

Advances in Sol-Gel Derived Materials and Technologies

Series Editors: Michel A. Aegerter · Michel Prassas

Mario Aparicio
Andrei Jitianu
Lisa C. Klein *Editors*

Sol-Gel Processing for Conventional and Alternative Energy



 Springer

Advances in Sol-Gel Derived Materials and Technologies

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The success of this society has been built on the forward thinking of the past presidents and boards. They have created the necessary infrastructure for an international society and they have shown a sustainable path forward. Today, our novel mission with you is to establish a stronger sense of global community in sol-gel science.

I wish you a very educative and pleasant reading.

Geraud Dubois
President of the International Sol-Gel Society

Mario Aparicio · Andrei Jitianu
Lisa C. Klein
Editors

Sol-Gel Processing for Conventional and Alternative Energy

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*Dedicated to Charo, Mihaela, and Tim
for their patience and understanding*

Preface

Energy is on everyone's mind these days because of the expanding need for electricity, lighting, heating, cooling, and transportation fuels. Finding more efficient ways to produce energy is a global priority. In addition, the production of energy needs to be sustainable and clean. At the core of the energy infrastructure is the need for materials for energy conversion, energy storage, and energy distribution.

The focus of this book is on ways to synthesize, assemble, and modify materials that find use in systems designed for energy conversion and energy storage. The sol-gel process has been used for a variety of systems that serve the energy market. The singular advantage of the sol-gel process is its being a low-temperature route to simple and complex oxide materials. Low-temperature processing allows the combination of organic and inorganic materials, such as hybrid membranes and ion conductors. Another advantage of the sol-gel process is that it begins in liquid form, so that it is easily adapted to coatings and surface treatments, such as electrochromic windows and multilayer thin film stacks. Furthermore, the sol-gel process leads to high surface area materials and porous materials, meaning it has applications in catalysis, environmental remediation, and carbon dioxide sequestration.

Through the lens of sol-gel processing, this book is about the selection and preparation of materials for batteries, fuel cells, photovoltaics, thermoelectrics, energy harvesting ferroelectrics, and supercapacitors. The properties of these materials are explored in detail. Their applications and performance are described and evaluated. The interested reader can gain a sense of the state of the art and, at the same time, the need for further improvement.

Since new solutions are needed to solve the problem of increasing energy consumption, it would bring the co-editors great satisfaction if this book motivates some or all of its readers to double their efforts toward finding new ways to use the sol-gel process to address materials, needs. The co-editors wish to thank Mike Luby of Springer for his encouragement to take on this project. Merry Stuber is thanked for her editorial assistance. This project would not have come together if it were not for the outstanding response from the chapter authors and their wonderful

contributions. Also, the co-editors appreciate the chance to work together on this project, which has led to further opportunities for research collaborations.

On behalf of my co-editors, Mario Aparicio and Andrei Jitianu,

Lisa C. Klein

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Chapter 1

Conventional Energy Sources and Alternative Energy Sources and the Role of Sol-Gel Processing

Lisa C. Klein

Abstract Energy is an ever-present concern. Materials are in some cases a limiting factor in energy production. It is necessary to improve the available materials for energy storage, energy conversion and energy distribution. One way to address some of these materials issues is sol-gel processing. This chapter briefly introduces the role of sol-gel processing for energy applications.

Keywords Alternative energy · Biomass · Clean energy · Conventional energy · Energy conversion · Energy storage · Fossil fuels · Hydrogen · Non-renewable energy · Renewable energy

1.1 Introduction

This book is intended to be a comprehensive source of information about the use of sol-gel processing in materials in energy systems, energy conversion, energy storage and energy generation. Both conventional energy (e.g., nuclear) and alternative energy (e.g., solar) are included. The goal is to cover the present applications, such as nuclear fuel processing, electrolytes for fuel cells and electrochromics, and dye-sensitized solar cells (DSSC), among others. For each of the existing technologies, the plan is to cover the processing, properties and industrial applications that are known today. Related topics such as carbon sequestration, wastewater treatment and photocatalysis are covered as well.

The authors in reviewing and assessing the methods and applications are able to identify materials challenges presented by conventional and alternative energy

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Table 1.1 2006 National Academy of Engineers “Engineering Challenges” [2]

Make solar energy affordable
Provide energy from fusion
Develop carbon sequestration methods
Manage the nitrogen cycle
Provide access to clean water
Restore and improve urban infrastructure
Advance health informatics
Engineer better medicines
Reverse-engineer the brain
Prevent nuclear terror
Secure cyberspace
Enhance virtual reality
Advance personalized learning
Engineer the tools for scientific discovery

generation that require new materials and innovative processing. Overall, these specialists provide state-of-the-art information about different aspects of materials for energy production, with a focus on their processing. The need for materials innovation, in general, to promote renewable energy has been reviewed recently [1].

1.2 Motivation

What is the motivation for surveying sol-gel processing in the context of energy? It is safe to say that energy, and especially alternative energy, is on the minds of everyone, including no doubt materials scientists. In the compilation of “Engineering Challenges” by the National Academy of Engineers (NAE) the first on the list is “make solar energy affordable” (see Table 1.1). Sol-gel processing is one of the ways that this challenge is being met. This book will go beyond this challenge to address other ways to make conventional energy and alternative energy affordable and clean.

1.3 Conventional Versus Alternative Energy Sources

To be clear about what is meant by the many terms used to classify and describe energy, a few definitions are in order. In discussing alternative and renewable energy, there are several terms that are frequently used to describe the different technologies. In general, alternative energy, renewable energy, clean energy and sustainable energy broadly are used interchangeably to include all forms of energy that are not classified as conventional fossil fuels, meaning coal, oil and

Table 1.2 Non-renewable versus renewable

Non-renewable	Renewable
Fossil fuels	Solar energy
Petroleum	Wind power
Natural gas	Hydropower
Coal	Geothermal
Nuclear	Tidal power
	Biomass

natural gas. Alternative energy includes nuclear energy, clean coal, hydrogen, recycled energy and other non-traditional fossil fuel energy sources such as landfill gas. Energy sources are classified as non-renewable or renewable in Table 1.2.

