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Designing Perovskite Oxides for Solid Oxide Fuel Cells

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Abstract

Perovskite-type oxides with the general formula ABO_3 have been widely studied and are utilized in a large range of applications due to their tremendous versatility. In particular, the high stability of the perovskite structure compared to other crystal arrangements and its ability, given the correct selection of A and B cations, to maintain a large oxygen vacancy concentration makes it a good candidate as electrode in solid oxide fuel cell (SOFC) applications. Utilizing this novel structure allows the engineering of advanced, effective electrolytes for such devices. This review details the development of current state-of-the-art perovskite-type oxides for solid oxide fuel cell (SOFC) applications.

Keywords: SOFC, Nanostructure

1. Introduction

The development of new energy technologies has become important with the present situation of increasing energy demand, rising energy prices, and reinforcement of countermeasures for global warming and its detrimental climatological, ecological, and sociological effects [1]. The supplies of fossil fuels are constantly decreasing and some believe that we have reached the peak for oil production. A reappearing problem in the energy field is the conversion from available to usable form. This concerns the conversion of chemical energy in the form of fossil resources and derivatives, such as hydrogen and alcohols, into electrical energy. It has become increasingly important to reduce the losses associated with the applied conversion techniques partly due to industrialization and technological progress. Traditional conversion to electrical energy is by gas turbine, steam turbine, or reciprocating engine driving a generator, where the

Carnot cycle sets a limit to the efficiency [2]. A fuel cell provides an alternative, whereby electrical energy can be made available with small losses, and no Carnot limit [3]. The effluents are in principle water, heat and CO₂ if the fuel is clean.

The energy situation has caused a push for sustainable energy technologies. Here, fuel cells play an important role in the renewable energy sector because of their highly efficient energy conversion and their especially high reliability. During the last decades, fuel cells have attracted much attention because of their potential for producing electricity more efficiently than conventional power generation like heat engines, which normally are limited by the Carnot cycle. The discovery of the fuel cell is ascribed to Sir William Grove (1839), demonstrating the reversibility of electrolytic water separation [4]. In 1899, Nernst contributed by demonstrating that certain oxides attained remarkably high electrical conductivity by doping with other oxides [5]. In the late twentieth century, the development accelerated and the interest in fuel cell technology increased. Today, there are five different types of fuel cells, all named after their electrolyte materials:

- Alkaline fuel cells (AFC)
- Polymer exchange membrane fuel cells (PEMFC)
- Phosphoric acid fuel cells (PAFC)
- Molten carbonate fuel cells (MCFC)
- Solid oxide fuel cells (SOFC)

Depending on the electrolyte, each fuel cell has certain characteristics such as operation temperature, electric efficiency, and demands for fuel composition (Table 1).

Fuel Cell	AFC	PEMFC	PAFC	MCFC	SOFC
Electrolyte	KOH	Polymer	H ₃ PO ₄	Li ₂ CO ₃ +K ₂ CO ₃	ZrO ₂ +Y ₂ O ₃
Charge carrier	OH ⁻	H ⁺	H ⁺	CO ₃ ²⁻	O ²⁻
Fuel	Pure H ₂	Pure H ₂	Co-free H ₂	H ₂ , CO, CH ₄	H ₂ , CO, CH ₄ , NH ₃
T _{oper} (°C)	65%–220	60%–130	150%–220	650	700%–1000
Electrical efficiency	45%–60%	40%–60%	35%–40%	45%–60%	45%–60%

Table 1. Most important characteristics for different types of fuel cells

Low-temperature fuel cells (AFC, SPFC, and PAFC) have potential for the propulsion of cars, where a short heating time is needed and the efficiency has to be compared with about 20% for a combustion engine, whereas high-temperature fuel cells (MCFC and SOFC) are suitable for continuous power and heat production, where the cell temperature can be maintained. The high-temperature fuel cells have higher efficiency and are more tolerant to the choice of fuel compared to the low-temperature fuel cells [3].

2. What is a solid oxide fuel cell?

Solid oxide fuel cells (SOFC) are electrochemical devices which convert chemical energy directly into electrical energy with high efficiency and low environmental impact and are expected to become the emerging technology for stationary power production [6].

SOFCs are considered by many researchers to be the most suitable for generating electricity from hydrocarbons because of their simplicity, efficiency, and ability to tolerate some degree of impurities. There are many advantages of SOFC with respect to other fuel cells. Some of the main advantages are [7]:

- The highest efficiencies of all fuel cells (50–60%)
- A potential long-life expectancy of more than 40,000–80,000 h
- Constructed from readily obtainable ceramic materials
- Few problems with electrolyte management
- High-grade waste heat is produced, for combined heat and power (CHP) applications increasing overall efficiencies to over 80%, and
- Internal reforming of hydrocarbon fuels is possible

However, there are some drawbacks related to the choice of materials in relation to costs. There are roughly two design types, tubular and flat plate. For the tubular cell, the material problems are less, but fabrication costs are high, whereas for the flat plate design, fabrication costs are less but more materials problems arise [8].

The operating principle of the solid oxide fuel cells is illustrated in Figure 1.

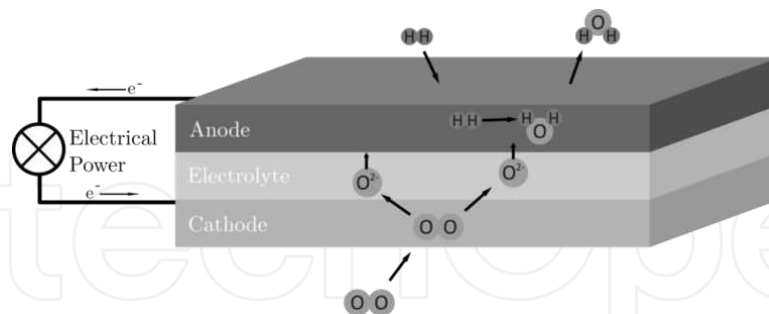


Figure 1. Sketch of solid oxide fuel cell operated on hydrogen and air.

SOFCs consist of three layers of functional materials: the anode, the electrolyte and the cathode. The anode is where the oxidation reaction takes place, and the cathode is where the reduction takes place. The cathode is fed with air or oxygen while the anode is fed with fuel gas. At the cathode, oxygen molecules are reduced to oxygen ions ($\frac{1}{2} \text{O}_2 (\text{g}) + 2 \text{e}^- \rightarrow \text{O}^{2-}$). The oxygen ions are conducted through the electrolyte to the anode. At the anode, oxygen ions oxidize the fuel gas and forms water and carbon dioxide, while the resulting free electrons are transported via the external circuit back to the cathode ($\text{H}_2 (\text{g}) + \text{O}^{2-} \rightarrow \text{H}_2\text{O} (\text{g}) + 2 \text{e}^-$).

To limit cathode overpotential, the traditional SOFC with yttria-stabilized zirconia (YSZ) electrolyte and strontium-doped lanthanum manganite (LSM) cathodes operate at relatively high temperatures (800°C–1000°C). These high temperatures encourage cell degradation—increasing cell, stack, and system maintenance. In addition, even higher temperatures are required for fabrication, encouraging electrode–electrolyte reactions, often forming undesirable, insulating secondary phases and consequently increasing cell resistance. Lowering the operating and fabrication temperature to 400°C–800°C could reduce both cell degradation and manufacturing costs. Cells which operate in this temperature range are known as intermediate temperature SOFCs (IT-SOFC). The advancement of this technology, limited by the high temperatures required, can be overcome by reducing operating temperatures, thus increasing theoretical efficiency. In order to operate efficiently at these reduced temperatures and to develop the next generation of hydrogen-related energy devices, new materials are required and the utilized processing routes must be optimized [6,9].

Among the new generation of materials, those with ABO_3 -type perovskite structures stand out due to their great versatility. Through the correct choice of A and B site cations and the introduction of dopants, it is possible to obtain a large variety of materials with a wide range of properties and applications. This chapter will cover a selection of key materials developed for use in SOFC devices, their advantages and disadvantages and the optimization strategies published so far.

3. Evolution of perovskite-type structured materials as electrodes in SOFCs

The general formula unit of the perovskite is ABO_3 , where A is a larger cation with a coordination number of 12 and B is a smaller cation with a coordination number of 6 (Figure 2). The large A cations can be rare earth, alkaline earth, alkali, and others [10] whereas the smaller B site accommodates many transition metals. These elements are typically the source of electronic conductivity. Cations of a rather wide range of ionic radii and valence are able to enter one or another site in the perovskite structure, exhibiting versatile physical and chemical properties and, thus, high concentrations of oxide vacancies and high ionic conductivity may be achieved [11]. This ability to hold a large content of oxygen vacancies makes them good candidates as electrodes in SOFC applications.

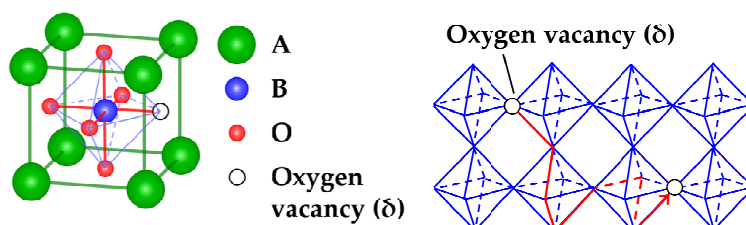


Figure 2. Atomic structure and oxygen transport in mixed conducting perovskites. On the left, the positions of the ions in a cubic structure. On the right, corner-sharing BO_6 octahedra and oxygen vacancy migration path.

The B cations are located in the corners of the cube and the A cation occupies the center. The oxygen is placed at the centers of the twelve cube edges, giving corner-shared strings of BO_6 octahedra. The A cation has the same size as the oxide ion, while the B cation is smaller. Depending on the type of cations, it is possible to create oxygen vacancies in the structure. These oxygen vacancies move along the structure giving rise to ionic conduction (Figure 2).

The composition and the microstructure of electrode materials greatly influence the performance of SOFCs. The high temperature and the reducing or oxidizing atmospheres limit the choice of these materials.

