

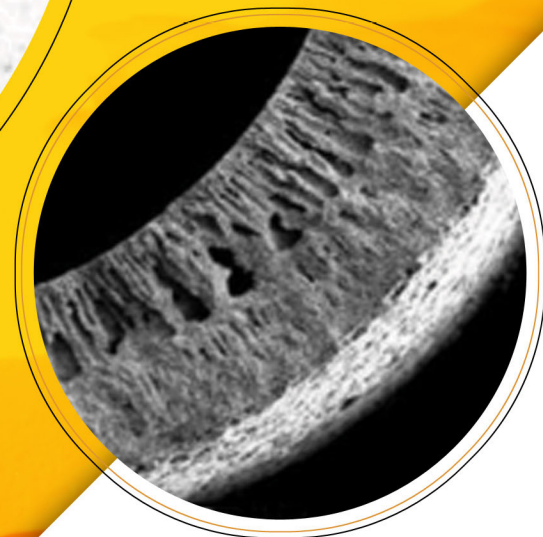
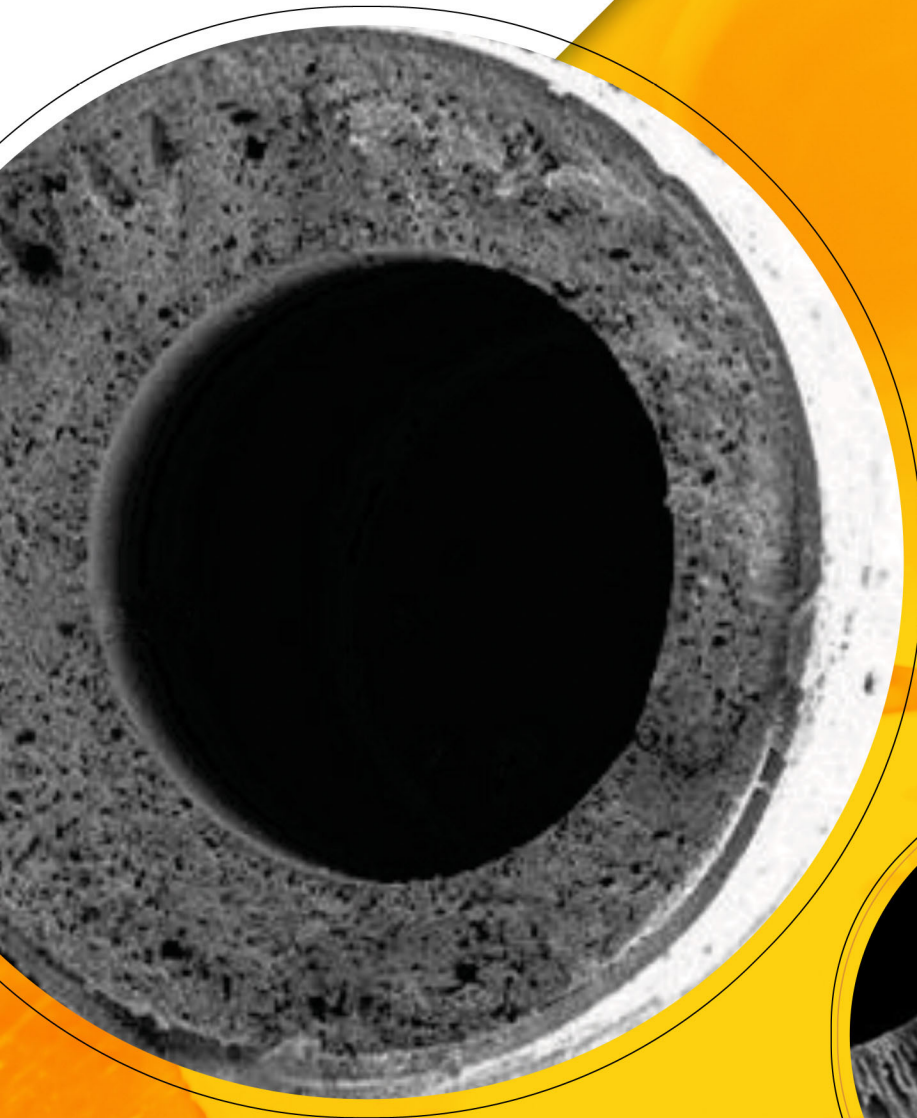
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FRONTIERS IN CERAMIC SCIENCE

FUNCTIONAL MATERIALS FOR SOLID OXIDE FUEL CELLS: PROCESSING, MICROSTRUCTURE AND PERFORMANCE

VOLUME 1



Editors:
Moisés R. Cesário
Daniel A. de Macedo

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Frontiers in Ceramic Science

(Volume 1)

*(Functional Materials for Solid Oxide Fuel Cells:
Processing, Microstructure and Performance)*

Edited by

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Volume # 1

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FOREWORD

This fascinating e-book clusters contributions from researchers who have dedicated the last years of their career to study materials, manufacturing processes and characterization techniques applied to the development of Solid Oxide Fuel Cells (SOFCs). These electrochemical devices that convert chemical energy into electricity are promising alternatives to traditional mobile and stationary power sources. Among their many advantages deserve special attention the high energy conversion efficiency and the excellent fuel flexibility. The development of high-performance functional SOFC is an important step towards reducing the operating temperature to 500 – 750 °C or lower. By doing this, the cell components can be easily and cost-efficiently produced. With this in mind, recent research around the world has focused on novel synthesis methods and processing routes to develop high performance components and single cells operating at reduced temperatures.

I am sure that this e-book reviews how processing conditions affect both microstructure and performance of functional SOFC materials.

Dr. Daniel Araújo de Macedo
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PREFACE

Solid Oxide Fuel Cells (SOFCs) are identified as a major technological promise for clean energy production. The development of functional materials for SOFC operating at intermediate temperatures (550 – 750 °C) requests not only a strict control of synthesis and processing conditions of ceramic/composite powders, but also a good understanding about the correlation between microstructure and electrochemical properties.

This e-Book aims to cluster contributions from the most productive and well-recognized researchers studying SOFC functional materials. Emphasis is on novel chemical/physical/mechanical processing routes towards the attainment of electrolyte and electrodes powdered/layered materials. Furthermore, the potential of the resulting microstructures toward SOFC applications has been checked using a combination of electron microscopy and electrical/electrochemical characterization techniques using symmetrical and/or single fuel cell configurations.

The book begins with an introductory chapter addressing the working principle of a SOFC and basic characteristics of SOFC electrodes. The second chapter is dedicated to cathode materials applied to intermediate and low-temperature SOFCs. The author proposes a comprehensive discussion on the cathode development, emphasizing its reaction mechanism, microstructural, characterization, and electrical performance. Studies of long-term chemical and mechanical stability have also been discussed.

The third chapter describes a review on anode materials, with focus on materials composition, synthesis methods, and electrical properties.

The fourth chapter reports on the study of lanthanum silicate apatite based materials, drawing attention to their properties as electrolytes for SOFC. The authors propose a discussion on different synthetic methods to obtain apatite type electrolytes.

The fifth chapter presents a brief review on chemical/physical routes to prepare electrolyte and electrode materials for SOFC.

The sixth chapter reports on a recently phase inversion technique that is used to fabricate micro tubular solid oxide fuel cells (MT-SOFC). The authors propose a discussion on the development of this important manufacturing technique and their effects on the fuel cell performance.

The seventh chapter also discusses the use of the phase inversion based extrusion technique to fabricate MT-SOFC. Emphasis is given on the fabrication of electrolyte and how the fabrication parameters could affect the structure of the obtained electrolyte layer.

The eighth chapter reports on the study of proton conducting ceramic oxides with perovskite structure. The authors propose the development of electrolyte and electrode materials with combined properties of proton conductivity, high sinterability (in case of electrolytes), and chemical stability which make quite innovative research.