Nuclear energy is sometimes classified in a category by itself, because it has a large role in the global energy picture, representing nearly 20% of electrical power generation in the United States alone. Notwithstanding recent events, nuclear energy will likely play a significant role in reducing greenhouse gases and achieving energy independence goals. Currently, for example, the use of nuclear power avoids ~2.5 billion metric tons of carbon dioxide emissions annually on a global basis.

Clean coal refers to a set of technologies that are aimed at reducing the level of pollution associated with the burning of coal and minimizing the amount of carbon dioxide that is emitted into the atmosphere. It includes technologies such as coal gasification, coal liquefaction, and carbon capture and storage (CCS). Given the worldwide abundance of coal, these technologies are expected to be central to any energy future involving coal.

Hydrogen is a carrier of energy and not an energy source. It is considered an alternative energy because it does not generate CO₂ during combustion. Today, however, hydrogen is mainly produced from fossil fuel and to a lesser extent by electrolysis of water using energy produced from fossil fuels. In the future, hydrogen could be a stored form of energy produced from other forms of renewable energy such as wind.

Recycled energy refers to high quality waste heat from industrial processes that can be captured and then used to generate electricity through the use of a steam turbine generator or to produce steam or hot water for heating applications. Thermoelectrics are a material class aimed at using waste heat to generate electricity directly.

Landfill gas is another source of alternative energy. It is a natural by-product of the decomposition of organic waste in landfills, and typically it comprises primarily methane. Since methane is a greenhouse gas that is about 20 times more potent than carbon dioxide at trapping the sun’s heat within the earth’s atmosphere, it is critical to capture landfill gases (LFG) and to prevent their escape into the atmosphere.

1.4 Renewable Energy Resources

In general, renewable energy includes a broad range of technologies that generate energy from non-fossil fuel resources, including wind, sun, rivers, oceans and deep drilling underground in the case of geothermal resources. Wind energy is converted into electrical energy when the wind turns propeller-like blades, which spin a shaft that is connected to a generator.

Solar energy is the sun's energy that reaches the surface of the earth. In energy terms it represents approximately $1 \text{ KW/m}^2/\text{h}$ depending on the time of year, weather, longitude and altitude. Solar energy systems can be divided into two major types. Concentrating solar power technologies use mirrors to reflect and concentrate sunlight onto receivers that heat a fluid, such as water, which in turn drives a steam turbine.

Photovoltaic solar energy systems, which are referred to as PV solar, use semiconductor materials to convert light energy into electrical energy. Some PV solar energy systems are already considered cost competitive in the 10 most expensive energy markets in the US with some experts predicting that PV may become cost competitive with coal within the next 10 years.

Hydroelectric power is produced from flowing water, typically rivers and streams. It is estimated that approximately 20% of the world's electricity is generated through hydro power, which currently accounts for over 80% of electricity derived from renewable sources.

Biomass refers to all forms of organic matter that can be converted into energy through combustion, directly or as a liquid fuel. There are enormous biomass resources, such as wood wastes, primary mill residues, forest residues, agricultural waste and dedicated energy crops. Other biomass resources exist, but are more distributed and not easy to quantify.

Geothermal energy is a form of renewable energy derived from heat deep within the earth's crust. Geothermal energy has wide applicability for heating and cooling residential homes and commercial facilities, and it currently represents about 0.5% of US generation capacity.

Ocean energy involves harnessing the power of the tides, currents or waves. These forms of energy hold significant potential but they are still in the early stages of development with typically only prototype units in operation.

1.5 Energy Storage and Energy Conversion

For an excellent review of electrochemical systems, including batteries, fuel cells and supercapacitors, the review by Winter and Brodd [3] is recommended. For a progress report on sol-gel processing in batteries and fuel cells, as of 2004, there is a chapter in Sakka's comprehensive three-volume set on sol-gel technology [4]. Since that time, there has been an explosion in research on sol-gel processing for

fuel cells, especially proton-exchange membrane fuel cells (PEMFC) [5–7] and direct-methanol fuel cells (DMFC) [8]. The development of DSSC has been a major achievement for sol-gel processing, due in large part to the success of the titania-based work of Grätzel [9].

In summary, energy, its sources, its storage and its conversion is a worldwide concern. Many ways to address this concern are dependent on materials and their processing. This book collects the present-day approaches using sol-gel gel processing. A positive result of this book is that it catalyzes new ideas to address energy needs.

Acknowledgments Tim Kinsella is thanked for sharing his vast knowledge of the energy industry and for working to promote alternative energy.

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Chapter 2

Solid Oxide Fuel Cells

Chendong Zuo, Mingfei Liu and Meilin Liu

Abstract Solid oxide fuel cells (SOFCs) have potential to be the most efficient and cost-effective system for direct conversion of a wide variety of fuels to electricity. The performance and durability of SOFCs depend strongly on the microstructure and morphology of cell components. As a unique synthesis and processing technique with easy control of composition, structure, morphology, and microstructure, sol-gel processes have been widely used for fabrication of key SOFC materials or critical components with desired properties or functionalities unattainable otherwise. In this chapter, we provide an overview on sol-gel processes applied for preparation of homogeneous and fine powders of electrolyte, electrode, and ceramic interconnect materials, for deposition of dense electrolyte membranes or porous electrode films, and for modification of electrode or metallic interconnect surface or interface to enhance catalytic activity, to improve tolerance to coking or contaminant poisoning, and to increase stability against oxidation, reduction, or other degradation mechanisms. While significant progress has been made in controlling and tailoring the composition, microstructure, morphology, and hence functionality of materials and components, many challenges still remain to make sol-gel processes cost-effective and versatile for many applications. The development of novel sol-gel processes as well as the exploration of the existing ones to new applications continues to be an intriguing research pursuit.