3.1. Cathode materials

One of the major research efforts in SOFC technology is directed towards decreasing the cell operating temperature. The best performance of the electrolyte, anode, and cathode materials typically is seen at an operating temperature above 800°C . This makes the use of expensive alloys as interconnectors and current collectors necessary. Decreasing the operating temperature would make it possible to use soft steel alloys with a remarkable decrease of the initial cost of the device. It is necessary, however, to develop new materials which exhibit good performance at lower temperatures in terms of conductivity, and chemical and mechanical compatibility. The widely used materials also need to be optimized in order to minimize technical problems at elevated temperatures. These problems are often associated with a mismatch between the thermal expansion coefficients of the electrolyte and cathode or as a consequence of oxygen loss from the cathode material.

The role of the cathode as the active site for the electrochemical reduction of oxygen is an important parameter to take into account in the material's design. SOFCs operate at high temperatures for long periods of time and, therefore, some requirements must be fulfilled [12]: (i) high electronic conductivity ($\sigma > 100 \text{ S cm}^{-1}$); (ii) a thermal expansion coefficient (TEC) match with other SOFC components; (iii) chemical compatibility with the electrolyte and interconnect materials; (iv) adequate porosity to allow mass transport of oxygen; (v) high thermal stability; (vi) high catalytic activity for the oxygen reduction reaction (ORR); and (vii) low cost.

The cathodic reaction is quite complex and comprises a number of single steps such as diffusion, adsorption, dissociation, ionization, and finally, incorporation of oxygen into the electrolyte [13]. Oxygen molecules adsorb on the surface where they form partially reduced ionic/atomic species. These electroactive species must be transported along surfaces, interfaces, or inside the bulk of the electrode material to the electrolyte, where they are fully incorporated as O^{2-} .

The cathode materials can be classified into two groups: mainly, electronic conductors (with poor ionic conduction) and mixed ionic-electronic conductors (MIECs). Depending on the type of material, the conduction mechanism in the cathode will be different (Figure 3). In a poor ionic conductor, adsorption, dissociation, and diffusion of oxygen between the gas phase, electrode, and electrolyte [14] occurs through the triple phase boundary (TPB). In the MIECs, the conduction mechanism also occurs through the double phase boundary (DPB) [15,16]. The

mixed conducting nature of the oxide ensures that electrochemical reactions occur at the MIEC/gas double phase boundary (DPB).

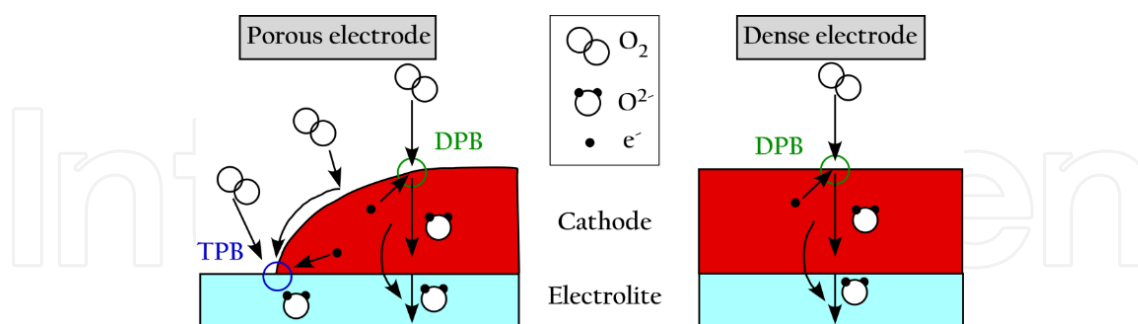


Figure 3. Schematic representation of conduction mechanisms (DPB: double phase boundary; TPB: triple phase boundary).

The deposition technique is also an important parameter which influences the electrochemical behaviour. Conduction in porous electrodes occurs through the three-phase boundary (TPB), whereas in MIECs, this also occurs through the DPB. In the case of dense electrodes, there is no direct contact between the cathode, electrolyte, and gas (hence, no TPB conduction exists). In this case, the oxygen reduction reaction occurs anywhere on the cathode surface, forming oxide anions which diffuse into the bulk of the electrode material towards the electrolyte. The material must present mixed ionic and electronic conduction [17].

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC) have been widely used as cathodes in SOFC. LSM has high electronic conductivity due to the introduction of Sr^{2+} on the La^{3+} site which will be charge-compensated by the Mn (Mn^{3+} – Mn^{4+}), making it a good cathode at high temperatures (1000°C). At intermediate temperatures (500°C – 700°C), however, a large increase in the cell overpotential (from <1 to 2000 ohm cm^2) is observed, which hinders its use as a cathode [18]. One of the main limitations of LSM is its low ionic conductivity ($\sim 10^{-7} \text{ S/cm}$ at 900°C), which is related to the Mn charge compensation where oxygen vacancies are not generated. The ease with which oxygen vacancies form is strongly influenced by the Sr content [19]. The influence of the cation vacancy on the transport properties of these materials has led to a study of the defects in these materials, such as LMO, and the effect of substitutions on the lanthanide site [20]. DeSouza et al. found that in both rhombic and rhombohedral structures, nonstoichiometry leads to the formation of vacancies on both cation positions, presenting a tendency toward the formation of vacancies [21]. These details are essential in understanding the behaviour of the materials and the degradation processes which can lead to the formation of insulating phases affecting the cathode performance. To obtain better performance from dense or porous LSM on YSZ electrolytes, a two-layer cathode is necessary—a 0.3 mm porous layer and in between a dense film of YSZ ($\sim 1 \text{ }\mu\text{m}$) [22]. This structure combines the best properties of both types of cathode in a single process and with more favorable properties than when using only the porous cathode.

Several authors have investigated other rare earths in the lanthanide position such as Pr, Sm, or Nd in order to improve the performance of manganites and avoid problems associated with

the formation of the pyrochlore-insulating phases at the LSM/YSZ interface [23]. By substituting La with Sm, new materials with lower energetic barriers for adsorption and diffusion of oxygen species have been obtained [24]. In addition, they present excellent compatibility with YSZ and electronic conductivity well above that required in a SOFC (100 S/cm) [25]. The most promising electrode materials are $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ and $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ in terms of thermal expansion coefficient, reactivity, and conductivity [26]. The study of the compatibility of $(\text{Ln}, \text{Sr})\text{MnO}_{3-\delta}$ with electrolytes has been limited to YSZ due to its widespread use. The performance of $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ with gadolinia-doped ceria electrolyte (most suitable for use in IT-SOFC), however, revealed no reaction between the components at the interface after prolonged high-temperature treatments [27]. The same authors indicated that $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3-\delta}$ shows very promising properties with an electrical conductivity of 226 S/cm at 500°C [28]. Most studies on manganites have focused on doping the lanthanide site with Sr. In terms of chemical compatibility and electrical conductivity, however, the use of calcium as a dopant can offer very promising results, as in the case of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$, which does not react with the electrolyte and has a maximum conductivity of 266 S/cm [29].

While looking for alternative materials to manganites, lanthanum cobaltites doped with bivalent metals such as Ca or Sr emerged [30]. These materials exhibit high conductivity values when 30% or 40% of Ca or Sr are added, respectively. In addition, the substitution of La by other lanthanides such as Pr and Sm has also lead to promising results. Despite the good results that these cobaltites exhibit, other drawbacks such as their high TECs and the appearance of secondary phases, limit their application.

In order to use the beneficial properties of these cobaltites, these materials are doped with Fe. Although, the addition of Fe promotes the decrease of the conductivity of the orthoferrites, lower TEC values are also achieved. Among these cobalto-ferrites, the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ material stands out for SOFC cathode application. Shao et al. reported excellent performance at intermediate temperatures, proving that the orthoferrites are an interesting alternative for IT-SOFCs [30]. At the same time, the use of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ has been widely investigated [31–33]. These cobalt-based cathodes exhibit higher electrocatalytic performances than those of the conventional LSM cathodes. Unfortunately, they have high TEC, high cost of cobalt, and easy evaporation and reduction of cobalt [34,35].

Rare earth orthoferrites with perovskite-type structure are interesting materials for many electronic applications because of their mixed conductivity [36,37]. A site-doped rare earth orthoferrite compounds have been studied as candidates to replace manganites and cobaltite cathodes due to its high catalytic activity and mixed ionic and electronic conductivities at reduced temperature ($\sigma_{\text{total}} = 100 \text{ S/cm}$ at 600°C–800°C) [35,38]. Lanthanum is a common element and key component of most SOFC, where several of its oxides provide the necessary electronic conductivity and high catalytic activity for oxygen reduction and some, in addition, combine ionic and electronic conductivity [39]. The choice of using Pr as the rare earth element is due to its peculiarity to show 3+ and 4+ oxidation states, which might induce interesting electrical properties [35]. Some of the Pr-doped orthoferrites display good performance as cathode materials in high-temperature solid oxide fuel cells because of their mixed, electronic and ionic, conductivity [40]. In particular, $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ presents

low electrical resistivity and good oxygen ion conductivity [41]. Fe-based perovskite oxides have also attracted much attention as possible alternatives to cobaltites due to their interesting transport properties. When the Fe fraction is higher than 0.5, the materials exhibit its highest electronic conductivity as observed for the $\text{LaNi}_{0.2}\text{Fe}_{0.8}\text{O}_3$ phase in which a conductivity of 135 S/cm, at 800°C, was obtained [42,43]. Calcium is another effective dopant for the A site, with low cost. For example, $\text{Pr}_{0.4}\text{Ca}_{0.6}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ material exhibits an ASR value of 0.09 ohm cm^2 at 850°C [35]. Taking into account the low ASR value and the electrical conductivity of this cathode (at temperatures above 600°C, which is over 100 S/cm), this material is a promising cathode for IT-SOFC applications. $\text{Pr}_{1-x}\text{M}_x\text{MnO}_3$ (M = Ca, Sr) have also been studied where Ca-doped PrMnO_3 phases exhibit better performance than those doped with Sr. Ca-doped materials show higher electrical conductivity, lower cathodic overpotential and more similar thermal expansion coefficient [44]. Moreover, calcium could be a good candidate because of the similarity of its ionic radius with La^{3+} giving rise to higher stability than that of strontium-substituted phases [45].