We would like to express our gratitude to all the eminent contributors for their excellent contributions and we believe that this e-book will be a reference to academic/industrial scientists from chemistry, physics, and materials science interested in the processing-microstructure-performance of SOFC materials.

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INTRODUCTION

The Solid Oxide Fuel Cell (SOFC) technology has attracted significant attention due to the fuel flexibility and environmental advantages of this high efficient electrochemical device. However, typical SOFC operating temperatures near 1000 °C introduce a series of drawbacks related to electrode sintering and chemical reactivity between cell components. Aiming to solve these problems, researchers around the world have attempted to reduce the SOFC operating temperature to 500 – 750 °C or lower. It would result in the use of inexpensive interconnect materials, minimization of reactions between cell components, and, as a result, longer operational lifetime. Furthermore, decrease the operation temperature increases the system reliability and the possibility of using SOFCs for a wide variety of applications such as in residential and automotive devices. On the other hand, reduced operating temperatures contributes to increase ohmic losses and electrode polarization losses, decreasing the overall electrochemical performance of SOFC components. Thus, to attain acceptable performance, reducing the resistance of the electrolyte component and polarization losses of electrodes are two key points. Losses attributed to the electrolyte can be minimized by decreasing its thickness or using high conductivity materials such as doped ceria and apatite-like ceramics. Regarding electrode losses, the higher activation energy and lower reaction kinetics of the cathode compared with those of the anode, limits the overall cell performance. Therefore, the development of new functional SOFC materials with improved electrical/electrochemical properties combined with controlled microstructures become critical issues for the development of solid oxide fuel cells. These topics are systematic discussed along this e-book.

Introduction to Solid Oxide Fuel Cells

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Abstract: Fuel cells are electrochemical devices that convert chemical energy into electrical energy with high potential for commercial power generation applications. Among various types of existing fuel cells, solid oxide fuel cell (SOFC) is one of the most promising types of fuel cells, due mainly to its ability to utilize several types of fuels such as hydrogen, CO, hydrocarbon fuels, and ethanol. This chapter introduces the reader into the fundamentals of SOFCs, including its working principle and the main components used as electrodes.

Keywords: Anodes, Cathodes, Ceramics, Chemical energy, Electrochemical, Electrodes, Electrolyte, Porous, Sealant, Solid Oxide Fuel Cells.

INTRODUCTION

Fuel cells are electrochemical devices that convert directly and efficiently chemical energy of a fuel gas into electrical energy. Furthermore, fuel cells are environmentally friendly devices whose efficiency is not limited to the Carnot-cycle and compared to others power generation systems with internal combustion, they do not produce significant amount of NO_x, SO_x, CO_x, and pollutants. The main fuel of fuel cells is hydrogen or hydrogen-rich fuels, this requirement makes fuel cell development a great challenge to researchers worldwide due to a number of problems involving hydrogen generation and storage. Fuel cells technology usage can be done in large stationary industrial plants as well as in vehicles and portable devices [1 - 5].

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Solid Oxide Fuel Cell (SOFC) is one of the most widely studied fuel cells, mainly because of their larger stability compared to other cell types, since it has a solid electrolyte, high efficiency and fuel flexibility. The main SOFC components are: porous cathode, porous anode, dense electrolyte, and sealants. The cathode is typically a solid state oxide which catalyzes oxygen reduction reaction, while anode is an oxide or cermet which catalyzes oxidation of a fuel, which can be either hydrogen or reformed hydrocarbons. The SOFC electrolyte must be an electronic insulating but ion-conducting material that allows only oxygen ions to pass through. Furthermore, this SOFC component must be dense to separate air and fuel, chemically and structurally stable over a wide range of partial pressures of oxygen and temperatures. Sealant materials, often used during the manufacture of single SOFCs, should provide a viscous behavior for coupling the compensating tolerances and other materials avoiding failures, which guarantees a hermetic seal.

Usually a SOFC operates at high temperatures in a range of 600 - 1000 °C allowing internal reforming of fuel. The characteristics of high operating temperature of SOFC present great challenges related to the cell lifetime and materials degradation. Therefore, there is a great interest in reducing the SOFC operating temperature to a range of 500 – 800 °C or lower, which reduces their production costs as well as stability and degradation issues. The operating principle of SOFC is schematically illustrated in Fig. (1). The fuel, hydrogen or a hydrocarbon gas, permeates into the anode compartment and the oxygen, from the air, into the cathode. At the anode (fuel electrode side), fuel is oxidized according to the reaction (Eq. 1):



The electrons are transported to the cathode through an external circuit. At the cathode the oxygen is reduced with the incoming electrons from external load according to the reaction (Eq. 2):



Generated oxygen ions migrate to anode across the electrolyte, hence, the fuel is oxidized by incoming oxygen ions. Therefore, this electrical connection allows a continuous supply of oxygen ions from the cathode to the anode, whilst maintaining an overall balance of electrical charge, thus producing electrical energy. The products of these reactions (Eq. 1 and 2) are only water and heat (Fig. 1). Most of the electrochemical reactions in a cell occur in the so-called triple

phase boundary (TPB), which is the contact region between gas phase, electrode and electrolyte [2, 6 - 8].

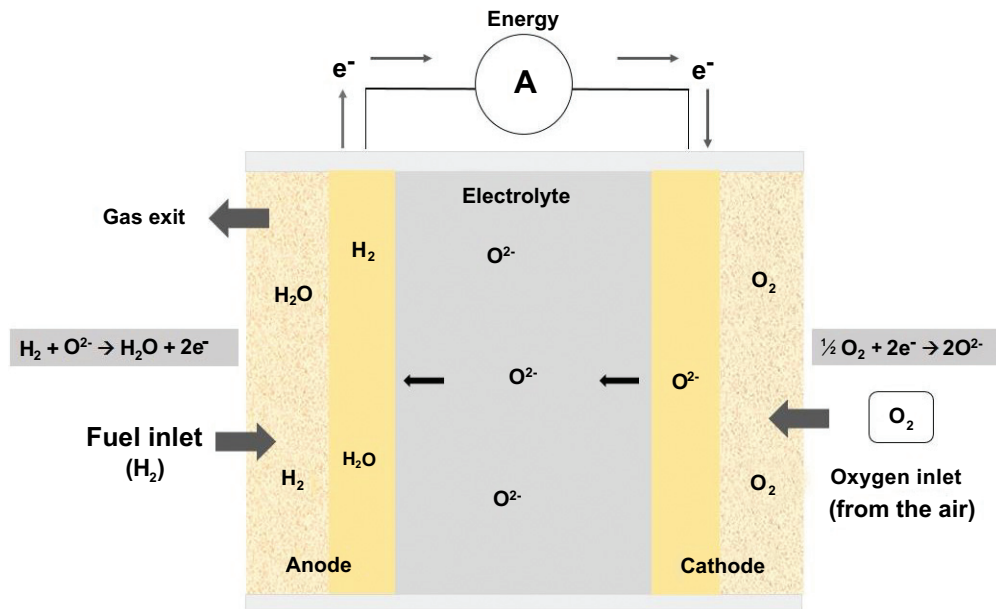


Fig. (1). The working principle of a SOFC.

Besides showing the working principle of a typical SOFC, this chapter is also focused on a brief review on the main SOFC electrodes (cathode and anode). Materials, processing and obtaining methods of electrodes and electrolyte materials will be discussed in the following chapters.