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Keywords Anode · Cathode · Coatings · Electrode/electrolyte interface · Electrolyte · Gadolinia-doped ceria (GDC) · ILTSOFC · Lanthanum strontium manganese (LSM) · Magnesium doped lanthanum chromate · NiO/YSZ · Sol-gel · Solid oxide fuel cell (SOFC) · Surface modification · Ytria-stabilized Zirconia (YSZ)

2.1 Introduction

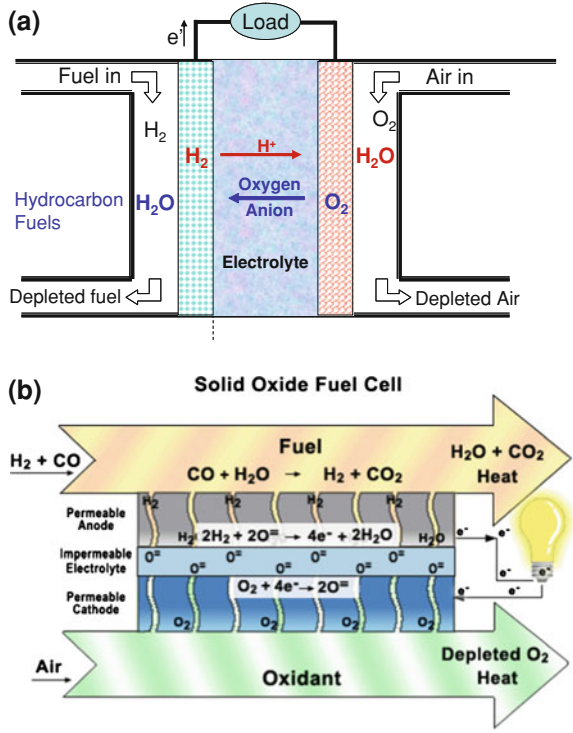
A fuel cell is a system that converts the chemical energy of a fuel directly to electricity. Compared to other types of fuel cells, a solid oxide fuel cell (SOFC) is an all-solid-state fuel cell based on a solid oxide electrolyte [1], which potentially offers the highest energy efficiency with minimum emissions and hold promise for direct utilization of a wide variety of fuels, from hydrogen to natural gas, coal gas, reformed gasoline or diesel, and gasified carbonaceous solids (e.g. municipal solid waste and biomass) [2–4]. SOFCs are simple, reliable, environmentally benign, and highly efficient (up to ~85% energy efficiency when combined with gas turbine) compared to engines and modern thermal power plants (~30%) [5].

2.1.1 Configuration of a SOFC

A single SOFC consists of an anode and a cathode separated by a solid oxide electrolyte (an ionic conductor), as schematically shown in Fig. 2.1a [6]. The solid electrolyte can be an *oxygen ion*, a *proton*, or a *mixed oxygen ion–proton* conductor, but it must be an electronic insulator (prohibiting the conduction of electrons or electron holes) and gas impermeable (in a dense membrane form). While SOFCs based on proton conductors (e.g., $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ —based electrolytes) have attracted much attention in recent years, the most studied SOFC systems to date are based on oxygen ion conductors such as yttria-stabilized zirconia electrolyte (YSZ, with a composition of 8 mol.% Y_2O_3 –92 mol.% ZrO_2 , sometimes referred as 8YSZ); the anode is a porous nickel-YSZ cermet; and the cathode is a porous composite that usually contains YSZ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM, usually x varies from ~0.15 to ~0.20). YSZ-based SOFCs usually operate at high temperatures (750–1,000°C) to be efficient because of the limited transport and catalytic properties of the SOFC materials at low temperatures. To reduce the operating temperature, doped ceria (such as $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ or GDC and $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$ or SDC) have been used as the electrolyte and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) as the cathode for SOFCs to be operated at low temperatures (<700°C). Figure 2.1b is a schematic for a typical single SOFC based on an electrolyte of an oxygen ion conductor using hydrogen as the fuel and oxygen as the oxidant.

During operation, oxygen molecules are adsorbed, dissociated, and reduced on the cathode surface to ionic oxygen species before incorporated into the lattice as

Fig. 2.1 Schematics of (a) SOFC based on different types of solid electrolyte [6] and (b) operating concept of an SOFC based on an oxygen ion conducting electrolyte [7]



oxygen ions, which then move through the electrolyte to the anode and combine with fuel molecules to form water and carbon monoxide/dioxide (if a hydrocarbon fuel is used). Outside the cell, electrons move from the anode to the cathode through an external circuit, converting chemical energy of the fuel to electrical energy. In Kroger’s notation, oxygen reduction on the cathode can be described as follows:

$$\frac{1}{2}O_2 + 2e + V_O^{\bullet\bullet} = O_O^X \tag{2.1}$$

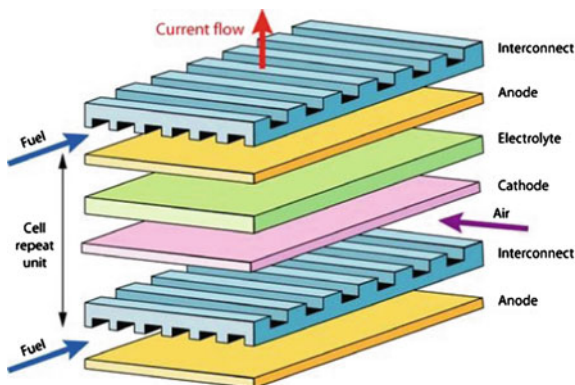
At the same time, fuel molecule (e.g., hydrogen) is oxidized on the anode by combining with oxygen ions and release electrons:

$$H_2 + O_O^X = H_2O + 2e + V_O^{\bullet\bullet} \tag{2.2}$$

The combination of the reactions (2.1) and (2.2) yields the overall reaction of the fuel cell,

$$H_2 + \frac{1}{2}O_2 = H_2O \tag{2.3}$$

Fig. 2.2 Schematic for a planar SOFC design [8]



2.1.2 Solid Oxide Fuel Cell Structure

For practical applications, SOFCs have different structures, and each of them has its own advantages and disadvantages, though the materials for cell components in these different designs are either the same or very similar in nature.