While a large number of studies concerning cathode materials report the presence of secondary phases, they are often left unidentified [46] and are typically considered undesirable and associated with insulating phases that give rise to low conductivity values and poor performance [47]. Conversely, actual research in SOFC cathodes is focused on the development of composite materials, as the inherent requirements are so wide-ranging that no single material is capable of fulfilling every aspect [48]. The creation of composite cathodes is a good way to enhance the cathodic performance. They are composed of a solid electrolyte and an electronic conducting electrocatalytic material as in the $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ /samarium-doped ceria (SDC) symmetrical cells reported in a previous work [49]. The investigated composite cathodes include $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC)- $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF)-SDC, LSCF- $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ (CGO), and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (BSCF)-SDC, all of which exhibit low polarization resistance at 600°C [50,51]. The electrochemical performance of these cathodes is generally governed by triple phase boundary (TPB) kinetics, mass transport, and ohmic drop. The primary disadvantages of utilizing composite materials arise from the need for two independent materials; this increases both production complexity and the possibility of undesirable phases forming through inter-reaction of the component phases. Recently, the $\text{La}_{1-x}\text{Ca}_x\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LCFN) system has been proposed and applied as a cathode featuring highly competitive performance [48]. Contrary to expectations, the formation of perovskite brown-millerite pseudo-composites resulted in a clear enhancement of the electrochemical performance and excellent thermomechanical compatibility with conventional electrolytes. Furthermore, new insights are gained into material surface properties controlling oxygen reduction processes.

The development of double perovskite materials such as $\text{GdBaCo}_2\text{O}_{5+x}$ [52], $\text{PrBaCo}_2\text{O}_{5+x}$ [53], $\text{SmBaCo}_2\text{O}_{5+\delta}$ [54], or $\text{NdBaCo}_2\text{O}_{5+\delta}$ [55] have also been investigated for IT-SOFCs. Their ORR activity is higher than many single perovskites [56]. They present high thermal expansion coefficients, however, which make them incompatible with the electrolytes developed so far. Table 2 summarizes the most widely study cathode materials for SOFC.

Composition	TEC (K ⁻¹)	Resistivity		Conductivity		Diffusion		Ref.
		ASR (Ω cm ²)	T (°C)	σ (S/cm)	T (°C)	k* (cm/s)	D* (cm ² /s)	
La _{1-x} Sr _x MnO ₃	11.6×10 ⁻⁶	0.18	750	180	800	—	3 × 10 ⁻⁹	[57,58]
La _{1-x} Sr _x FeO _{3-δ}	12.1 × 10 ⁻⁶	0.1	800	125	800	1 × 10 ⁻⁵	6 × 10 ⁻⁷	[59–61]
La _{1-x} Sr _x Fe _{0.8} Co _{0.2} O _{3-δ}	15.4 × 10 ⁻⁶	0.34	750	404	550	6 × 10 ⁻⁶	3 × 10 ⁻⁵	[62–65]
La _{1-x} Sr _x Fe _{0.8} Ni _{0.2} O ₃	15.6 × 10 ⁻⁶	0.16	700	435	800	—	—	[66,67]
La _{0.6} Ca _{0.4} Fe _{0.8} Ni _{0.2} O ₃	11 × 10 ⁻⁶	0.10	800	260	600	—	—	[6]
La _{0.6} Sr _{0.4} Fe _{0.8} Cu _{0.2} O ₃	14.6 × 10 ⁻⁶	0.138	750	135	275	---	---	[68]
Pr _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O ₃	19.6 × 10 ⁻⁶	0.046	800	1040	300	---	9.4 × 10 ⁻⁵	[69]
LaNi _{0.6} Fe _{0.4} O ₃	11.4 × 10 ⁻⁶	0.018	800	600	600	---	2 × 10 ⁻⁷	[70,71]
Pr _{1-x} Sr _x Co _{0.2} Fe _{0.8} O ₃	14 × 10 ⁻⁶	0.454	600	2190	600	---	---	[72,73]
Sm _{0.5} Sr _{0.5} CoO _{3-δ}	22.8 × 10 ⁻⁶	0.20	600	1000	850	6 × 10 ⁻⁵	8.6 × 10 ⁻⁷	[74,75]
Ba _{0.5} Sr _{0.5} Zn _{0.2} Fe _{0.8} O _{3-δ}	16.5 × 10 ⁻⁶	0.48	650	9.4	590	---	---	[76]
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O ₃	19.9 × 10 ⁻⁶	0.15	600	30	600	---	7.3 × 10 ⁻⁵	[77,78]
PrBaCo ₂ O _{5+δ}	20 × 10 ⁻⁶	0.11	600	2000	150	1 × 10 ⁻³	1 × 10 ⁻⁵	[56,79,80]
PrBaCoFeO _{5+δ}	21 × 10 ⁻⁶	0.049	800	321	350	---	---	[81]
NdBaCoFeO _{5+δ}	19.5 × 10 ⁻⁶	0.062	800	172	350	---	---	[81]
GdBaCo ₂ O _{5+δ}	20.1 × 10 ⁻⁶	0.15	750	512	500	2 × 10 ⁻⁶	3 × 10 ⁻⁷	[82,83]
SmBaCo ₂ O _{5+δ}	16 × 10 ⁻⁶	0.098	750	815	500	---	---	[84]
SmBa _{0.5} Sr _{0.5} Cu ₂ O _{5+δ}	14.1 × 10 ⁻⁶	0.25	650	277.7	485	---	---	[85]
YBaCo ₂ O _{5+δ}	16.3 × 10 ⁻⁶	0.11	700	315	325	---	---	[86]

Table 2. The main properties of SOFC cathodes with both single and double perovskite structures

In recent years, advancements in cathode material properties have been made where a variety of perovskite oxides with a wide range of properties have been investigated. There are still, however, many chemistries to investigate which may yield superior performance in the future.

3.2. Anode materials

The requirements for a SOFC anode are quite similar to those for cathodes (changing the oxidizing atmosphere by a reducing environment), including: (i) proper electronic conductivity; (ii) thermomechanical and chemical compatibility with the electrolyte and interconnect materials; (iii) adequate porosity to allow gas transport to the reaction sites; and (iv) low cost. High ionic and electronic conductivity over a wide pO₂ range and high surface oxygen exchange kinetics and good catalytic properties for the anode reactions are also desirable properties for a good anode material. Nickel-YSZ cermet has been widely used in the SOFC

anode. This material fulfills most requirements: Ni exhibits good catalytic activity for the dissociation of hydrogen while remaining stable at operating conditions and YSZ provides structural support for the Ni particles and inhibits their coarsening while matching the thermal expansion properties of the rest of the cell components [87]. Areas where this anode composition is lacking, however, include poor redox stability, low sulphur and carbon deposition tolerance when hydrocarbon fuels are used, and the tendency for nickel to agglomerate after prolonged operation [88]. In the search for alternative anode materials that are capable of withstanding sulphur contamination and carbon deposition, oxides with perovskite structure have drawn considerable attention [87]. Several authors have studied anode materials based on the perovskite structure as very promising alternatives [89,90]. Among the numerous materials with perovskite structure, SrTiO_3 -type titanates have received a great deal of attention due to their high stability under reducing atmospheres and high temperatures [91]. This material, however, suffers from poor electronic conductivity, but this can be overcome through the introduction of appropriate dopants in the structure [92]. Marina et al. studied the effect of La doping in SrTiO_3 with a clear effect seen from the substitution of the Sr and the oxygen partial pressure on the total electrical conductivity with values as high as 500 S/cm at 500°C for the $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ phase [93]. Furthermore, doping with Sr in the A site and Nb in the B site, it was possible to increase the conductivity to 10 S/cm; however, these materials exhibited a poor ionic conductivity [94]. Ti has also been substituted by other cations such as Al, Fe, Ga, Mg, Mn, or Sc, affecting significant changes on the redox properties of the material and conductivities [95]. By adding multivalent cations such as Mn or Fe, reduction or oxidation occurs in these cations in preference to or together with Ti, leading to a general decrease in the presence of Ti (III), resulting in a decrease in conductivity [96]. The effect of Co has also been analyzed, observing that after reduction with H_2 , the segregation of Co nanoparticles occurs on the anode surface, which favors the oxidation of the fuel, thus reducing the resistance under anodic polarization [97]. To improve the behaviour of titanates, various dopants have been introduced on the A site (Y, La, Ce) [98,99]. The introduction of Ce^{3+} leads to decomposition into a variety of phases due to its ready oxidation in air. Some Ce-rich phases migrate to the grain boundaries, which result in an increase in the catalytic properties of up to an order of magnitude [100]. It is particularly interesting to note the results obtained by Morales-Ruiz et al., where $(\text{La,Sr})(\text{Ti,M})\text{O}_3$ ($\text{M} = \text{Ga, Mn}$) anodes exhibited comparable performance to those of conventional Ni-YSZ anodes [101]. Recently, AMoO_3 perovskite types ($\text{A} = \text{Ca, Sr, and Ba}$), containing Mo^{4+} ions have received interest for their potential use as anodes [102]. While these materials have high electrical conductivities (10^4 S/cm) they also present problems associated with the diffusion of oxide ions [102]. This limitation can be overcome by doping with other metals such as Fe or Cr on the Mo site [103,104]. Co is another suitable dopant which also creates oxygen vacancies, supplying sufficient ionic transport making a material with excellent catalytic properties for the oxidation of hydrogen [105]. Another alternative is to create composites with materials which have high ionic conductivity [106]. In this regard, the most commonly used materials are $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_2$ (YSZ), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM), and $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_2$ (GDC), which have been traditionally used as electrolytes, facilitating greater thermal, mechanical, and chemical compatibility with the anode composite. From these systems, a new material with the general formula $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ (SFMO) and perovskite-type structure has been developed, which features suitable mixed ionic-electronic conductivity and interesting catalytic activity [107]. It exhibits great stability when H_2 , fuel or natural gas is used

and high tolerance to sulfides [108]. Recently, Sutirakun et al. developed a theoretical model for analyzing the electrochemical oxidation of H_2 on the surface of this material [109]. One strategy for optimizing the material is to increase either the Mo content or add a small amount of active transition metal such as Ni in order to reduce the energy required for the formation of vacancies on the surface of SFMO. The other family of materials which has been widely studied are the chromites ($LaCrO_3$). These materials initially developed as interconnectors for SOFCs, which will be discussed later, because of their high stability in both oxidizing and reducing atmospheres and low tendency to accumulate carbon [110]. Their low catalytic activity, however, makes their use with some fuels such as methane impossible. To solve this problem, the effect of different dopants on the properties of this material (Ca and Sr on the A site and Mg, Mn, Fe, Co, and Ni in the B site) has been studied [111]. $(La, Sr)(Cr, Fe)O_3$ is the best candidate due to its high redox stability, high conductivity, and electrochemical activity [111]. In addition, this material works well as a catalyst for methane [112] and has a thermal expansion coefficient very similar to YSZ and LSGM [113]. Fowler et al. have also studied these materials, finding that the $La_{0.6}Sr_{0.4}Cr_{0.4}Fe_{0.6}O_{3-\delta}$ composition presents the best performance and highest stability [114]. In recent years, a new generation of anode materials with the double perovskite structure, such as Sr_2MgMoO_6 (SMMO) [115], $PrBaM_2O_5$ ($M = Co, Mn$) [116,117], and $La_4SrTi_5O_{17}$ [118] have been developed. These materials have very interesting properties which permit the use of multiple fuels.