SOFC ELECTRODES

Cathode

The cathodes for SOFC must have several properties, including: (a) high electrical conductivity; (b) high catalytic activity for the oxygen reduction; (c) good compatibility with others cell components; (d) suitable porosity (approximately 30-40%); (f) thermal expansion coefficient matching those of other components; (g) chemical stability during fabrication and operation; (h) low manufacturing cost and (i) extensive TPB (triple phase boundary). In the early development of SOFC, platinum was used as cathode, nevertheless it seemed very costly for commercial use. The cathode has the function to reduce the oxygen molecule, transport ion to the electrolyte and provides electrical current resulting from

Cathode Materials for High-Performing Solid Oxide Fuel Cells

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Abstract: It is well recognized that the development of low-temperature solid oxide fuel cells (LT-SOFCs) relies on the exploration of new functional materials and optimized microstructures with facilitated oxygen reduction reaction (ORR) that involves complicated electrochemical processes occurring at triple-phase boundaries (TPB). This urgent and critical demand promotes great research efforts on pursuing superior catalysts as electrodes owing comprehensive electrochemical and physicochemical properties, and relevant catalyst optimization on materials and microstructures. The material development is mostly based on perovskite with extensive doping strategies to maximize the catalytic activity while other properties such as stability, thermal and chemical compatibility, *etc.* are well compromised. Other types of materials such as K_2NiF_4 , double perovskite were also studied as potential candidates, owing to the excellence of catalytic activity resulting from the special features of crystal structures. In this chapter, the fundamental knowledge of cathode is briefly introduced, such as reaction processes of ORR, catalysis mechanism and defect transport. Several typical perovskites are reviewed to better understand the required specific material properties for an excellent ORR catalyst as cathode material that can be operated at practical low temperatures (350~500 °C). Particularly, recent development of the layered perovskites is specifically introduced because they show very promising performance at low temperatures due to the fast oxygen exchange and oxygen diffusion yielded by the ordered cation distribution in crystal.

Keywords: Catalysis mechanism, Catalytic activity, Cathode, Layered perovskite, Oxygen diffusion, Oxygen reduction reaction, Oxygen surface exchange, Perovskite, Solid oxide fuel cells, Three-phase boundary.

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INTRODUCTION

In this chapter, the recent development of cathode materials, which are operated at low operating temperature (350 ~ 600 °C) is discussed. With emphasis on how the candidate materials are selected as potential low-temperature operating cathodes, mechanism of oxygen reduction reaction, criteria of promising cathode and role of mixed ionic-electronic conductors are also discussed.

Technical Parameters for SOFC Cathodes

As an air electrode, the oxygen reduction reaction (ORR) occurs at the three phase boundaries where the oxygen gas, electrolyte and cathode surfaces meet. The produced negatively charged oxygen ions transfer through the electrolyte conducting membrane and then react with hydrogen molecules to form water while the electrons released from fuel of hydrogen have to pass the external circuit to form the current. Therefore, the ORR is a very critical step to determine the initial kinetics of total reaction. The oxygen reduction on the cathode surface is believed to include several sub-steps which separately determine the limiting step, such as oxygen absorption, charged, dissociation and desorption, *etc.* (Fig. 1) shows the reaction steps at TPB area (pure electronic conductor is used to illustrate for simplicity). The oxygen molecules are absorbed on the surface or the TPB sites first and then move towards TPB area to be dissociated, where oxygen ions are formed through electrochemically charged by the electrons. Consequently, the oxygen ions should have to leave the sites and move towards electrolyte and incorporate into it. If a mixed ionic and electronic conductor is used, the places for oxygen dissociation can be extended to the whole cathode surface. Therefore, the oxygen ions can reach the electrolyte membrane by another pathway of bulk cathode. The reaction kinetics can be significantly increased by this extension of reaction sites and diffusion paths.

In order to facilitate ORRs to proceed fast, several technical requirements have to be satisfied. (a) Electrical conductivity: since ORR is an electrochemical reaction, a certain conductivity is needed to allow electron conduction. The mixed conductor of electrons and oxygen ions is preferred because the more active sites are created; (b) Catalytic activity: the property of surface chemistry need to allow the absorption and desorption of various oxygen-related species on the cathode surface; (c) porosity: the gas diffusion from the layer surface to the cathode/electrolyte interface should be fast to minimize the concentration over-potential; (d) thermal and chemical compatibility with electrolyte: the thermal expansion of cathode bulk should be close to that of electrolyte to avoid the potential delamination between two layers and to increase the resistance against

thermal shocks. The cathode should not react with electrolyte to form any insulating phases that slower down or block the further proceeding of oxygen reduction; (e) chemical stability: the cathode must be chemically stable in some case of low oxygen partial pressures when large amount of oxygen is consumed by reactions, causing the oxygen absent at electrolyte/cathode interface area. Overall, the cathode performance is determined by all of these physical, chemical, or electrochemical parameters; one bad-done aspect can deteriorate the cathode behavior in operation.

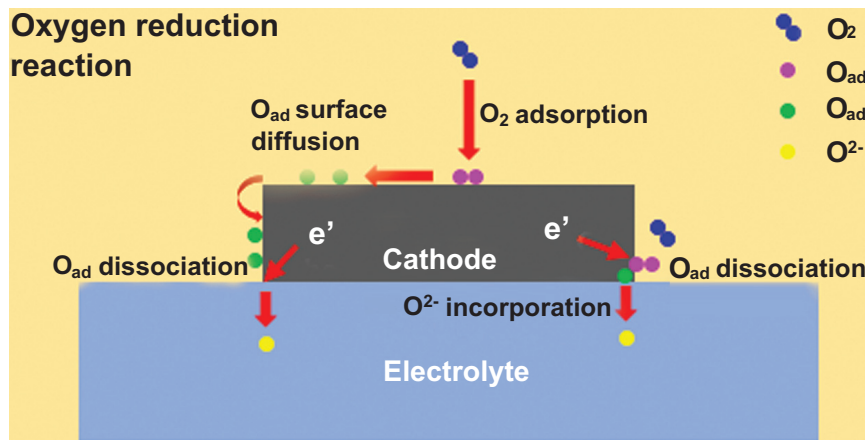


Fig. (1). The schematic of catalysis mechanism for ORR on the cathode surface (pure electronic conductor).

Typical Materials for Cathode and their Conducting Nature

Perovskite

Searching for a conductive oxide which can sustain good relevant properties after the processes of material synthesis and fuel-cell fabrication conditions. Many oxides with perovskite structure are ideal material candidates, which are still in great interest in current activities. Perovskite is a class of compounds which have the same type of crystal structure as CaTiO_3 ($\text{A}^{2+}\text{B}^{4+}\text{X}^{2-}_3$). Due to the high tolerance factor of the crystal structure, perovskite offers wide flexibility for improving the properties of materials, such as catalytic activity, electronic or ionic conductivity, chemical stability and thermal behavior, *etc* [1]. Many useful properties of the perovskite oxides are primarily determined by the B-site cations while they can be also tuned by A-site cations. In this perovskite structure as shown in Fig. (2), oxides typically adopt a cubic structure (sometimes it also distorts to other crystal structure depending on the atoms and preparation conditions).

A Brief Review on Anode Materials and Reactions Mechanism in Solid Oxide Fuel Cells

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Abstract: This chapter presents a state-of-art brief review on anode materials for SOFC. Materials, processing and synthesis routes to attain porous anodes are highlighted. Especial attention is given to Ni-ceramic phase (especially fluorite-type structure ceramics) cermets. Some aspects about prospects and problems of the currently developed electrodes materials are elucidated. Electrodes for intermediate temperature SOFCs (IT-SOFCs) are discussed in relation to other conventional electrodes. The electrochemical characterization of anodes, as mixed ionic-electronic conductors, is briefly outlined.

Keywords: Anodes, Ceramics, Cermets, chemical routes, conventional routes, Electrical properties, Electrodes, Mixed Ionic-Electronic Conductor, Porous, Solid Oxide Fuel Cell.

INTRODUCTION

The anode is the electrode where the fuel oxidation occurs. As the cathode, this component must also exhibit high electronic conductivity, good catalytic activity for the fuel oxidation reactions and sufficient porosity to allow the transport of fuel to the anode/electrolyte interface and the removal of reaction products. In addition, the anode should be chemically stable and thermally compatible with the other SOFC components [1, 2].