- Planar versus tubular solid oxide fuel cells

Currently, there are two basic types of SOFCs in terms of cell structure: one is planar and the other is tubular. For planar SOFCs, each cell is made into a flat disk, square, or rectangular plate. The cells are put in series and connected by the interconnect plates, as schematically shown in Fig. 2.2. For tubular SOFCs, usually the electrode (either cathode or anode) is made into a long-tube with a porous wall. Outside the electrode tube are the electrolyte and then another electrode. Cells are also connected in series through interconnects, as schematically shown in Fig. 2.3. Earlier studies in SOFCs were focused on high temperature tubular SOFC systems; since the late 1990s, accompanied with the reduction of electrolyte thickness in the planar SOFC technology, the development of planar SOFC systems has drawn great interest due to its apparent advantages in power density and the ease of fabrication. However, tubular SOFC is still favorable for portable applications where rapid start-up and cool-down are required. The comparisons of planar and tubular structures are summarized in Table 2.1 [1].

- Electrolyte-supported versus electrode-supported solid oxide fuel cells

As illustrated in Fig. 2.1, a single SOFC has three layers: a porous anode and a porous cathode separated by a dense electrolyte membrane. The relative thickness for each cell component depends on the cell structure, electrolyte-supported or electrode-supported SOFCs, as illustrated in Fig. 2.4. In terms of processing technique, electrode-supported cells are more demanding than electrolyte-supported cells. However, electrode-supported structures are now more widely used. For example, for the tubular structure, Siemens adopts the cathode-supported

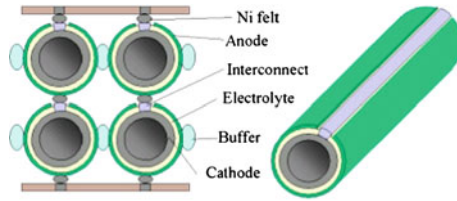


Fig. 2.3 Schematic for a tubular SOFC design [9]

Table 2.1 Comparison of planar and tubular structure for solid oxide fuel cells [1]

	Planar	Tubular
Power per unit area	Higher	Lower
Power per unit volume	Higher	Lower
Ease of fabrication	Easier	Difficult
Cost of fabrication	Higher	Lower
Ease of sealing	Difficult	Easy
Long-term stability	Fair	Excellent
Thermo-cycling stability	Fair	Good

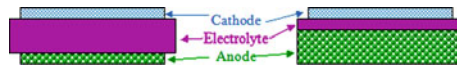


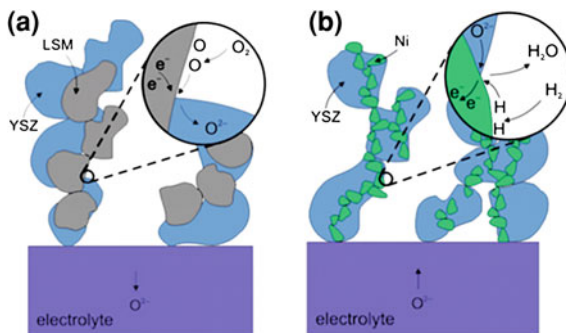
Fig. 2.4 Schematic for the cross-section of (a) an electrolyte-supported SOFC and (b) an anode supported SOFC

structure, and for the planar structure, most industrial teams adopt the anode-supported structure. The main advantage of the electrode-supported structure is that it provides thinner electrolyte and thus lower electrolyte ohmic resistance, which enables the operation of SOFC at lower temperatures, especially for the anode-supported planar structure [1].

2.1.3 Advanced Intermediate- and Low-Temperature SOFCs (ILT-SOFCs)

SOFC is currently attracting tremendous interest because of its huge potential for power generation in stationary, portable, and transport applications and of the increasing need for sustainable energy resources. The major current impediment of commercializing SOFCs is the high cost which results from high operating temperature (800–1,000°C). By lowering the operating temperature (500–750°C), the advanced intermediate- and low-temperature SOFCs (ILT-SOFCs) have the potential to greatly reduce the cost of interconnect, manifolding, and sealing materials, in addition to improved reliability, portability, and operational life [10]. However, the interfacial polarization resistances between electrolyte and

Fig. 2.5 Schematic of (a) Reduction reaction on the TPB of a cathode made of LSM-YSZ and (b) Oxidation reaction on the TPB of an anode made of Ni-YSZ [13]



electrodes increase dramatically as the operating temperature is reduced [11]. Thus, the development of novel electrode materials and/or unique microstructure is one of the critical issues in development of new generation SOFCs.

As shown in Fig. 2.5, a critical part of most fuel cells is often referred to as the triple-phase boundary (TPB), where the actual electrochemical reactions take place, are found where reactant gas, electrolyte, and electrode meet each other. For a site or area to be active, it must be exposed to the reactant, be in electrical contact with the electrode, be in ionic contact with the electrolyte, and contain sufficient electro-catalyst for the reaction to proceed at a desired rate. The density of these regions and the microstructure of these interfaces play a critical role in the electrochemical performance of SOFCs [12]. Thus porous electrodes with fine particle size are preferred in SOFCs to achieve high surface area which significantly increases the length of TPB. In order to reduce the operating temperature, the resistive loss occurring in the electrolyte should also be minimized. One of the solutions is to decrease the thickness of the solid electrolyte from several hundred micrometers, the usual thickness in conventional electrolyte-supported cell, to a range close to ten micrometers (electrode-supported cell). Therefore, advanced fabrication processes are desirable in order to create dense, thin electrolyte and porous electrode films with fine microstructures so that electrochemical performance can be enhanced at lower operating temperatures.

