and exhibit less vibration than a conventional engine during operation; they therefore represent a competitive alternative in distributed, stationary power generation.

For SOFCs operating at higher temperatures, there are added advantages. High-temperature operation, typically in the range of 600–1000 °C, not only provides high-quality waste heat, but also effectively activates the processes of reforming and electrochemical oxidation of hydrocarbon fuels in the presence of catalysts. This realization is technically important for several reasons. First, it opens the opportunity for SOFCs to use most hydrocarbon fuels, either in the gaseous or liquid state, provided that they are properly cleaned and reformed into simple fuels such as H_2 and CO. This is in contrast to low-temperature fuel cells such as proton exchange membrane (PEM) fuel cells where CO poisons the anode. The second is that excessive heat produced from the electrochemical oxidation of fuels can be utilized by the highly endothermic steam reforming reaction simultaneously occurring, which makes internal on-cell reformation possible. Such integration further increases the overall system efficiency. Co-production of heat and power, often known as combined heat and power (CHP), is the third added advantage of high-temperature SOFCs. The recovery of waste heat along with the production of electricity enables the total energy efficiency of such a system to be in the range of 85–90%. Another way of recovering waste heat is to combine a micro gas turbine with an SOFC stack to form a hybrid system. In order to maximize the electrical efficiency, the SOFC/micro gas turbine hybrid is often operated under pressurization that would boost both the performance of the SOFC stack and the effectiveness of the micro gas turbine. In order to be even more efficient, a bottom cycle steam turbine can be added into the above hybrid system. This is particularly preferable for generators over 100 MWe. The hybrid SOFC generator system has been reported by Siemens/Westinghouse to achieve a net AC electrical efficiency of 53% for a 220 kWe class.

When compared with another type of high-temperature fuel cell, the molten carbonate fuel cell (MCFC), the all-solid components used in an SOFC system avoid the corrosion issues caused by the liquid electrolyte of the MCFC system, which prolongs the lifetime of an SOFC. In fact, with over 35000 operating hours at an acceptable degradation rate, a Siemens/Westinghouse 100 kWe unit is the longest-running SOFC generator.

1.3 Applications of solid oxide fuel cells

Determined largely by the unique advantages presented above, the best application of SOFC systems is distributed, stationary power generation. Depending on the size of the SOFC generator, stationary power generation can be further grouped into the following markets.

- *Residential*. The SOFC is targeted for powering a home with a power rating of 1–10 kWe. Hot water, house heating, and chilling can also be provided as a by-product. Pipeline natural gas or coal gas is the fuel of choice. The net AC efficiency is expected to be >35%.
- *Industrial*. The SOFC is targeted for powering a small industrial unit such as a credit-card data processing center or a hospital that cannot tolerate a power outage. The power rating typically ranges from 100 to 1000 kWe. Quality heat can also be provided as a by-product. Pipeline natural gas can be used as the fuel. The net AC efficiency is expected to be >45%.
- *Dispersed*. An extension of industrial SOFC generators can be targeted for powering a larger industrial unit or a small community with a power rating of 2–10 MWe. Natural gas or coal-derived fuel is the fuel of choice. The net AC efficiency is expected to be >48%.
- *Central*. The largest SOFC generator system would have a power rating of 100 MWe. In such a system, producing electricity by the most efficient way is the ultimate goal. Therefore, a hybrid SOFC system is the design choice. Natural gas and coal-derived gas can be used as fuels. The net AC efficiency is expected to be >60%.