4. Perovskite oxides as electrolytes and interconnectors for SOFC

Electrolyte ceramic materials must meet the following requirements: high ionic conductivity and low electronic conductivity; the charge carrier must either be from the oxidizer (O_2) or fuel (H_2), i.e. O^{2-} or protons [119]. To date, SOFC electrolytes are, in most commercial cases, 8 mol % yttria stabilized zirconia (8-YSZ) [120]. This material belongs to the group of fluorite-type solid solutions and up to now is the O^{2-} ion conductor most used as electrolyte material for SOFC due to its high ionic conductivity and thermomechanical stability. Doping ZrO_2 with Y_2O_3 has two main functions. First, to stabilize the cubic, fluorite phase, otherwise only stable at elevated temperatures, and second, to compensate the insertion of the trivalent Y^{3+} ions by oxygen vacancies in the zirconia lattice, giving rise to an enhancement of the oxygen ion conductivity. Generally, yttria-doped zirconia with 8 mol% Y_2O_3 exhibit an ionic conductivity higher than 0.1 S/cm at 1000°C and an electrical conductivity lower than 10^{-4} S/cm [121].

An important aspect to be considered is the chemical stability of the candidate materials at cell operation conditions, presenting high ionic conductivity (>0.1 S/cm) at intermediate temperatures and thermal expansion coefficients similar to the components of the cell [119]. The decrease in operating temperature can lead to an increase in chemical stability and cell lifetime, as well as a reduction in manufacturing costs; however, in the case of YSZ, cell performance decreases at lower temperatures due to the thermally activated ionic conductivity [122].

In order to obtain materials with improved properties at temperatures below 800°C, two families with perovskite type structure: gallates and cerates have been developed [123]. Most studies focus on Sr-doped $LaGaO_3$, but other dopants such as Ba have also been investigated [124]. Phase segregation occurs when Ba is used due to its large size compared to Sr which

forms a mixture of $\text{LaBaGa}_3\text{O}_7$ and LaGaO_3 resulting in poor conductivities [125]. The ionic conductivity of this material can be increased by introducing Mg in the perovskite B site due to the introduction of compensating defects in the structure [126,127]. It has also been shown that the presence of a stoichiometry deficient in Ga may result in an increase in the concentration of oxygen vacancies [128]. In fact, this material is stable in CO-rich atmospheres, which allows its use as an electrolyte in direct coal solid oxide fuel cells (DC-SOFCs) [129]. Another strategy to increase the ionic conductivity of the material is through the production of composites with doped ceria electrolytes [130]. Through this method, it has been possible to optimize conduction through the grain boundaries, resulting in up to 10 times higher conductivity than ceria electrolytes at 500°C. In summary, the cells employing $(\text{La,Sr})(\text{Ga,Mg})\text{O}_{3-\delta}$ electrolytes have high power densities at 800°C, which makes them excellent candidates for IT-SOFC electrolytes [131,132].

The other family of materials with perovskite structures is based on BaZrO_3 and BaCeO_3 , which traditionally have been developed as proton-conducting oxides, especially the cerates [133]. The production method, the temperatures employed in the process and the type and concentration of the dopant will affect proton conduction in the material. The cerates allow the introduction of precious metals such as Pd, which facilitates oxygen mobility, although the best results were obtained by using metal nanoparticles and by decorating the surface of the perovskite which acts as active catalysts [134]. Other dopants, both divalent and trivalent (Y, Yb, Gd, Sm, Nd, and La) have been employed [135–137]. This makes it possible to design materials resistant to reducing atmospheres with high conductivity and thermal and chemical stability in IT-SOFC operating conditions, even at temperatures as low as 500°C.

SOFC interconnect material requirements are as follows: (i) electronic conductivity $> 100 \text{ S/cm}$; (ii) ionic transport number < 0.01 to avoid chemical shortcut permeation; (iii) gas tight; (iv) tolerate both reducing (H_2) and oxidizing (air/ O_2) atmospheres; (v) be compatible with anode and cathode electrode materials (TEC and chemistry); and (vi) mechanical strength. LaCrO_3 chromites are the most widely used SOFC interconnects and, doped with other elements, their properties are shown to be improved [138]. The dopants most widely employed in the A site of the perovskite are Sr, Mg, and Ca, with dissolution limits of 50% [139], 15% [140], and 50% [141], respectively. Furthermore, the B site is also doped with Co or Fe, in order to limit the Cr content as much as possible due to its volatility [142]. Doped lanthanum chromites seem ideal materials for use as interconnects as they are highly stable in both oxidizing and reducing atmospheres and, at SOFC operating temperatures, do not react with the other cell components. Regarding thermal compatibility, through appropriate doping, it is possible to tailor the thermal expansion coefficient to that of the other components of the cell. LaCrO_3 is a p-type conductor that, upon divalent cation substitution on the La site, is seen to charge compensate by a valence change in the Cr (Cr^{3+} – Cr^{4+}), accompanied by an increase in the electronic conductivity of the material. The main problem associated with these compounds is their sinterability, as at high temperatures and under high oxygen pressure, volatilization of chromium oxide can occur. To avoid this, various strategies such as more reactive synthesis methods at lower temperatures, the introduction of cationic vacancies, and new fabrication techniques (including microwave sintering, freeze drying with EDTA, and more) have been analyzed [143].

5. Nanostructured perovskites for improving solid oxide fuel cells

Nowadays, the research in solid oxide fuel cells (SOFCs) is focused on lowering the operating temperature below 800°C in order to overcome problems such as the ageing of the materials. Concurrently, lowering the operating temperature has the detrimental consequences of decreasing the rate of surface reactions and bulk diffusion in the cathode, giving rise to a worsening of the cell performance. Surface exchange and ionic conduction must therefore be improved to maximize the yield of the cathode reaction. This improvement can be carried out not only by new material selection but also by the detailed control of the microstructure [144]. As stated before, a common strategy for improving the electrochemical performance of the electrodes is the fabrication of composite materials, combining ionic and mixed ionic electronic conducting materials, where the ionic conductor is homogeneously distributed [49]. Using composites, the ionic conductivity across the electrode will be enhanced and, simultaneously, a higher thermomechanical compatibility with the electrolyte can be achieved. The catalytic activity of the material is associated with its microstructure, so if the latter is improved, the active surface area will be increased, and a higher electrochemical durability will be obtained [145]. A significant number of studies have also been conducted to increase active surface area via microstructural control: the use of organic materials as pore formers, template materials such as colloidal crystals, meshes, foams or microfibers, glassy carbon microspheres, or membrane-based templates [146]. These methods look for higher catalytic activities for electrode reactions and lower annealing temperatures due to the numerous active sites and large surface areas. The same goal can be achieved using a new tool that has been developed during the last two decades: nanotechnology [147].

Recently, nanotechnology has been shown to overturn many established theories in a wide range of scientific fields, often with highly desirable properties [148]. This has naturally resulted in a great deal of interest from both scientific and industrial communities in the properties of nanostructured materials. This interest arises from new and unexpected behaviour when compared with bulk materials. Enhancements have been reported in electrical and ionic conductivity, chemical reactivity, and other properties. The shift from bulk to nanomaterials is therefore a promising approach in the development of new advanced technologies capable of achieving higher performance and low environmental impact.

Nanomaterials have typically been considered for low-temperature devices, as high temperatures could promote coarsening and therefore loss of the desired properties. This has generally kept nanomaterials from application in solid oxide fuel cells (SOFCs), but constant material advances have led to the decrease in their operational temperature. These so-called intermediate temperature SOFCs (IT-SOFCs), operating at 500°C–850°C, allow new possibilities for the use of nanomaterials.

The high surface area to volume ratio inherent in nanomaterials provides a large active area for SOFC electrodes. Nanomaterials are defined as a range of materials where at least one dimension is below 100 nm, resulting in nanostructures in zero- to three-dimensions. Nanoparticles, 0-D in nature, are well suited for use in composite electrodes, 1-D nanostructures, including nanotubes and nanowires, are thought to operate as promising electrodes, and thin

films, 2-D in nature are of interest for application in micro-SOFCs (μ -SOFCs) and interlayers. Although the electrical properties of these nanostructures have been analyzed as independent 0- or 1-dimensional structures, the 2- or 3-dimensional behavior is more frequently reported, as it provides reliable results.

When working with SOFCs, there are two main approaches to develop nanomaterials with improved properties: optimizing existing composites by transforming them to nanocomposites and exploring novel nanostructured materials with high mixed ionic and electronic conductivity. In order to fabricate nanocomposites, wet impregnation/infiltration has been gaining increasing attention in recent years [149]. The infiltration process consists of placing a drop of a metal salt solution, with the chemistry required to give rise to the MIEC electrode material after decomposition, on top of a porous material (typically the ionic conductor) [150].