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The electrochemical performance of the anode depends on the charge transport resistance (electrons and ions), inside the anode and the anode/electrolyte interface, and the resistance of gas transport. The increase of the triple phase boundaries (TPB) length, by microstructural optimization and phase composition, are the most efficient ways to improve the electrochemical performance of anodes [3, 4].

Internal reform and tolerance to sulfur-containing compounds are also essential to the anodes, especially when a hydrocarbon fuel is used, *e.g.* methane. The porosity of the anodes is a very important factor, not only because it is related to high densities of triple phase boundaries, but also because it avoids mass transport limitation. In this regard, many studies have reported the use of pore formers (graphite, starch, citric acid, *etc.*) in order to obtain suitable porosity in anodes [5, 6]. However, due to the tendency to agglomerate of pore-forming agents, it is sometimes difficult to ensure good structural performance and permeation of gases in these electrodes [7].

Anode Materials

Porous metal electrodes are the most suitable materials to work in reducing atmosphere conditions. These materials have good electronic conductivity and good fuel permeability. Metals such as Ag, Pt, Ru, Co, Fe, and Mn have been tested as anode materials [8 - 11]. In these studies it was observed that platinum lost adhesion with the electrolyte after a few hours of cell operation. Nickel, despite its low cost, good chemical stability and excellent catalytic activity for oxidation of hydrogen, had a serious drawback with microstructural stability. Ni has very low melting point and sintering temperature (1453 and 1000 °C respectively) which enable the grain growth during operation, this behavior can difficulty the passage of gases. Ni also has poor adhesion on dense electrolytes. Furthermore, pure Ni has an incompatible thermal expansion coefficient (TEC) with that of the most used electrolyte materials, YSZ and GDC (gadolinium doped ceria) ($13.3 \times 10^{-6} \text{ K}^{-1}$, $10.5 \times 10^{-6} \text{ K}^{-1}$, $12.0 \times 10^{-6} \text{ K}^{-1}$ respectively) [12, 13].

Spacil proposed an easy way to solve the grain growth issue in Ni based anodes [14]. In his patent, Spacil proposed a mixture of YSZ and nickel particles (Ni), creating the Ni – YSZ cermet. This new material had superior properties than those of pure nickel electrodes. Nickel, characterized by its high electrocatalytic activity and relatively low price, makes the anode an electronic conductor with the possibility to perform steam reforming operations [15]. The ceramic phase basically suppress grain growth during cell operation, which prevents electrode pores obstruction; and improve the thermal and chemical compatibility at the

electrolyte/electrode interface. In addition, the presence of the ceramic phase creates TPB in the entire anode extension where the fuel oxidation reaction occurs [16, 17]. Ni – YSZ cermets became the reference for SOFC anodes.

The idea of using cermets as anode materials began to be adopted in the development of new SOFC systems containing electrolytes with properties higher than YSZ. Examples of these materials are doped ceria, lanthanum gallates, and barium zirconate/barium cerate. For each SOFC system based on a new electrolyte, nickel can be mix with the corresponding electrolyte material, forming a Ni cermet – electrolyte. In these two-phase systems, the percolation limit is about 30 vol % of the metal phase (Ni), it is a required content to occur the transition from predominantly ionic to predominantly electronic conductivity. Furthermore, these materials are used in order to minimize the operating temperature of SOFCs, restricting the possibility of grain growth during the operation of the cell [18].

In recent years, the replacement of YSZ for doped ceria in nickel based cermets has been an increasingly common practice in the development of SOFC anodes. Compared to Ni-YSZ, Ni-GDC cermets have several advantages especially because of the properties of ceria based compounds (GDC has ionic conductivity at 800 °C equivalent to that of YSZ at 1000 °C, approximately 10^{-1} S/cm) which become mixed conductors in an atmosphere of hydrogen [19, 20]. As a mixed conductor, ceria can reduce the ions and transport electrons, promoting the charge transfer reaction in the entire area of electrode/gas interface. A notable feature of ceria-based anodes in relation to those containing YSZ is the ability to resist to carbon deposition on Ni surface, mainly when using methane-rich atmospheres [21, 22]. The good thermal compatibility with the ceria-based electrolytes is another great advantage of Ni-doped ceria cermets.

The electrochemical activity of these materials is strongly influenced by the electrical conductivity of each component and microstructural parameters such as grain size, composition, phase distribution, and connectivity between the ionic conductor (doped ceria), catalytic metal (Ni) and pore. The microstructure is influenced, among other factors, by the characteristics of the starting powders. The use of nanoparticles provides significant microstructural changes, especially increasing the number of contacts between Ni and the ceramic phase, which implies in extension of the TPB area and, as a result, improvement of the electrochemical performance. Considerable electrode microstructural changes have been observed by varying the starting powders [23 - 25]. The improvement of the electrochemical performance by increasing the TPB length can be provided

Recent Advances in Synthesis of Lanthanum Silicate Apatite Powders as New Oxygen-Ion Conductor for IT-SOFCs: A Review

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Abstract: YSZ (yttrium stabilized zirconia) with fluorite structure is the traditional electrolyte used in SOFC (solid oxide fuel cell), where the operating temperatures are above 900 °C. In those high temperatures, reactions between the components may occur, in addition to the thermal expansion and contraction, causing the diminution of the cell life. Therefore, the reducing of operating temperature to development of the intermediate temperature SOFs (IT-SOFCs) is one of important task to the power production area. Find an alternative electrolyte for IT-SOFCs became the interest of researchers. Recently, rare earth silicate-based compositions materials with apatite-type structure, with general formula $\text{Ln}_{10-a}\text{Si}_6\text{O}_{26+b}$, (where Ln is La, Sm, Nd, Dy or Gd, and $a = 8$ to 11), have attracted significant attention as electrolyte. This is because of the structure allows high ionic conductivity with low activation energy at intermediate temperatures. For example, the lanthanum silicate apatite (LSA) solid electrolyte, with the composition $\text{La}_{10}\text{Si}_6\text{O}_{27}$ has exhibited high oxygen ionic conductivity at 500 °C. However, several problems in obtaining the pure apatite single phase and the low sinterability of LSA are disadvantageous for its application as electrolyte. Therefore, the development of a viable synthesis process to attain LSA apatite crystalline powder, with high sinterability for applying in the production of IT-SOFCs electrolytes, turned out to be a challenge for SOFC researchers. Efforts have focused to reach the pure single phase of apatite with the reduction of temperature and time of the sintering process. In this review, different methods, of LSA synthesis, are summarized and discussed.

Keywords: Apatite, Characterization, Electrolyte, Ionic conductivity, $\text{La}_{10}\text{Si}_6\text{O}_{27}$, Lanthanum silicate, Methods comparison, SOFC, Synthesis, X-ray Diffraction.

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INTRODUCTION

The main challenge in the development of fuel cell technology involves the production of the component layers of SOFC (solid oxide fuel cell) cell stack. High ionic conductivity in addition to low electronic conductivity at operation temperature [1] and be secure in equally oxidizing and in reducing environments is essential for electrolyte of SOFC. The mechanism of the flow current in the electrolyte consists on the oxygen ions in movement through the crystal lattice. The moving of thermally activated ions, from one crystal lattice to its neighbor site [2], results the current. This mechanism occurs in stabilized zirconia in SOFC electrolyte, where the oxygen vacancies created by reducing of Zr^{4+} ion in the lattice site, establishes the ion oxygen conductivity. The operating temperature of SOFC must be satisfactory to permit achieving the ionic conductivity into the electrolyte. Typical SOFC electrolyte is yttria doped zirconia with 8 mol% (8YSZ), in which the electronic conductivity is negligible even under highly reducing environments [1]. Other electrolytes under considering are Ga-doped ceria (GDC), Sm-doped ceria (SDC), Sc-stabilized zirconia (SDZ) and La-Sr--a-Mg oxide (LSGM), because of their high ionic conductivities at reduced temperatures [3].