2.1.4 Applications of Sol-Gel Process in SOFCs

Sol-gel processes have been widely used for synthesis of an inorganic network through a chemical reaction in a solution at low temperatures. The most obvious features of this reaction, the transition from a liquid into a solid (di- or multi-phasic gel), led to the expression “sol-gel process” [14]. An overview of the sol-gel process is presented in a simplified chart (Fig. 2.6).

Sol-gel chemistry is a remarkably versatile approach for fabricating materials and components. The advantages of the sol-gel processes include excellent control

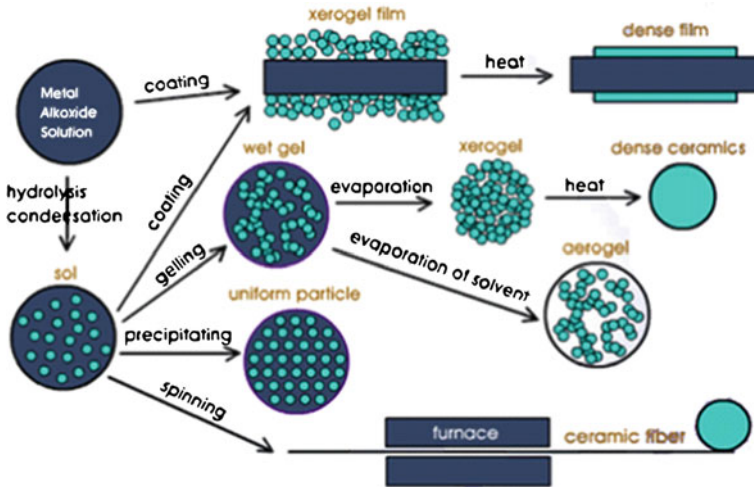


Fig. 2.6 Simplified Chart of sol-gel processes [14]

of microstructure and ease of compositional modification at relatively low temperatures by using simple and inexpensive equipment [15]. Sol-gel techniques have been used not only for powder synthesis or thin-film coating but also for modification of electrode surfaces or electrode/electrolyte interfaces.

2.2 SOFC Material Powders Derived from a Sol-Gel Process

The sol-gel method of obtaining ceramic oxide materials has been extensively developed and consists essentially of three steps [15, 16]:

1. Preparation of a starting solution. It involves mixing low viscosity (to ensure homogenization at molecular level) solutions of suitable ‘precursors’, i.e., metal derivatives; these precursors can in some instances be the ‘metal oxide’ sols themselves
2. Gelling stage: consists of forming a uniform sol and causing it to gel; this is the key step in the process to endow chemical homogeneity on the ceramic product during desiccation. The transition from the sol to the gel state can be achieved in three different ways:
 - growth of polymeric molecules (which crosslink randomly to a three dimensional network)
 - growth of individual particles (which grow together as they become larger)
 - stabilization of colloids by surface charges (change of the zeta potential and a following interparticle condensation process leads to gelation).

3. Thermal conversion treatment to the final material: shaping during or after gelation into the final form (bulk materials, hollow spheres, fibers, surface coatings, etc.) before firing.

For the preparation of multicomponent ceramic materials, the most commonly employed precursors include metal alkoxides, and other derivatives of metals, such as, metal oxides (sols or solids), nitrates, acetates (carboxylates), and β -diketonates.

Sol-gel techniques have been applied to fabricate SOFC materials with favorable physical and chemical properties that conventional solid state reaction method are unable to provide, which will significantly increase the number of reaction site (TPB) in electrodes or decrease the sintering temperature of the dense electrolyte. More details are described in the following sections.

2.2.1 Electrolyte Materials

- Synthesis of YSZ electrolyte powders

The most widely used electrolyte material for SOFCs is yttria-stabilized zirconia (YSZ) with a typical composition of $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ or 8YSZ. The ionic conductivity of YSZ varies with dopant concentration and increases exponentially with temperature [1].

Figure 2.7 illustrates a flow chart for the synthesis of ultrafine YSZ powders through a sol-gel process [17]. The precursors were the zirconium propoxide ($\text{Zr}(\text{OPr})_4$) and yttrium nitrate hexahydrate in 1-propanol. After the gelation step at 50°C, samples were dried at 80°C for a minimum of 24 h to obtain a xerogel. Then, they were calcined at 950°C for 2 h. XRD analysis indicates that the obtained powders have a single phase [18]. Figure 2.8 illustrates these nano-structured YSZ powders form an agglomerate with an average primary particle size of 50–100 nm and have nearly spherical morphology. These nano-engineered YSZ particles with controlled morphology and particle size can aid in the packing of particles in the green films and hence enhance sintering kinetics. This, in turn, assists densification of electrolyte films at lower firing temperatures.

- Synthesis of doped ceria electrolyte powders

With high ionic conductivity between 500 and 700°C, doped cerias have been extensively studied as electrolytes in reduced-temperature SOFCs. Gadolinia-doped ceria (GDC, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) is considered to be one of the most promising electrolytes for SOFCs to be operated below 650°C [19]. Further, doped cerias have also been successfully used as part of anodes for SOFCs, especially those using hydrocarbon fuels [20, 21]. Nano-crystalline GDC powder has been prepared by a sol-gel thermolysis method [20]. After the GDC gel precursors calcined at 400°C, the powders showed cubic fluorite structure with an average crystallite size

Fig. 2.7 **a** Procedure of synthesis with AcAc; **b** Procedure of synthesis in acid environment [17]