In parallel, MIEC nanostructured materials have also been developed in order to find further optimization of current state-of-the-art electrode materials. This kind of material features one dimension below 100 nm, giving rise to different structures such as nanoparticles, nanotubes, nanofibers, etc. There are several techniques for obtaining these unique phase nanomaterials with enhanced active areas and lower particle sizes with one of the most commonly used being via templating. Only some examples utilizing this procedure will be shown, although a large number of articles have been published on this topic. However, the excellent review by Ruiz-Morales et al. is recommended for those interested in a more detailed description of this method [146]. There are just a few materials able to act as templates because they must fulfill requirements such as removability, compatibility with the process conditions, wettability with the network forming precursor solution and a narrow particle size distribution to achieve optimal packing. Some of the most interesting templates are the organic polymer spheres of polycarbonate (PC), polystyrene (PS), and polymethyl methacrylate (PMMA) [151]. It has been demonstrated that templated porosity is maintained and highly influences electrochemical behavior, presenting an effective means of enhancing the triple phase boundary (TPB), and thus improving cell performance [152]. Another interesting method to obtain economical nanostructures is based on the use of carbon nanotubes (CNTs) as particle growth controller templates [153,154]. The growth controller material must fulfill the following two characteristics for the desired application: thermal stability and either an ease of removal or sufficient electrical properties to form a composite material. This facile and economical route allows to synthesize perovskite nanoparticles with grain sizes as small as 16 nm and surface areas of 151 m²/g, improving electrochemical performance of the electrode by approximately one order of magnitude [153].

Of all possible nanostructures, nanotube-shaped materials seem to exhibit the most interesting improvements to electrode performance [155]. Although inorganic nanowires have been synthesized by several methods such as hydrothermal reaction [156], vapor transport [157], and electrospinning [158], the complexity of perovskite nanotube synthesis has resulted in the template-assisted syntheses becoming the most employed method. There are currently several membranes with different properties which can be used as templates, with anodized alumina (AAO) membranes being the most common [159]. The most important advantage of these membranes is their thermal stability, which allows the control of the morphology at high

temperatures. Their high cost and the problems associated with their anodization do, however, limit their use. These membranes are classified in the literature as hard membranes while there is another group of templates known as soft membranes, which are primarily polymeric in nature. While not costly, they decompose between 200°C and 300°C, which means that the morphology cannot be completely controlled at higher synthesis temperatures. There are several types of polymeric membranes, with polycarbonates being the most commonly used [160]. The use of the pore wetting technique with polycarbonate membranes as templates and subsequent freeze-drying allows the fabrication of highly ordered three-dimensional nanostructures [161]. The electrospinning technique has also been used for the production of MIEC lanthanum strontium cobalt orthoferrite nanofibers [162]. This nanofiber-based cathode architecture is highly stable at intermediate temperatures (600°C–800°C) and provides continuous pathways for charge transport throughout the cathode.

Finally, there is a third generation of materials consisting of nanostructured nanocomposites. An improvement in oxygen reduction reaction (ORR) activity was reported when LSM nanoparticles were loaded on a porous YSZ framework [163–166]. Also, electrocatalytic nanoparticles could be produced in oxide anodes for solid oxide fuel cell (SOFC) by an ex-solution method, i.e., by incorporating metals into a perovskite oxide phase in air followed by the reduction of the perovskite oxide [167]. The improvement in the performance of the cell by using these nanocomposites lies in the extension of the TPB to the newly generated surfaces [168]. Templates such as polycarbonate membranes have also been used for the production of composite nanotubes with 20 nm wall thicknesses [169]. With this strategy, a clear decrease in polarization resistance of the electrode is observed, giving rise to higher efficiencies at temperatures as low as 700°C. Recently, an electrolyte-supported SOFC was fabricated with all-nanocomposite components and operated below 600°C [170]. The highly active nanocomposite electrodes and easily sintered nanocomposite electrolyte allow an in situ low-temperature sintering while preserving the microstructure and electrochemical performance stability upon thermal cycling.

The performance of intermediate temperature SOFCs can be improved by engineering the electrode architecture on the nanoscale. Lowering the temperature facilitates the use of nanotechnology in synthesizing new nanostructured materials in which parameters such as porosity, the distribution of generated pores, and surface area can be closely controlled. These parameters have a significant influence on the performance of the materials used for energy conversion and storage, which means that these methods are an important starting point for the design and optimization of these types of energy devices.

6. Conclusions

The great versatility of the perovskite structure allows for different doping to obtain a variety of properties, which is a key feature in the development of materials for solid oxide fuel cells (SOFCs). This chapter not only briefly introduces the foundation and operation of SOFCs but also shows the evolution of perovskite materials for device components. Among the electro-

lytes, BaCeO_3 -based cerates exhibit the highest ionic conduction at intermediate temperatures while chromites doped with Sr find potential as interconnector materials. By introducing Fe in the Cr site, these chromites become interesting alternatives to the traditional NiO anode, in addition to the new trend of double perovskite-type materials such as $\text{Sr}_2\text{MgMoO}_6$, which present very promising results for anode application. It is in the area of SOFC cathodes in which the most progress has been made. Initially, in the 1960s, doped manganese perovskites ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ —LSM) were used as cathodes, but the low ionic conduction forced the development of new materials based on Co and/or Fe-containing perovskites. In addition, they have mixed ionic-electronic conductivity, allowing the active electrode area to extend across the surface. This leaves $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ perovskite as the most promising cathode material, although as in the case of anodes, double perovskites are also alternative materials with interesting properties.

Finally, it is worth mentioning the importance of not only the material composition but also its structure, morphology and porosity. It has been found that a higher catalytic electrode area results in a significant improvement in the electrochemical system efficiency. Reducing operating temperatures of the SOFC has allowed nanotechnology to become a useful tool for the development of future generations of materials for IT-SOFCs.

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References

- [1] Goto S, Oguma M, Chollacoop N, editors. EAS-ERIA Biodiesel Fuel Trade Handbook: 2010, Jakarta: ERIA, 2010. p. 6–15.
- [2] Ruiz de Larramendi, I. $\text{Ln}_{1-x}\text{Sr}_x\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_{3-\delta}$ (Ln = Pr, Gd; M = Co, Ni, Cr, Ga; $x = 0.1, 0.2, 0.3$) Perovskite Type Oxides as Cathode Materials for Solid Oxide Fuel Cells [thesis]. University of the Basque Country (UPV/EHU), Bilbao; 2007.
- [3] Primdahl, S. Nickel/Yttria-Stabilized Zirconia Cermet Anodes for Solid Oxide Fuel Cells [thesis]. University of Twente, Faculty of Chemical Technology, The Netherlands and Risø National Laboratory, Materials Research Department, Denmark; 1999.
- [4] Grove, W.R. Philos. Mag. 1839; Ser. 3–14: 127–130.
- [5] Nernst, W. Material for electric-lamp glowers. USA, US patent No.: U 00685730, 1901.
- [6] Ortiz-Vitoriano N, Bernuy-López C, Ruiz de Larramendi I, Knibbe R, Thydén K, Hauch A, Holtappels P, Rojo T. Optimizing solid oxide fuel cell cathode processing route for intermediate temperature operation. Appl. Energy. 2013;104:984–991.
- [7] Tu H, Stimming U. Advances, aging mechanisms and lifetime in solid-oxide fuel cells. J. Power Sources. 2004;127:284–293.
- [8] Blenow, P. Strontium-Titanate-Based Anodes for Solid Oxide Fuel Cells [thesis]. Lund University, Sweden. 2007.
- [9] Zhao Y, Xia C, Jia L, Wang Z, Li H, Yu J, Li Y. Recent progress on solid oxide fuel cell: Lowering temperature and utilizing non-hydrogen fuels. Int. J. Hydrogen Energ. 2013;38:16498–16517.
- [10] West AR. Inorganic functional materials: optimization of properties by structural and compositional control. The Chem. Rec. 2006;6:206–216.
- [11] Mogensen M, Lybye D, Bonanos N, Hendriksen PV, Poulsen FW. Factors controlling the oxide ion conductivity of fluorite and perovskite structured oxides. Solid State Ionics. 2004;174:279–286.
- [12] Sun C, Hui R, Roller J. Cathode materials for solid oxide fuel cells: a review. J Solid State Electrochem. 2009;14:1125–1144.
- [13] Zhou W, Ran R, Shao Z. Progress in understanding and development of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -based cathodes for intermediate-temperature solid-oxide fuel cells: A review. J. Power Sources. 2009;192:231–246.
- [14] Janardhanan VM, Heuveline V, Deutschmann O. Three-phase boundary length in solid-oxide fuel cells: A mathematical model. J. Power Sources. 2008;178:368–372