YSZ, the most important electrolyte used as SOFCs electrolyte, exhibits the fluorite structures and has high mechanical strength. However, it requires high temperatures (800 – 1000 °C) in order to obtain its efficient performance. Working at this range of temperatures reduces the useful life of SOFC and limits the selection of materials. Therefore, the main feature of the SOFC researches focuses in the development of high ionic conductivity solid electrolytes at reduced temperatures. It is one of the important tasks to overcome for the development of named intermediate temperature solid oxide fuel cells (IT-SOFC), to operate at temperatures between 500 and 750 °C [2].

As CeO_2 and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-x}$ (LSGM) exhibit higher ionic conductivity than YSZ [4] at reduced temperatures, they may be considered as alternative electrolyte for IT-SOFC. However, they develop electronic conduction under reducing environments.

The high electric conductivity of apatite-type lanthanum silicate has recently attracted significant interest of the researchers. Nakayama *et al.* [5, 6] first reported that lanthanum silicates ($Ln_{10-a}Si_6O_{26+b}$ ($Ln = La, Sm, Nd, Dy, Gd, a = 8$ to 11)) with hexagonal crystal system similar to calcium phosphate $Ca_{10}(PO_4)_6O_2$ called apatite, exhibited ionic conductivity. In their studies, one with the composition $La_{10}Si_6O_{27}$ has exhibited oxygen ionic conductivity of $10^{-3} Scm^{-1}$ at

500 °C, which is higher than that of YSZ electrolytes [5, 7] at that temperature. Lanthanum silicate has hexagonal crystal system similar to calcium phosphate $\text{Ca}_{10}(\text{PO}_4)_6\text{O}_2$. Later, detailed investigation [8 - 10] of crystal structure and conduction mechanism of this oxide electrolyte revealed that the conductivity in apatite systems involves interstitial oxide ions in addition to oxygen vacancies mechanism. Various studies performed by theoretical atomistic simulations [4, 10 - 13], neutron powder diffraction [14 - 18] and Mössbauer [16] spectroscopies, have recognized the conductivity within the apatite structure occurs by interstitial migration of oxide anions. Interstitial oxide dominates ionic conductivity of lanthanum silicate and pass in a *c*-axis direction [2, 3]. By doping other elements into sites in the crystals, the ionic conductivity may be improved. The conductivity of lanthanum silicate apatite (LSA) increases with La content in $\text{La}_{9.33+x}\text{Si}_6\text{O}_{26+1.5x}$ because of excess oxygen ions introduced into the interstitial position of lattice [19]. $\text{La}_{9.92}\text{Si}_6\text{O}_{26.88}$ shows higher conductivity than YSZ below 650 °C [19]. Through lattice doping, the conductivity of LSA can further improved. The conductivity of oxygen ions can be enhanced to a value of 88 $\text{mS}\cdot\text{cm}^{-1}$, with activation energy as low as 0.42 eV at 800 °C, by a small Mg substitution amount, in the Si site [20]. This conductivity is higher than YSZ below 900 °C and similar to doped LaGaO_3 , below 550 °C. Doping Al and Ba into Si site and La site respectively is reported to enhance the conductivity [21, 22], as well as excess oxide ion and vacancy in La site contribute to the improvement of ionic conductivity in the LSA [23, 24]. Therefore, LSA is a potential candidate as a new electrolyte. Materials for use as electrolyte are required to be dense [22, 25, 26]. The difficulty in obtaining dense ceramic of LSA is the main trouble for its application in SOFC. For example, to achieve ceramic bodies with relative densities higher than 90%, temperatures as higher as 1650 °C is need for sintering process using LSA powders synthesized by solid-state reaction. Densities higher than 93% require grinding of the powders, hot pressing and sintering at high temperatures [23, 27]. Additional trouble of LSA consists on the difficulty to obtain the pure apatite single phase. $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ and La_2SiO_5 are the well-known crystalline phases found in the samples of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ sintered below 1775 °C. Therefore, the major research efforts have been focused to reach the pure single phase of apatite and reduction of temperature and time of the sintering process. To obtain a homogeneous mixture of the precursor oxides, La_2O_3 and SiO_2 , by conventional solid-state reaction, is difficult. Secondary crystalline phases, such as La_2SiO_5 and $\text{La}_2\text{Si}_2\text{O}_7$, are often associated to LSA. Using sol-gel technique, the formation of those secondary phases may avoid, because the process allows distribution of the components more homogeneously. Nevertheless, in this method, parameters of the processing, such as, the concentration and molar ratio

A Review on Synthesis Methods of Functional SOFC Materials

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Abstract: Many properties of ceramic materials depend largely on its composition and structure, being also affected by the synthesis method. Intense research activity has been carried out for the development of materials and processes to components of solid oxide fuel cells (SOFCs). Regarding ceramic powders preparation to be used as SOFC components, chemical approaches such as polymeric precursor method, sol-gel, combustion, and co-precipitation have been mentioned in literature. This chapter aims to present some methods that have been used to prepare functional SOFC materials, highlighting its main advantages and disadvantages in the performance of these materials.

Keywords: Ceramic materials, Co-precipitation, Combustion, Fuel cells, Gelatin, Polymeric complexing method, SOFCs, Sol-gel, Solid state reaction, Synthesis methods.

INTRODUCTION

Several technologies are used for the development of SOFCs and currently much we advance in the process of preparing the components that make up the cell: cathode, anode and electrolyte. Technologically, the use of these cells lies some limitations related to materials selection and processing. This fact is mainly due to the high temperatures usually employed, which accelerates corrosion processes, thermal stresses and fatigue of components. In addition, it is essential to exist a

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good compatibility between electrode (anode and cathode), electrolyte and interconnector materials. Accordingly, the scientific community has been studying and trying to develop materials and processes that may allow the production and effective industrial use of the SOFCs.

The choice of composition, doping concentration and processing conditions during the preparation of a ceramic material must be made taking into consideration several characteristics of the final product since all these parameters influence the electrical conductivity, as indicated in Fig. (1). In an ideal ceramic processing is expected that the obtained material presents: high chemical purity, chemical homogeneity, high sinterability, good control of particle size distribution and reduced particle size. For the processing of advanced ceramic materials various physical and chemical methods have been reported in the literature, such as:

- Physical or Ceramic methods
 1. Solid state reaction (mixture of oxides)
 2. Combustion synthesis
- Chemical Methods
 1. Sol-gel
 2. Polymeric complexing method
 3. Modified Polymeric complexing method – Use of gelatin
 4. Co-precipitation

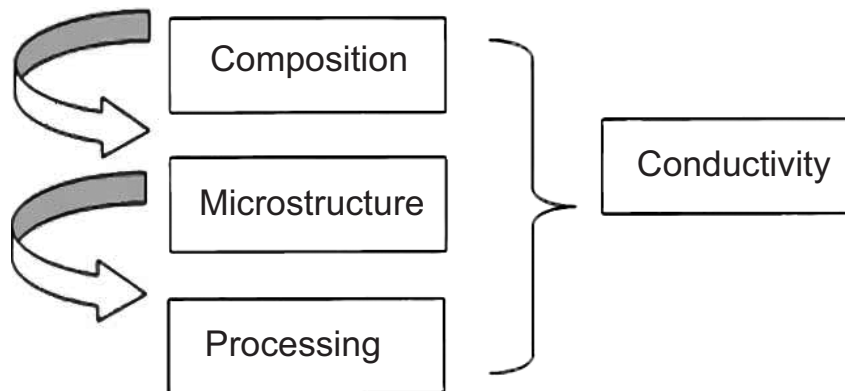


Fig. (1). Correlation between microstructure, composition, processing and conductivity of ceramic materials.

The development of new functional materials and advanced manufacturing techniques are fundamental in reducing the SOFC operating temperature, and as a result, decrease the costs to fabricate these electrochemical devices. Furthermore,

the optimization of synthesis techniques are important for the cost reduction during the manufacturing. With this in mind, the flowchart in Fig. (2) shows the procedure usually adopted to synthesize particulate materials.