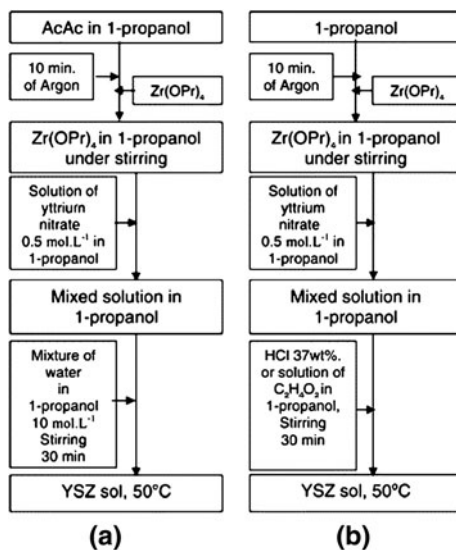
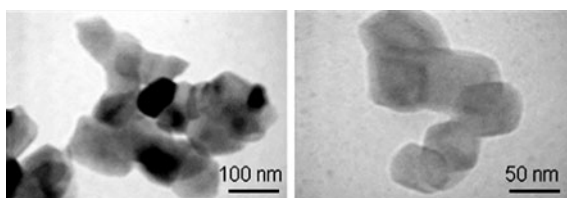


Fig. 2.8 TEM features of a micrograph of gel calcinated at 400°C with a CA/EG RATIO = 2.4 [18]

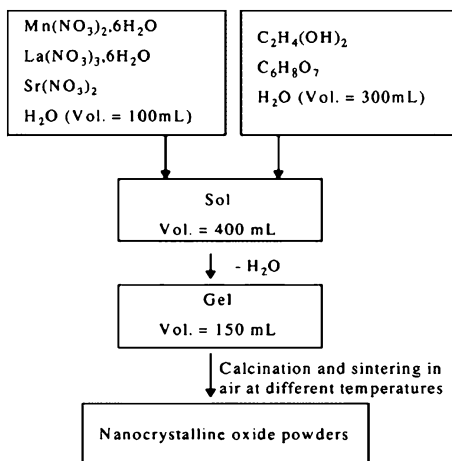


of 10 nm. The powders calcined at lower temperatures showed better sinterability and higher ionic conductivity ($\sim 2.21 \times 10^{-2} \text{ S cm}^{-1}$ at 700°C in air).

2.2.2 Cathode Materials

Sol-gel process has been widely used for synthesis of cathode materials, such as perovskite LSM [22], $(\text{Pr}_{0.7}\text{Ca}_{0.3})_{0.9}\text{MnO}_{3-\delta}$ [23], Fe-doped LSM [24], LSCF [25, 26], $\text{Pr}_{1-x}\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [27], La, Pr, Sm and/or Ba co-doped $\text{Ln}_{0.58}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ [28, 29], Sc doped SrCoO_3 [30], BSCF [31], $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{3-\delta}$ [32]; layered perovskite oxide of $\text{PrBaCo}_2\text{O}_{5+\delta}$ [33], $\text{PrBaCuCoO}_{5+\delta}$ [34], $\text{GdBaCo}_2\text{O}_{5+\delta}$ [35], and K_2NiF_4 type cathode materials $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ [36], $\text{La}_{2-x}\text{NiO}_{4+\delta}$ [37] etc. In order to reduce interfacial polarization resistance, an important factor to consider is the grain size of the porous cathode. The TPBs can be increased by decreasing grain size or increasing the surface to volume ratio. Sol-gel process has been studied for the preparation of highly homogeneous and fine cathode powders [38, 39].

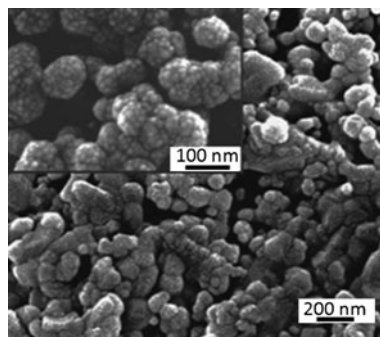
Fig. 2.9 A flow chart illustrating the processing procedure for LSMx powders preparation [22]



LSM is known to be a classical cathode material for SOFCs based on yttria-stabilized zirconia electrolyte because of its high electrical conductivity, excellent thermal, chemical stability and compatibility with the zirconia-based electrolyte at the working temperatures. Shown in flow chart of Fig. 2.9 is a typical sol-gel process for LSM powders [22]. In this process, the $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Sr}(\text{NO}_3)_2$ precursors were dissolved into water. Ethylene glycol and citric acid were used as polymerization/complexation agents, respectively. The stable solution was then heated on a thermal plate, where polymerization occurs in the liquid solution and leads to a homogeneous sol. When the sol is further heated to remove the excess solvent, an intermediate resin is formed. Calcination of the resin at 400°C in air was performed before final sintering at various temperatures ($600\text{--}1,000^\circ\text{C}$). LSM powder has a cubic crystalline structure with particle sizes as small as 40 nm.

Recently, Zhou et al. [40] developed a simple in situ sol-gel derived carbon templating process to synthesize nano-sized $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM). These perovskite oxides were prepared using an EDTA-citrate complexing process to facilitate homogeneous mixing of the metal ions in the molecule level. After calcination of the dried gel under a reducing condition at high temperatures, perovskite oxide and carbon particles were formed simultaneously, producing nano-sized LSCF-carbon and LSM-carbon composites with a grain size of 20–30 nm. Further calcination of the obtained composites in air removes the carbon, resulting in nano-sized LSCF and LSM with a crystalline size of 14 nm, which is smaller than that prepared by the calcination of the solid precursor in air directly (18–22 nm). Such a decrease in crystalline size of perovskite via the indirect calcination process was ascribed to the suppressing effect of carbon in the grain growth of perovskite. Furthermore, when the in situ created carbon was used as a template for pore forming, a highly porous microstructure was obtained. Figure 2.10 shows the typical surface morphology (SEM image) of a sintered pellet [40] with porosity of $\sim 75\%$, as determined by the

Fig. 2.10 Typical surface morphologies of a porous LSCF pellet prepared using the in situ carbon templating process after firing at 1,000°C in air for 5 h [40]



Archimedes method, which is much higher than those obtained from other processes (30–40%). The pores size with irregular pore shape was varied from several μm to nm while the particle size was in the range of 10–20 nm. The high porosity and high surface area make this in situ carbon templating process very promising for the preparation of porous electrode and catalysts for chemical and energy transformation applications.