- [15] Ciucci F, Chueh WC, Goodwin DG, Haile SM. Surface reaction and transport in mixed conductors with electrochemically-active surfaces: a 2-D numerical study of ceria. *Phys. Chem. Chem. Phys.*, 2011;13:2121–2135.
- [16] Muñoz-García AB, Ritzmann AM, Pavone M, Keith JA, Carter EA. Oxygen transport in perovskite-type solid oxide fuel cell materials: insights from quantum mechanics. *Acc. Chem. Res.* 2014;47:3340–3348.
- [17] Ruiz de Larramendi I, Vivès S, Ortiz-Vitoriano N, Ruiz de Larramendi JI, Arriortua MI, Rojo T. $\text{La}_{0.6}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ thin films obtained by pulsed laser ablation: effect of the substrate on the electrochemical behaviour. *Solid State Ionics.* 2011;192:584–590.
- [18] Jacobson AJ. Materials for solid oxide fuel cells. *Chem. Mater.* 2010;22:660–674.
- [19] Pavone M, Muñoz-García AB, Ritzmann AM, Carter EA. First-principles study of lanthanum strontium manganite: insights into electronic structure and oxygen vacancy formation. *J. Phys. Chem. C.* 2014;118:13346–13356.
- [20] Takeda, Y.; Sakaki, Y.; Ichikawa, T.; Imanishi, N.; Yamamoto, O.; Mori, M.; Mori, N. y Abe, T. Stability of $\text{La}_{1-x}\text{A}_x\text{MnO}_{3-z}$ ($\text{A}=\text{Ca}, \text{Sr}$) as cathode materials for solid oxide fuel cells. *Solid State Ionics.* 1994;72:257–264.
- [21] DeSouza RA, Islam MS, Ivers-Tiffée EJ. Formation and migration of cation defects in the perovskite oxide LaMnO_3 . *Mater. Chem.* 1999;9:1621–1627.
- [22] Herle JV, McEvoy AJ, Thampi KR. A study on the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ oxygen cathode. *Electrochim. Acta.* 1996;41:1447–1454.
- [23] Skinner SJ. Recent advances in perovskite-type materials for solid oxide fuel cell Cathodes. *Int. J. Inorg. Mater.* 2001;3:113–121.
- [24] Choi Y, Choi MC, Liu M. Rational design of novel cathode materials in solid oxide fuel cells using first-principles simulations. *J. Power Sources.* 2010;195:1441–1445.
- [25] Wen TL, Tu H, Xu Z, Yamamoto O. A study of $(\text{Pr}, \text{Nd}, \text{Sm})\text{SrMnO}$ cathode materials for solid oxide fuel cell. *Solid State Ionics.* 1999;121:25–30.
- [26] Sakaki Y, Takeda Y, Kato A, Imanishi N, Yamamoto O, Hattori M, Iio M, Esaki Y. $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$ and Gd) as the cathode material for solid oxide fuel cells. *Solid State Ionics.* 1999;118:187–194.
- [27] Kostogloudis GC, Ftikos C. Characterization of $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ SOFC cathode materials. *J. Eur. Ceram. Soc.* 1999;19:497–505.
- [28] Kostogloudis GC, Vasihkos N, Ftikos C. Preparation and characterization of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ ($x = 0, 0.15, 0.3, 0.4, 0.5$) as a potential SOFC cathode material operating at intermediate temperatures (500–700°C). *J. Eur. Ceram. Soc.* 1997;17:1513–1521.

- [29] Rim HR, Jeung SK, Jung E, Lee JS. Characteristics of $\text{Pr}_{1-x}\text{M}_x\text{MnO}_3$ ($M = \text{Ca}, \text{Sr}$) as cathode material in solid oxide fuel cells. *Mater. Chem. Phys.* 1998;52:54–59.
- [30] Shao Z, Halle SM. A high-performance cathode for the next generation of solid-oxide fuel cells. *Nature*. 2004;431:170–173.
- [31] Tai LW, Nasrallah MM, Anderson HU, Sparlin DM, Sehlin SR. Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. Part 2. The system $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$. *Solid State Ionics*. 1995;76:273–283.
- [32] Singhal SC, Kendall K, editors. *High Temperature Solid Oxide Fuel Cells*. Elsevier. 2004.
- [33] Mai A, Haanappel BAC, Uhlenbruck S, Tietz F, Stöver D. Ferrite-based perovskites as cathode materials for anode-supported solid oxide fuel cells: Part I. Variation of composition. *Solid State Ionics*. 2005;176:1341–1350.
- [34] Wang H, Tablet C, Feldhoff A, Caro J. A cobalt-free oxygen-permeable membrane based on the perovskite-type oxide $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$. *Adv. Mater.* 2005;17:1785–1788.
- [35] Ortiz-Vitoriano N, Ruiz de Larramendi I, Gil de Muro I, Larrañaga A, Ruiz de Larramendi JI, Rojo T. A novel one step synthesized Co-free perovskite/brownmillerite nanocomposite for solid oxide fuel cells. *J. Mater. Chem*, 2011;21:9682–9691.
- [36] Stevenson JW, Armstrong TR, Carneim RD, Pederson LR, Weber WJ. Electrochemical properties of mixed conducting perovskites $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($M = \text{Sr}, \text{Ba}, \text{Ca}$). *J. Electrochem. Soc.* 1996;143:2722–2729.
- [37] Liu X, Cheng B, Hu J, Qin H, Jiang M. Preparation, structure, resistance and methane-gas sensing properties of nominal $\text{La}_{1-x}\text{Mg}_x\text{FeO}_3$. *Sens. Actuator B-Chem.* 2008;133:340–344.
- [38] Plonczak P, Gazda M, Kusz B, Jasinski P. Fabrication of solid oxide fuel cell supported on specially performed ferrite-based perovskite cathode. *J. Power Sources*. 2008;181:1–7.
- [39] Yoon KJ, Zink PA, Gopalan S, Pal UB, Pederson LR. Defect chemistry and electrical properties of $(\text{La}_{0.8}\text{Ca}_{0.2})_{0.95}\text{FeO}_{3-\delta}$ fuel cells and energy conversion. *J. Electrochem. Soc.* 2009;156:B795–B800.
- [40] Hashimoto SI, Kammer K, Larsen PH, Pulsen FW, Mogensen M. A study of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ as a cathode material for SOFCs with intermediate operating temperature. *Solid State Ionics*. 2005;176:1013–1020.
- [41] Ruiz de Larramendi I, López Antón R, Ruiz de Larramendi JI, Baliteau S, Mauvy F, Grenier JC, Rojo T. Structural and electrical properties of thin films of $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$. *J. Power Sources*. 2007;169:35–39.

- [42] Chiba R, Yoshimura F, Sakurai Y. An investigation of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ as a cathode material for solid oxide fuel cells. *Solid State Ionics*. 1999;124:281–288.
- [43] Ruiz de Larramendi I, Ortiz N, López-Antón R, Ruiz de Larramendi JI, Rojo T. Structure and impedance spectroscopy of $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ thin films grown by pulsed laser deposition. *J. Power Sources*. 2007;171:747–753.
- [44] El-Himri A, Marrero-López D, Ruiz-Morales JC, Peña-Martínez J, Núñez P. Structural and electrochemical characterisation of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Cr}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ as symmetrical solid oxide fuel cell electrodes. *J. Power Sources*. 2009;188:230–237.
- [45] Ortiz-Vitoriano N, Ruiz de Larramendi I, Ruiz de Larramendi JI, Arriortua MI, Rojo T. Synthesis and electrochemical performance of $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3$) material for solid oxide fuel cell cathode. *J. Power Sources*. 2009;192:63–69.
- [46] Taguchi H, Masunaga Y, Hirota K, Yamaguchi O. Synthesis of perovskite-type $(\text{La}_{1-x}\text{Ca}_x)\text{FeO}_3$ ($0 \leq x \leq 0.2$) at low temperature. *Mater Res. Bull.* 2005;40:773–780.
- [47] Montini T, Bevilacqua M, Fonda E, Casulla MF, Lee S, Tavagnacco C, Gorte RJ, Fornasiero P. Relationship between electrical behavior and structural characteristics in Sr-doped $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ mixed oxides. *Chem. Mater.* 2009;21:1768–1774.
- [48] Ortiz-Vitoriano N, Ruiz de Larramendi I, Cook SN, Burriel M, Aguadero A, Kilner JA, Rojo T. The formation of performance enhancing pseudo-composites in the highly active $\text{La}_{1-x}\text{Ca}_x\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ system for IT-SOFC Application. *Adv. Funct. Mater.* 2013;23:5131–5139.
- [49] Ortiz-Vitoriano N, Ruiz de Larramendi I, Ruiz de Larramendi JI, Arriortua MI, Rojo T. Optimization of $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3\text{--Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ composite cathodes for intermediate-temperature solid oxide fuel cells. *J. Power Sources*. 2011;196:4332–4336.
- [50] Dusastre V, Kilner JA. Optimisation of composite cathodes for intermediate temperature SOFC applications. *Solid State Ionics*. 1999;126:163–174.
- [51] Wang K, Ran R, Zhou W, Gu H, Shao Z, Ahn J. Properties and performance of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} + \text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ composite cathode. *J. Power Sources*. 2008;179:60–68.
- [52] Tarancón A, Morata A, Dezanneau G, Skinner SJ, Kilner JA, Estradé S, Hernández-Ramírez F, Peiró F, Morante JR. $\text{GdBaCo}_2\text{O}_{5+x}$ layered perovskite as an intermediate temperature solid oxide fuel cell cathode. *J. Power Sources*. 2007;174:255–263.
- [53] Frontera C, García-Muñoz JL, Castaño O, Ritter C, Caneiro A. The effect of oxygen disorder on magnetic properties of $\text{PrBaCo}_2\text{O}_{5.50}$ layered cobaltite. *J. Phys.: Condens. Matter*. 2008;20:104228(8)
- [54] Kim JH, Kim YM, Connor PA, Irvine JTS, Bae J, Zhou WZCS. Structural, thermal and electrochemical properties of layered perovskite $\text{SmBaCo}_2\text{O}_{5+d}$, a potential cathode

material for intermediate-temperature solid oxide fuel cells. *J. Power Sources*. 2009;194:704–711