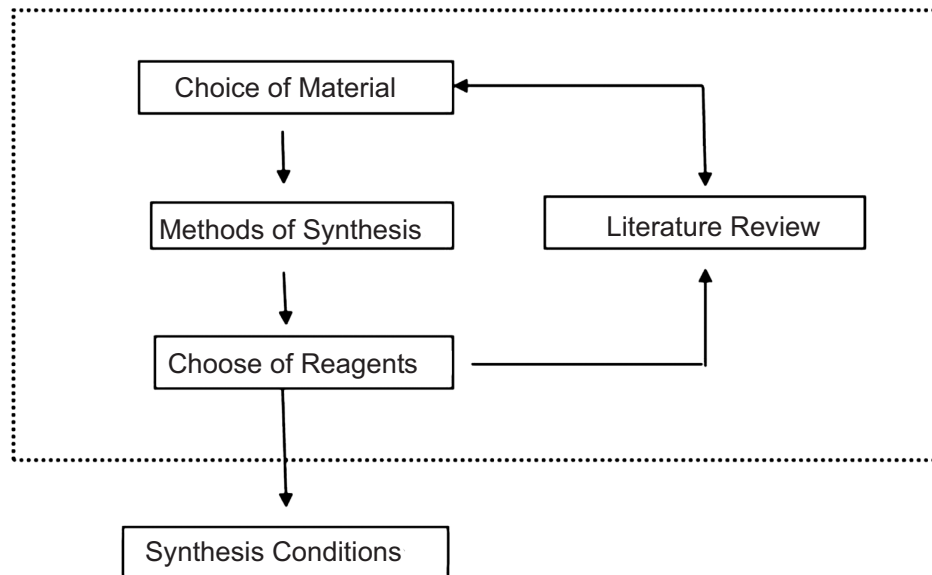


Fig. (2). Steps of the procedure usually adopted to prepared ceramic powders.

TYPES OF SYNTHESIS METHODS

Solid State Reaction (Mixture of Oxides)

The solid state reaction also known as conventional ceramic route is a synthesis method based on solid state diffusion, being characterized by the mechanical mixture of oxides and/or metal carbonates of interest *via* milling followed by heat treatment. In addition to oxides and carbonates other such as chlorides, nitrates, acetates may be used. It's a simple process, relatively inexpensive and is the most widely used industrially. In general, this method requires high temperatures and long calcining times to obtain the desired phases. The reproducibility of the method is limited, mainly due to large particle size distribution and material loss resulting of high temperature volatility. Below are summarized some disadvantages and advantages of this method.

Advantages:

1. Easy implementation and execution;
2. Production of large powder quantity (industrial method);

Ceramic Hollow Fibers: Fabrication and Application on Micro Solid Oxide Fuel Cells

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Abstract: Micro-tubular solid oxide fuel cells (MT-SOFC) have recently attracted increasing attention due to their advantages, such as quick start-up/shut-down, high volumetric power density and better mobile/portable characteristics comparing favorably with planar and tubular SOFCs. Basically, there are four fabrication techniques to prepare MT-SOFCs: extrusion, cold isostatic pressing, slip-casting and phase-inversion. Among these techniques, the phase inversion method is a recently emerging technology to prepare the MT-SOFCs, which can be easily scaled up to realize an automatic and continuous preparation process. Therefore, this chapter gives a detailed account of the fabrication skills of micro-tubular SOFCs based on the phase-inversion techniques and the brief review of their performance test results.

Keywords: Ceramic membranes, Co-spinning, Dual-layer, Hollow fibre, Microtubular, Mobile, Phase inversion, Portable, Quick start-up/shut-down, Solid oxide fuel cells.

INTRODUCTION

Along with the energy crisis and global climate change, clean energy application and exploration of high-efficiency power sources have attracted more and more attention not only from the research communities but also from the industries [1, 2]. Among these efficient energy conversion devices, fuel cell is one typical example with the advantages of low emission and high energy efficiency. Fuel cells can directly convert chemical energy to electrical power *via* electrochemical

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redox. Since no gas turbine is involved, the fuel cell system is not limited by Carnot cycle, and therefore the efficiency of fuel cells are up to 80% or more if the waste-heat could be fully recycled, which attract intense research interest in the recent thirty years. Fuel cells have been classified into several types: alkaline fuel cell, proton exchange membrane fuel cell, phosphoric fuel cell, molten carbonate fuel cell, and solid oxide fuel cell. Among these various types, solid oxide fuel cells (SOFCs) are one of the most promising electrochemical devices featuring the advantages of higher energy efficiency, long term durability, noble-metal-free electrodes, anti-poisoning catalysts and high fuel choice flexibility including hydrogen, methane, CO, gasoline and other combustible gases. Therefore, SOFC has been considered as a promising power generator, transforming chemical energy into electricity, either in a power plant station or in a domestic electricity-heat generating unit. As the major part of SOFC components is fabricated from ceramic materials, such as ZrO_2 electrolyte membrane, perovskite cathode, cermet anode, ceramic bipolar connector and oxide sealant, SOFCs are also referred as ceramic fuel cells.

There are several configurations of SOFC design, including the planar, tubular (or microtubular), or honeycomb structure; among which planar and tubular geometries are the preferred designs [3 - 7]. The planar configuration is relatively an easier and cheaper design due to its simple fabrication protocols including tape casting to prepare ceramic membrane, screen printing to form thin layer electrode, and co-firing; these processing steps have been fully developed in the past decades and now are becoming established and mature techniques. And the efficiency of a planar SOFC has also been proved to be the highest compared to other designs due to the inherently shorter path for electron/ion transport from anode to cathode. However, this design has been found some challenges on thermal and mechanical stability. The shape distortion under high temperature is becoming more serious with a larger dimension of the single planar cell. Sealing is another issue which is challenging the high temperature operation because the sealing area is very large and complex associated with the planar design.

Apparently, the tubular SOFC configuration is a promising alternative due to the easier sealing process for its relative smaller sealing area. And the thermo-cycling behavior of a tubular cell has also been improved compared to the planar ones because of less shape distortion under high temperature operation. However, fuel cells with a tubular shape are more difficult to prepare than the planar structure. For example, the dense electrolyte layer on tubular ceramic support needs to be prepared by CVD-EVD method, or plasma spraying process [8, 9], which are more expensive and complex techniques than those employed in the planar fuel

cells. Meanwhile, the energy efficiency, or power density in a tubular fuel cell is usually lower than the planar fuel cell. The reason is attributed to the long tubular structure, resulting in a long electronic path for current collection and leading to a higher ohmic loss.

MICRO TUBULAR SOLID OXIDE FUEL CELL: ADVANTAGES AND FABRICATIONS

Solid oxide fuel cells, either planar or tubular, are usually operated at the temperature of 750-900°C, which is too high to be practically applied, hindering their commercialization. High operation temperature will bring in many problems such as electrode sintering, chemical reaction between ceramic layers, corrosion of metal parts and finally damaging the life of the power generator. Furthermore, the start-up/set-down speed of the power source is an important threshold that limits the application of SOFC as an urgent power device or uninterruptible power supply (UPS). Large scale SOFCs are considered as promising power station due to their high efficiency of waste-heat and fuel recycling. On the other hand, small size of SOFC has been also emphasized, for its potential application as portable and mobile power unit [10].