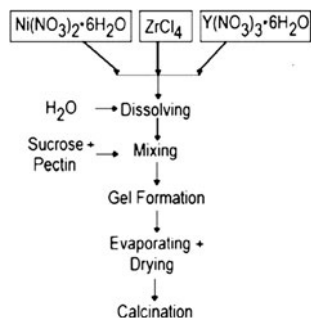
2.2.3 Anode and Interconnect Materials

Traditionally anode materials are binary mixtures of nickel (Ni) and yttria-stabilized zirconia (YSZ) particles with a porosity of above $\sim 30\%$. Such cermets meet all of the requirements for the anode: the interconnecting Ni network acts as a good catalyst for the electrochemical oxidation of hydrogen and provides an excellent conduction path for electrons released from the electrochemical oxidation of hydrogen; the interconnecting electrolyte material network provides a path for the oxygen ions from the electrolyte and also acts as a constraint for the growth and coalescence of nickel particles so that the fine nickel network could be maintained after long-term operation at elevated temperatures. The performance of the anode, in terms of minimal electrode polarization loss and minimal degradation during operation, depends strongly on its microstructure, and therefore on the precursor powders [41, 42]. It is important that both an ionic conducting network is formed by the YSZ particles and an electronically conducting one is formed by the Ni particles, and that the TPB between the two networks and the gas-phase is long. Furthermore, the relative size of the particles is important, the YSZ particles need to be much smaller than the Ni particles to minimize degradation due to Ni-particle sintering and coarsening during operation [41, 43].

- Synthesis of NiO–YSZ anode powders

The standard way of producing the anode precursor powder mixture is to produce YSZ and NiO particles separately and mix them in a mill [44]. However,

Fig. 2.11 A flow chart illustrating the preparation of samples [41]



it would be advantageous to produce the powder mixture in one single processing step via a sol-gel process (Fig. 2.11) because the mixing of species occurs on the atomic scale [41], Zirconium tetrachloride ($ZrCl_4$), yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$), and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) were used as precursors. The obtained xerogel is then calcined to obtain NiO/YSZ powder. During calcination this polymeric metal ion complex is decomposed into CO_2 and H_2O , and their escape from the reaction mixture prevents agglomeration by ensuring that the mixture remains porous. Thus fine particles, which only moderately agglomerated, are formed as the final powder. The Fig. 2.12 illustrated that the agglomerates of NiO/YSZ samples are quite similar in all final powders with different NiO/YSZ ratios. The mean particle sizes of the powders ranging from 28 to 31 nm and a well-crystallized NiO and YSZ powder mixture is formed even for the samples calcined at $800^\circ C$, as indicated by XRD analysis.

- Synthesis of LSCM anode powders

Significant effort has been devoted to the development of anode catalysts for SOFCs run on carbon-containing fuels [45, 46]. For example, $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) perovskite oxide exhibited excellent redox stability and catalytic activity in both methane and hydrogen SOFCs [47–49]. LSCM powders were prepared using a sol-gel combustion method [50]. $La(NO_3)_3$, $Sr(NO_3)_2$, $Cr(NO_3)_3 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ salts were first dissolved in deionized water. Then citric acid was added as a chelating agent. After being heated on a hot plate to evaporate water to become dry gel, the resulting powder was calcined at $1,000^\circ C$ to prepare LSCM powders. The XRD pattern showed that pure LSCM perovskite oxide was obtained and the TEM image (Fig. 2.13) showed that the average particle size was about 200 nm. Thus, when compared to the powders derived from a solid-state reaction method, the LSCM powders derived from the sol-gel combustion method at a relatively low calcination temperature had uniform morphology [51].

- Synthesis of LMC anode powders

Magnesium doped lanthanum chromate ($La_xMg_{1-x}CrO_3$) is considered as interconnect material for SOFC applications. The nano powder of this interconnect

Fig. 2.12 TEM images of the B samples calcined at 800 and 1,000°C [41]

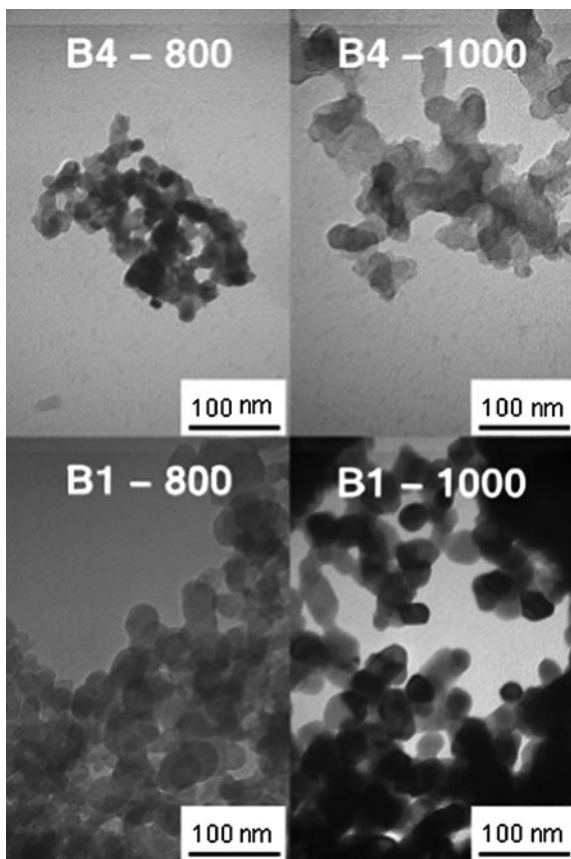
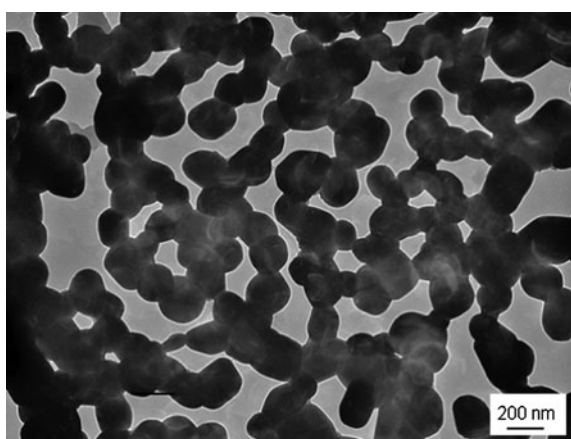