- [55] Zhao L, He BB, Xun ZQ, Wang H, Peng RR, Meng GY, Liu XQ. Characterization and evaluation of $\text{NdBaCo}_2\text{O}_{5+\delta}$ cathode for proton-conducting solid oxide fuel cells. *Int. J. Hydrogen Energ.* 2010;35:753–756.
- [56] Kim G, Wang S., Jacobson AJ, Reimus L, Brodersen P, Mims CA. Rapid oxygen ion diffusion and surface exchange kinetics in $\text{PrBaCo}_2\text{O}_{5+x}$ with a perovskite related structure and ordered A cations. *J. Mater. Chem.* 2007;17:2500–2505.
- [57] Bak T, Nowotny J, Rekas M, Sorell CC, Vance ER. A manometric method for the determination of chemical diffusion in non-stoichiometric oxides: Example of $(\text{La,Sr})\text{MnO}_3$. *Solid State Sci.* 2000;135:557–561.
- [58] Marrero-López D, dos Santos-Gómez L, Canales-Vázquez J, Martín F, Ramos-Barra-do JR. Stability and performance of nanostructured $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ cathodes deposited by spray-pyrolysis. *Electrochim. Acta.* 2014;134:159–166.
- [59] Bouwmeester HJM, Kruidhof H, Burggraaf AJ. Importance of the surface exchange kinetics as rate limiting step in oxygen permeation through mixed-conducting oxides. *Solid State Ionics.* 1994;72:185–194.
- [60] Søgaard M, Vang Hendriksen P, Mogensen M. Oxygen nonstoichiometry and transport properties of strontium substituted lanthanum ferrite. *J. Solid State Chem.* 2007;180:1489–1503.
- [61] Ralph JM, Rossignol Cc, Kumar R. Cathode materials for reduced-temperature SOFCs. *J. Electrochem. Soc.* 2003;150:A1518–A1522.
- [62] Zomorrodian A, Salamati H, Lu Z, Chen X, Wu N, Ignatiev A. Electrical conductivity of epitaxial $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ thin films grown by pulsed laser deposition. *Int. J. Hydrogen Energ.* 2010;35:12443–12448.
- [63] Cox-Galhotra RA, McIntosh S. Unreliability of simultaneously determining k_{chem} and D_{chem} via conductivity relaxation for surface-modified $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$. *Solid State Ionics.* 2010;181:1429–1436.
- [64] Lu H, Zhu L, Kim JP, Son SH, Park JH. Perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{B}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($B = \text{Ti, Cr, Co}$) oxides: Structural, reduction-tolerant, sintering, and electrical properties. *Solid State Ionics.* 2012;209–210:24–29.
- [65] Garcia LMP, Macedo DA, Souza GL, Motta FV, Paskocimas CA, Nascimento RM. Citrate-hydrothermal synthesis, structure and electrochemical performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathodes for IT-SOFCs. *Ceram. Int.* 2013;39:8385–8392.
- [66] Zhu G, Fang X, Xia C, Liu X. Preparation and electrical properties of $\text{La}_{0.4}\text{Sr}_{0.6}\text{Ni}_{0.2}\text{Fe}_{0.8}\text{O}_3$ using a glycine nitrate process. *Ceram. Int.* 2005;31:115–119.

- [67] Chiba R, Yoshimura F, Sakurai Y. Properties of $\text{La}_{1-y}\text{Sr}_y\text{Ni}_{1-x}\text{Fe}_x\text{O}_3$ as a cathode material for a low-temperature operating SOFC. *Solid State Ionics*. 2002;152–153:575–582.
- [68] Zhou Q, Xu L, Guo Y, Jia D, Li Y, Wei WCJ. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ perovskite oxide as cathode for IT-SOFC. *Int. J. Hydrogen Energ.* 2012;37:11963–11968.
- [69] Meng X, Lü S, Ji Y, Wei T, Zhang Y. Characterization of $\text{Pr}_{1-x}\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($0.2 \leq x \leq 0.6$) cathode materials for intermediate-temperature solid oxide fuel cells. *J. Power Sources*. 2008;183:581–585.
- [70] Hashimoto S, Kammer K, Poulsen FW, Mogensen M. Conductivity and electrochemical characterization of $\text{PrFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ at high temperature. *J. Alloys Compd.* 2007;428:256–261.
- [71] Rebello J, Vashook V, Trots D, Guth U. Thermal stability, oxygen non-stoichiometry, electrical conductivity and diffusion characteristics of $\text{PrNi}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$, a potential cathode material for IT-SOFCs. *J. Power Sources*. 2011;196:3705–3712.
- [72] Guo YQ, Yin YM, Tong Z, Yin JW, Xiong MW, Ma ZF. Impact of synthesis technique on the structure and electrochemical characteristics of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (PSCF) cathode material. *Solid State Ionics*. 2011;193:18–22.
- [73] Kostogloudis GC, Ftikos C. Crystal structure, thermal expansion and electrical conductivity of $\text{Pr}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($0 \leq x \leq 0.5$). *Solid State Ionics*. 2000;135:537–541.
- [74] Chang CL, Hsu CS, Hwang BH. Unique porous thick $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ solid oxide fuel cell cathode films prepared by spray pyrolysis. *J. Power Sources*. 2008;179:734–738.
- [75] Yang S, He T, He Q. $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cathode material from glycine-nitrate process: Formation, characterization, and application in LaGaO_3 -based solid oxide fuel cells. *J. Alloys Compd.* 2008;450:400–404.
- [76] Wei B, Lü Z, Huang X, Liu M, Li N, Su W. Synthesis, electrical and electrochemical properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite oxide for IT-SOFC cathode. *J. Power Sources*. 2008;176:1–8.
- [77] Lee S, Lim Y, Lee EA, Hwang HJ, Moon J-W. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LBCF) cathodes prepared by combined citrate-EDTA method for IT-SOFCs. *J. Power Sources*. 2006;157:848–854.
- [78] Wei B, Lü Z, Huang X, Miao J, Sha X, Xin X, et al. Crystal structure, thermal expansion and electrical conductivity of perovskite oxides $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($0.3 \leq x \leq 0.7$). *J. Eur. Ceram. Soc.* 2006;26:2827–2832.
- [79] Chen D, Ran R, Zhang K, Wang J, Shao Z. Intermediate-temperature electrochemical performance of a polycrystalline $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode on samarium-doped ceria electrolyte. *J. Power Sources*. 2009;188:96–105.

- [80] Meng F, Xia T, Wang J, Shi Z, Zhao H. Praseodymium-deficiency $\text{Pr}_{0.94}\text{BaCo}_2\text{O}_{6-\delta}$ double perovskite: A promising high performance cathode material for intermediate-temperature solid oxide fuel cells. *J. Power Sources*. 2015;293:741–750.
- [81] Jin F, Xu H, Long W, Shen Y, He T. Characterization and evaluation of double perovskites $\text{LnBaCoFeO}_{5+\delta}$ (Ln = Pr and Nd) as intermediate-temperature solid oxide fuel cell cathodes. *J. Power Sources*. 2013;243:10–18.
- [82] Li N, Lü Z, Wei B, Huang X, Chen K, Zhang Y, et al. Characterization of $\text{GdBaCo}_2\text{O}_{5+\delta}$ cathode for IT-SOFCs. *J. Alloys Compd.* 2008;454:274–279.
- [83] Taskin AA, Lavrov AN, Ando Y. Achieving fast oxygen diffusion in perovskites by cation ordering. *Appl. Phys. Lett.* 2005;86:091910.
- [84] Zhou Q, He T, Ji Y. $\text{SmBaCo}_2\text{O}_{5+x}$ double-perovskite structure cathode material for intermediate-temperature solid-oxide fuel cells. *J. Power Sources*. 2008;185:754–758.
- [85] Ding X, Kong X, Wu H, Zhu Y, Tang J, Zhong Y. $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Cu}_2\text{O}_{5+\delta}$ and $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{CuFeO}_{5+\delta}$ layered perovskite oxides as cathodes for IT-SOFCs. *Int. J. Hydrogen Energ.* 2012;37:2546–2551.
- [86] Xue J, Shen Y, He T. Double-perovskites $\text{YBaCo}_{2-x}\text{Fe}_x\text{O}_{5+\delta}$ cathodes for intermediate-temperature solid oxide fuel cells. *J. Power Sources*. 2011;196:3729–3735.
- [87] Zhu WZ, Deevi SC. A review on the status of anode materials for solid oxide fuel cells. *Mater. Sci. Eng. A* 2003;362:228–239.
- [88] Sun C, Stimming U. Recent anode advances in solid oxide fuel cells. *J. Power Sources*. 2007;171:247–260.
- [89] Atkinson A, Barnett S, Gorte RJ, Irvine JTS, McEvoy AJ, Mogensen M, Singhal SC, Vohs J. Advanced anodes for high-temperature fuel cells. *Nat. Mater.* 2004;3:17–27.
- [90] Boukamp BA. Fuel cells: The amazing perovskite anode. *Nat. Mater.* 2003;2:294–296.
- [91] Verbraeken MC, Ramos T, Agersted K, Ma Q, Savaniu CD, Sudireddy BR, Irvine JTS, Holtappels P, Tietz F. Modified strontium titanates: from defect chemistry to SOFC anodes. *RSC Adv.* 2015;5:1168–1180.
- [92] Yurkiv V, Constantin G, Hornes A, Gondolini A, Mercadelli E, Sanson A, Dessemond L, Costa R. Towards understanding surface chemistry and electrochemistry of $\text{La}_{0.1}\text{Sr}_{0.9}\text{TiO}_{3-\alpha}$ based solid oxide fuel cell anodes. *J. Power Sources*. 2015;287:58–67.
- [93] Marina OA, Canfield NL, Stevenson JW. Thermal, electrical, and electrocatalytical properties of lanthanum-doped strontium titanate. *Solid State Ionics*. 2002;149:21–28.
- [94] Hashimoto S, Kindermann L, Poulsen FW, Mogensen M. A study on the structural and electrical properties of lanthanum-doped strontium titanate prepared in air. *J. Alloys Compd.* 2005;397:245–249.