Since 1990s, Kendall and co-workers have proposed an advanced cell design referred as the microtubular solid oxide fuel cell (MT-SOFC) [3]. It is not just an improvement to minimize the tubular structure of SOFC, but shows some remarkable advantages such as quick start-up/shut-down, high volumetric power density and better mobile/portable characteristics. When the diameter of the micro tubes reduces to 1-2 mm or less, its heat and mass transfer rates, and ion permeation rates are much quicker than that from large-thickness tubes. Therefore, new theoretical or modeling works are required to predict the performance of MT-SOFC. During the last two decades, a lot of research works have been done focusing on fabrication, theoretical analysis, modeling, and applications of MT-SOFCs. The advantages of MT-SOFC are re-emphasized as below:

High Volumetric Power Density. It is calculated that, the specific area of a micro tube with the diameter of 2 mm is 20 times larger than a tube with the diameter of 20 mm. Thus the volumetric power density of MT- SOFC is much higher than that of the large tubular one [11]. A cubic SOFC stack based on micro tubular configuration, designed by Suzuki *et al.* shows a power output up to 30W in a volume of 30 cm³ (>1000 kW/m³) [12]. This implies that small device with micro SOFC stacks can be applied to light mobile and portable power sources. In 2004, Nano Dynamics Inc., USA launched a product

Electrolyte Hollow Fiber as Support *via* Phase-Inversion-Based Extrusion/Sintering Technique for Micro Tubular Solid Oxide Fuel Cell

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Abstract: This chapter focuses to discuss about the recently introduced phase-inversion based extrusion technique for fabrication of electrolyte hollow fiber support and multi-layer of the micro tubular solid oxide fuel cell (MT-SOFC). The effects of different fabrication parameters on the morphologies and electrochemical performances of developed electrolytes *via* the technique were critically discussed. The future direction of this advanced phase-inversion-based extrusion technique in the MT-SOFCs fabrication was also being discussed at the end of this book chapter.

Keywords: Anode-supported, Co-extrusion, Co-sintering, Electrolyte-supported, Hollow fiber, Multi-layer, Phase-inversion, Single-layer, SOFC, Thin layer.

INTRODUCTION

As solid oxide fuel cell becomes as the future electricity generation devices, its development is greatly explored. Currently, focus has been given to the materials, structures, and fabrications designs of SOFC components. Besides that, production cost and manufacturing processes were also considered so that the performance of SOFC can be enhanced to meet the requirement of economic power production. Besides that, production cost and manufacturing processes were also considered so that the performance of SOFC can be enhances to meet the requirement of economic power production.

The most common structural designs of SOFCs are planar and tubular designs

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which both designs have different shapes and structures. Due to planar design caused thermal shock problem, the tubular design has been introduced by extrusion technique to overcome the issue. However, as inverse tubular cell diameter affects the power density, efforts had been made by Kendall [1] to develop micro-tubular SOFCs (MT-SOFCs) that possess smaller tubular diameter and enhanced performance. In fact, this developed advanced cell design offers a quick start-up capability, an excellent thermal stability during rapid heat cycling, low capital cost, high power output density, and easy to mobile as compared to the conventional tubular and planar SOFCs [2].

Typically, the design of SOFCs can be constructed into either self-supporting or supported concept, as depicted in Fig. (1) [3]. From Fig. (1), electrolyte with thickness of ca. 80-250 μm is denoted as self-supporting geometry which acts as structural element. For the supported design, a thin layer electrolyte with approximate thickness of $<50 \mu\text{m}$ is deposited on cathode or anode which provide the mechanical strength to the hollow fiber. Depending on the support, the MT-SOFC materials can be constructed as anode, cathode or even electrolyte supported. Unlike electrolyte self-support, the use of anode-supported design possessed thinner electrolyte layer, and thus could offer a minimal electrolytic resistance losses and better production of conductance at lower temperatures [4]. Despite this design has excellent performance, precautions are needed to ensure the electrolyte layer is microcracks-free and completely gas-tight. Nonetheless, it should be noted that most of the recent works on the MT-SOFCs have developed the anode-supported design.

The recent trend in MT-SOFC development is to operate the system at lower temperature which is intermediate temperature (500-700 $^{\circ}\text{C}$) or lower ($< 500 \text{ }^{\circ}\text{C}$). Some drawbacks of commercialized high operating temperature system are durability of the cell components, limitation of the material selections, as well as high production cost. On the other hands, lower temperature operation offers enhanced durability, quicker start-up, and greater robustness, wider choice of selecting materials with simplified system requirements.

Other than that, lowering the operating temperature from 700-1000 $^{\circ}\text{C}$ to 500-700 $^{\circ}\text{C}$ has become as one of the major tasks in the development of SOFCs with improved performance. Since last decade, electrolytes with high oxygen-ion conductivity operated at low temperatures have received tremendous attentions. One of the good option of alternative electrolyte to yttria stabilized zirconia (YSZ) is Cerium gadolinium oxide (CGO). Like zirconia, ceria-based electrolytes have a cubic, fluorite-type crystal structure. However, it has superior oxygen ion

conductivity at low temperatures when compared to zirconia [6]. These features resulted to large oxygen ions conductivity with excellent mobility. Nevertheless, ceria will be partially reduced to be an electronic conductor when it is exposed to higher temperatures and at low oxygen partial pressures, which can cause short circuit [7]. Although the stability of ceria at low oxygen partial pressures is weaker than zirconia, its chemical stability of ceria with cathode materials is good. CGO has been proven with a wide variety of electrodes, including lanthanum strontium cobaltite (LSC), lanthanum nickel ferrite (LNF), lanthanum strontium manganite (LSM), lanthanum strontium ferrite (LSF) and lanthanum strontium cobalt ferrite (LSCF) [8].

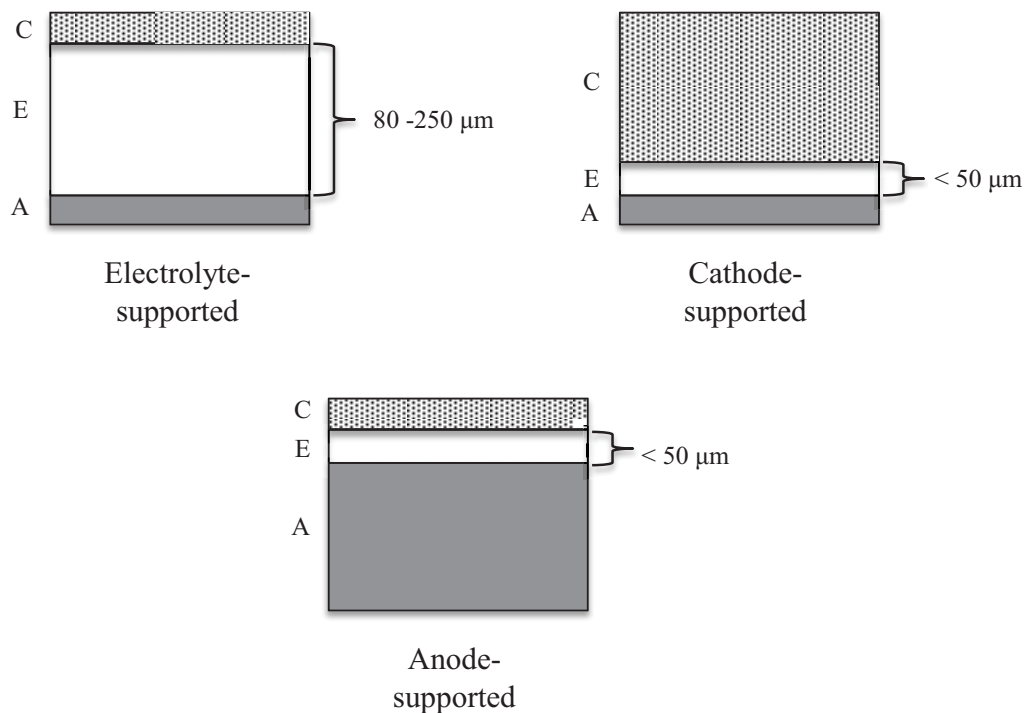


Fig. (1). Geometries of SOFCs (Reproduced from [5]).