Fig. 2.13 TEM image of as-prepared LSCM powders [50]



material was prepared using sol-gel process [52]. The precursors were $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the chelating agent was citric acid and the dispersant agent was ethylene glycol. The SEM images reveal that the particle size of $\text{La}_{0.7}\text{Mg}_{0.3}\text{CrO}_3$ powders achieved by sol-gel process is in the range of $\sim 50\text{--}200$ nm. The powders prepared using $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is more cost-effective than using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ since it also acts as fuel. The TGA plots depict that there is no further weight loss after reaching 350 and 575°C for the LMC gels prepared using AD and Cr-N, respectively, an indication of complete combustion of the precursors and formation of oxide phases.

2.3 Fabrication of SOFC Components Using a Sol-Gel Process

The performance of a SOFC depends strongly on the microstructures of its components. For a single cell, each component should have specific microstructures (in addition to the requirements on intrinsic properties of the materials) in order to achieve high efficiency: a porous, gas-permeable electrode (cathode and anode) with high specific surface area to increase the TPB length and thin, gas-tight electrolyte membrane to reduce the ohmic resistance. Sol-gel process has unique advantages for the fabrication of this kind of ceramic films because it does not require costly equipment, allows a lower processing temperature, and can control microstructure and chemical composition easily. The sol-gel process has been used not only for fabrication of thin electrolyte membranes but also for modification of electrode surfaces and electrode/electrolyte interfaces to improve the microstructure and electrochemical performance of cell components. More details of the sol-gel process for fabrication of cell components are described in the following sections.

2.3.1 Electrolyte

For efficient operation of a SOFC at low or intermediate temperatures, the electrolyte must be used in a thin-film form to reduce the ohmic losses. Further, the electrolyte membranes must be continuous and crack-free in order to prevent gas leakage, and must rest between two porous electrodes through which gases can pass freely to or away from the active sites for electrochemical reactions near the electrode–electrolyte interface. Thus, the fabrication of defect-free, dense electrolyte films on porous electrodes assumes significant importance.

There are a number of techniques for depositing thin films of ceramics on dense and porous substrates, including chemical vapor deposition, electrochemical vapor deposition, and various sputtering processes using ion beam, magnetron, electron beam, and so forth [53]. The drawbacks of these physical deposition techniques

include difficulties in obtaining good compositional homogeneity [54, 55] and high costs due to the requirements of vacuum conditions [55]. Sol-gel techniques, on the other hand, overcome these problems and offer many additional advantages [56, 57]. Certainly one of the most technologically important aspects of sol-gel process is that, prior to gelation, the fluid sol or solution is ideal for preparing thin films by such common processes as dipping, spinning, or spraying. Both dense and porous structures can be easily tailored through the precursors and there is no limitation on the shape or size of the substrate surface. However, the most important advantage of sol-gel process over conventional coating methods is the ability to control precisely the microstructure (pore volume, pore size, and surface area) and composition (stoichiometry) of the film [58–60]. The disadvantages of sol-gel process include the cost of the raw materials (especially alkoxide precursors), shrinkage that accompanies drying and sintering, and processing times. Thin-film coating is one of the well-known applications of sol-gel process which benefits from most of the advantages of sol-gel process just cited while avoiding these disadvantages [58, 61].

Starting from a molecular precursor, the polymeric sol can be prepared by partial hydrolysis of corresponding metal alkoxide. If the rate of hydrolysis or condensation is very fast, then some kinds of organic acids, beta-dicarbonyls, and alkanolamines have been used as chelating agent in sol-gel processes to control the extent and direction of the hydrolysis-condensation reaction by forming a strong complex with alkoxide. For this reason, extremely thin, dense, and well-defined electrolyte films can be derived from sol-gel coatings on a porous electrode to form an electrode supported SOFC and the thickness can be controlled by the number of applied coatings. Purity and uniformity can also be controlled by the solution chemistry of the sol-gel process.

YSZ films with different thicknesses, such as ultra-thin film (0.1–10 μm) [53–56] and thick YSZ (8–100 μm) films [58–60], have been successfully deposited onto dense or porous electrode using a sol-gel process. Since the internal resistance of the cell decreased with decreasing the electrolyte thickness, high performance of 477 mW/cm^2 at 600°C and 684 mW/cm^2 at 800°C were achieved in an anode supported SOFC, which consists of a Ni-YSZ anode, a 4YSZ electrolyte (0.5 μm), and a Pt/Pd cathode Cathode [62]. Other electrolyte materials, such as SDC [61], BCG [63], zirconia films doped with Sc_2O_3 and Al_2O_3 (85 mol.% ZrO_2 -11 mol.% Sc_2O_3 -4 mol.% Al_2O_3) [64], have also been successfully fabricated via a sol-gel process.

Sol-gel process was also used for preparing an electronic blocking layer, such as thin YSZ layer, on doped ceria electrolyte to enhance the OCV [65–67]. Kim et al. [67] successfully fabricated 2 μm thick YSZ layer on YDC electrolyte surface using a sol-gel spin coating method. The open circuit voltage (OCV) of a single cell based on this composite electrolyte was ~ 0.5 V higher than that for an uncoated YDC electrolyte at temperatures from 700 to 1,050°C. The maximum power density of the single cell with the bi-layer electrolyte was 122 mW/cm^2 at 800°C, comparable to that of an YSZ single cell with the same electrolyte thickness at 1,000°C (~ 144 mW/cm^2).