However, the fabrication processes of MT-SOFCs, specifically the fabrication parameters that affect the structures of electrolytes fabricated *via* phase-inversion based technique is fairly reported. Micro-tubular that has smaller cell size led to a more challenging fabrication procedures as compared to the typical tubular design. Therefore, in the context of this chapter, discussion is focused on the fabrication of electrolytes *via* phase-inversion technique. The discussion has been divided into three sub-sections. Section one mainly describes on the concept of

Proton Conducting Ceramic Materials for Intermediate Temperature Solid Oxide Fuel Cells

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Abstract: Solid oxide fuel cells (SOFCs) offer a large potential as a future green energy technology, as they show high fuel conversion efficiency with limited pollution and fuel flexibility for a wide range of applications [1]. These devices operate in the high temperature range (800-1000 °C), where cost and longevity related problems have slowed their commercialization. Nonetheless, the high operating temperature hurdle of SOFCs can be crossed by using proton conducting ceramic oxides as solid electrolytes, producing so called protonic ceramic fuel cells (PCFCs). The perovskite $AB_{1-x}M_xO_{3-\delta}$, (A=Ca, Ba, Sr; B=Ce, Zr; M=Y, Gd, Yb) materials have been suggested as electrolyte materials for PCFCs, since these materials show high protonic conductivity and lower activation energy (0.4-0.6 eV) in the intermediate temperature range 500-750 °C [2]. The alkaline earth doped cerate family possess high proton conductivity (about 10^{-2} S cm^{-1} at 600 °C) with low activation energy, but suffer from poor chemical stability due to degradation in the presence of acidic gases (e.g., CO₂) and steam, precluding their practical use as electrolytes in PCFCs. On the contrary, the alkaline earth doped zirconates exhibit good chemical stability, although their overall proton conductivity is limited (about 10^{-3} S cm^{-1} at 600 °C) due to a low grain boundary conduction, compounded by poor sinterability and limited grain growth [3]. By tailoring the chemical composition of these two material families, a compromise between good proton conductivity, good sinterability and chemical stability can be achieved [4]. Due to the novelty and potential of this technology, this chapter will be dedicated to recent developments in PCFCs, highlighting potential electrolyte and electrode materials, their microstructure and property relationships.

Keywords: Barium cerate, Barium zirconate, Cathode, Cermet anode, Combustion synthesis, Electrolyte, Perovskites, Proton conductors, Protonic ceramic fuel cell, Solid oxide fuel cell.

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INTRODUCTION

Solid oxide fuel cells (SOFCs) are amongst the most capable technologies to deliver sustainable and clean energy to the future. These high-temperature targeted devices operate around 800-1000 °C, with high efficiency, zero emissions and silent function. The use of non-noble catalysts in the electrode materials and the possibility of co-generation are some of the advantages [5, 6]. However, several key technical issues related to the high operating temperature have hindered the deployment of this transformative technology, such as high systems costs and high performance degradation rates, as well as slow start-up and shutdown cycles [7]. The elevated operation temperature leads to severe degradation of cell components, and demand expensive sealants and interconnection materials [5, 6]. Over the past decade, considerable effort has, therefore, been focused in reducing the operating temperature of SOFCs down to the intermediate temperature range. Recently, innovative proton conductive electrolytes have opened a new working window, in the temperature range of 400-700 °C. These electrolytes derive their ionic conductivity from the incorporation of protonic defects of sufficiently high mobility [8].

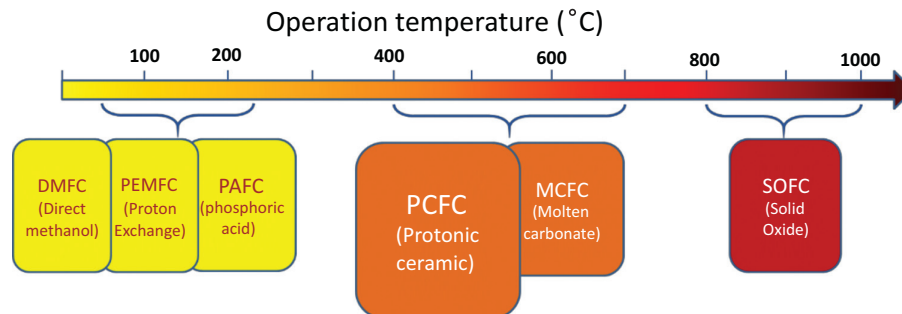


Fig. (1). Status of the current fuel cell technologies and their targeted operation temperature range.

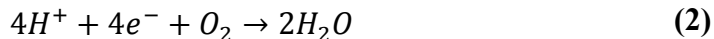
Fuel cells can use a diverse set of electrolytes and it is this component that normally defines the operation temperature (Fig. 1), the nature of the fuel and the kind of reforming demanded for the fuel (internal or external) [9]. In the low temperature range, the most advanced technology is by a wide margin the proton exchange membrane fuel cell (PEMFC), leaving a fringe role for the phosphoric acid fuel cell (PAFC) and the direct methanol fuel cell (DMFC). On the other hand, in the medium to high temperature range, the molten carbonate fuel cell (MCFC) and SOFC are mainly used for providing high power for stationary applications and often integrate cogeneration systems (production of electricity

and heat together) [10]. Amongst these, the more recent PCFC technology is very promising because it offers the same flexibility of SOFC in terms of the type of fuels that can be used (*e.g.* hydrogen or hydrocarbons) and also does not contain corrosive liquids, as opposed to MCFCs for instance, while being able to be operated at intermediate temperatures [11].

A PCFC is comprised of a proton conducting solid electrolyte, sandwiched between two porous electrodes (the anode and the cathode) [12]. The working principle is illustrated in Fig. (2). In PCFCs, the fuel (hydrogen or alternative hydrocarbons) is oxidised at anode side by creating protons and releasing electrons:



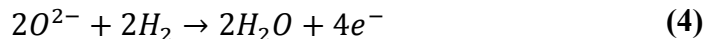
The protons formed at anode side migrate through the electrolyte towards cathode side where the formation of water takes place by reaction with oxygen:



Conversely, in the case of oxide-ion conducting electrolytes, these mobile ions are formed at the cathode by oxygen reduction:



While on the other side, the anodic reaction will be:



Global reactions, equations (1 + 2) or (3 + 4) and the corresponding cell Nernstian voltage ($V = -\Delta G/4F$), where the symbols have their usual meaning) are identical, however, the individual electrode reactions are distinct, as are the ionic transport mechanisms [13]. The difference in the chemical potential of gases at the electrodes is responsible for the movement of the ionic species. However, the electrochemical reactions occur mainly at electrode/electrolyte interface, within a range of few micrometers into the electrodes from the electrolyte. This interfacial zone is termed as the functional layer while the remaining part of the electrode is primarily a current collector microstructure that should be porous to allow gas access to the functional layer [14].

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Moisés R. Cesário

Moisés Cesário has a Ph.D. degree in physicochemical sciences from the University of Strasbourg (France) in co-supervision with the Federal University of Rio Grande do Norte (Brazil). Following a post doctorate at the University of Aveiro, Portugal, he was Assistant Professor and Researcher at the National Graduate School of Engineering and Research (ENSICAEN), France. He currently is a postdoctoral researcher at the University of the Littoral Opal Coast (ULCO), France.

New and cheap technologies for obtaining "clean" energy using catalytic materials prepared by techniques of easy handling has been the main goal of his work. Passionate about research, innovation and new challenges in the field of materials for fuel cells and catalysis, he participated in several research projects, namely on powder preparation of cathode/electrolyte materials, thin film preparations and their electrochemical performances in Solid Oxide Fuel Cells (SOFCs). He also worked with catalytic materials and their applications in chemical processes for hydrogen production. From his work resulted he is the author of articles published in scientific conferences and journals, book chapter writing and patent.



Daniel A. de Macedo

Prof. Daniel Macedo has devoted the last decade of his academic career to the study and improvement of ceramic and composite materials for energy conversion in Solid Oxide Fuel Cells. He is author of several scientific papers published in conferences and journals of national and international circulation, book chapters, and 4 patent requests. He is an adjunct professor at the Federal University of Paraíba, Brazil.