- [95] Canales-Vázquez J, Ruiz-Morales JC, Irvine JTS, Zhou W. Sc-substituted oxygen excess titanates as fuel electrodes for SOFCs. *J. Electrochem. Soc.* 2005;152:A1458–A1465.
- [96] Miller DN, Irvine JTS. B site doping of lanthanum strontium titanate for solid oxide fuel cell anodes. *J. Power Sources.* 2011;196:7323–7327.
- [97] Cui SH, Li JH, Zhou XW, Wang GY, Luo JL, Chuang KT, Bai Y, Qiao LJ. Cobalt doped $\text{LaSrTiO}_{3-\delta}$ as an anode catalyst: effect of Co nanoparticle precipitation on SOFCs operating on H_2S -containing hydrogen. *J. Mater. Chem. A.* 2013;1:9689–9696.
- [98] Ma Q, Tietz F. Comparison of Y and La-substituted SrTiO_3 as the anode materials for SOFCs. *Solid State Ionics.* 2012;225:108–112.
- [99] Park BH, Choi GM. Ex-solution of Ni nanoparticles in a $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ alternative anode for solid oxide fuel cell. *Solid State Ionics.* 2014;262:345–348.
- [100] Périllat-Merceroz C, Gauthier G, Roussel P, Huvé M, Gélin P, Vannier RN. Synthesis and study of a Ce-doped La/Sr titanate for solid oxide fuel cell anode operating directly on methane. *Chem. Mater.* 2011;23:1539–1550.
- [101] Ruiz-Morales JC, Canales-Vázquez J, Savaniu C, Marrero-López D, Zhou W, Irvine JTS. Disruption of extended defects in solid oxide fuel cell anodes for methane oxidation. *Nature* 2006;439:568–571.
- [102] Chamberland BL, Danielson PS. Alkaline-earth vanadium (IV) oxides having the AVO_3 composition. *J. Solid State Chem.* 1971;3:243–247.
- [103] Martínez-Coronado R, Alonso JA, Aguadero A, Fernández-Díaz MT. Optimized energy conversion efficiency in solid-oxide fuel cells implementing $\text{SrMo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ perovskites as anodes. *J. Power Sources.* 2012;208:153–158.
- [104] Martínez-Coronado R, Alonso JA, Aguadero A, Fernández-Díaz MT. New $\text{SrMo}_{1-x}\text{Cr}_x\text{O}_{3-\delta}$ perovskites as anodes in solid-oxide fuel cells. *Int. J. Hydrogen Energ.* 2014;39:4067–4073.
- [105] Martínez-Coronado R, Alonso JA, Fernández-Díaz MT. $\text{SrMo}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$: A potential anode for intermediate-temperature solid-oxide fuel cells (IT-SOFC). *J. Power Sources.* 2014;258:76–82.
- [106] Du Z, Zhao H, Yang C, Shen Y, Yan C, Zhang Y. Optimization of strontium molybdate based composite anode for solid oxide fuel cells. *J. Power Sources.* 2015;274:568–574.
- [107] Zheng K, Świerczek K, Bratek J, Klimkowicz A. Cation-ordered perovskite-type anode and cathode materials for solid oxide fuel cells. *Solid State Ionics.* 2014;262:354–358.
- [108] Liu Q, Dong X, Xiao G, Zhao F, Chen F. A novel electrode material for symmetrical SOFCs. *Adv. Mater.* 2010;22:5478–5482.

- [109] Suthirakun S, Ammal SC, Muñoz-García AB, Xiao G, Chen F, zur Loye HC, Carter EA, Heyden A. Theoretical investigation of H₂ oxidation on the Sr₂Fe_{1.5}Mo_{0.5}O₆ (001) perovskite surface under anodic solid oxide fuel cell conditions. *J. Am. Chem. Soc.* 2014;136:8374–8386.
- [110] Sfeir J. LaCrO₃-based anodes: stability considerations. *J. Power Sources.* 2003;118:276–285.
- [111] Lü MF, Tsipis EV, Waerenborgh JC, Yaremchenko AA, Kolotygin VA, Bredikhin S, Kharton VV. Thermomechanical, transport and anodic properties of perovskite-type (La_{0.75}Sr_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-δ}. *J. Power Sources.* 2012;206:59–69.
- [112] Tao SW, Irvine JTS. Catalytic properties of the perovskite oxide La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-δ} in relation to its potential as a solid oxide fuel cell anode material. *Chem. Mater.* 2004;16:4116–4121.
- [113] Wei T, Liu XJ, Yuan C., Gao QY, Xin XS, Wang SR. A modified liquid-phase-assisted sintering mechanism for La_{0.8}Sr_{0.2}Cr_{1-x}Fe_xO_{3-δ}—A high density, redox-stable perovskite interconnect for solid oxide fuel cells. *J. Power Sources.* 2014;250:152–159.
- [114] Fowler DE, Haag JM, Boland C, Bierschenk DM, Barnett SA, Poeppelmeier KR. Stable, low polarization resistance solid oxide fuel cell anodes: La_{1-x}Sr_xCr_{1-x}Fe_xO_{3-δ} ($x = 0.2$ – 0.67). *Chem. Mater.* 2014;26:3113–3120.
- [115] Huang YH, Dass RI, Xing ZL, Goodenough JB. Double perovskites as anode materials for solid-oxide fuel cells. *Science* 2006;312:254–257.
- [116] Choi S, Yoo S, Kim J, Park S, Jun A, Sengodan S, Kim J, Shin J, Jeong HY, Choi Y, Kim G, Liu M. Highly efficient and robust cathode materials for low-temperature solid oxide fuel cells: PrBa_{0.5}Sr_{0.5}Co_{2-x}Fe_xO_{5+δ}. *Sci. Rep.* 2013;3:2426-6.
- [117] Sengodan S, Choi S, Jun A, Shin TH, Ju YW, Jeong HY, Shin J, Irvine JTS, Kim G. Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells. *Nat. Mater.* 2015;14:205–209.
- [118] Périllat-Merceroz C, Roussel P, Huvé M, Capoen E, Rosini S, Gélín P, Vannier RN, Gauthier GH. Pure and Mn-doped La₄SrTi₅O₁₇ layered perovskite as potential solid oxide fuel cell material: Structure and anodic performance *J. Power Sources.* 2015;274:806–815.
- [119] Ruiz de Larramendi I, Ortiz-Vitoriano N, Acebedo B, Jimenez de Aberasturi D, Gil de Muro I, Arango A, Rodríguez-Castellón E, Ruiz de Larramendi JL, Rojo T. Pr-doped ceria nanoparticles as intermediate temperature ionic conductors. *Int. J. Hydrogen Energ.* 2011;36:10981–10990.
- [120] McEvoy AJ. Thin SOFC electrolytes and their interfaces—A near-term research strategy. *Solid State Ionics.* 2000;132:159–165.

- [121] Chen XJ, Khor KA, Chan SH, Yu LG. Influence of microstructure on the ionic conductivity of yttria-stabilized zirconia electrolyte. *Mater. Sci. Eng. A* 2002;A335:246–252
- [122] Vlasov AN, Perfiliev MV. Ageing of ZrO_2 -based solid electrolytes. *Solid State Ionics* 1987;25:245–253.
- [123] Slater PR, Irvine JTS, Ishihara T, Takita Y. The structure of the oxide ion conductor $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ by powder neutron diffraction. *Solid State Ionics*. 1998;107:319–323.
- [124] Kim S, Chun MC, Lee KT, Lee HL. Oxygen-ion conductivity of BaO- and MgO-doped LaGaO_3 electrolytes. *J. Power Sources*. 2001;93:279–284.
- [125] Sood K, Singh K, Pandey OP. Structural and electrical behavior of Ba-doped LaGaO_3 composite electrolyte. *J. Renew. Sust. Energy*. 2014;6:063112.
- [126] Kurumada M, Hara H, Munakata F, Iguchi E. Electric conduction in $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_{3-\delta}$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$. *Solid State Ionics*. 2005;176:245–251.
- [127] Mineshige A, Izutsu J, Nakamura M, Nigaki K, Abe J, Kobune M, Fujii S, Yazawa T. Introduction of A site deficiency into $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and its effect on structure and conductivity. *Solid State Ionics*. 2005;176:1145–1149.
- [128] Ahamd-Khanlou A, Tietz F, Stöver D. Material properties of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.9+x}\text{Mg}_{0.1}\text{O}_{3-\delta}$ as a function of Ga content. *Solid State Ionics*. 2000;135:543–547.
- [129] Zhang L, Xiao J, Xie Y, Tang Y, Liu J, Liu M. Behavior of strontium- and magnesium-doped gallate electrolyte in direct carbon solid oxide fuel cells. *J. Alloys Compd.* 2014;608:272–277.
- [130] Wang XP, Zhou DF, Yang GC, Sun SC, Li ZH, Fu H, Meng J. Nonstoichiometric $(\text{La}_{0.95}\text{Sr}_{0.05})_x\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ electrolytes and $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}-(\text{La}_{0.95}\text{Sr}_{0.05})_x\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ composite electrolytes for solid oxide fuel cells. *Int. J. Hydrogen Energ.* 2014;39:1005–1013
- [131] Feng M, Goodenough JB, Huang K, Milliken C. Fuel cells with doped lanthanum gallate electrolyte. *J. Power Sources*. 1996;63:47–51.
- [132] Lo Faro M, Aricò AS. Electrochemical behaviour of an all-perovskite-based intermediate temperature solid oxide fuel cell. *Int. J. Hydrogen Energ.* 2013;38:14773–14778
- [133] Yamazaki Y, Blanc F, Okuyama Y, Buannic L, Lucio-Vega JC, Grey CP, Haile SM. Proton trapping in yttrium-doped barium zirconate. *Nat. Mater.* 2013;12:647–651.
- [134] Liu Y, Ran R, Li S, Jiao Y, Tade MO, Shao Z. Significant performance enhancement of yttrium-doped barium cerate proton conductor as electrolyte for solid oxide fuel cells through a Pd ingress–egress approach. *J. Power Sources*. 2014;257:308–318.

- [135] Stevenson DA, Jiang N, Buchanan RM, Henn FEG. Characterization of Gd, Yb and Nd doped barium cerates as proton conductors. *Solid State Ionics*. 1993;62:279–285.
- [136] Oishi M, Yashiro K, Sato K, Mizusaki J, Kitamura N, Amezawa K, Kawada T, Uchimoto Y. Oxygen nonstoichiometry of the perovskite-type oxides $\text{BaCe}_{0.9}\text{M}_{0.1}\text{O}_{3-\delta}$ (M = Y, Yb, Sm, Tb, and Nd). *Solid State Ionics*. 2008;179:529–535.
- [137] Nguyen NTQ, Yoon HH. Preparation and evaluation of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) electrolyte and BZCYYb-based solid oxide fuel cells. *J. Power Sources*. 2013;231:213–218.
- [138] Fergus JW. Lanthanum chromite-based materials for solid oxide fuel cell interconnects. *Solid State Ionics*. 2004;171:1–15.
- [139] Devi PS, Rao MS. Preparation, structure, and properties of strontium-doped lanthanum chromites: $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$. *J. Solid State Chem*. 1992;98:237–244.
- [140] Flandermeyer BK, Nasrallah MM, Agarwal AK, Anderson HU. Defect structure of Mg-doped LaCrO_3 model and thermogravimetric measurements. *J. Am. Ceram. Soc*. 1984;67:195–198.
- [141] Coutures JP, Badie JM, Berjoan R, Coutures J, Flamand R, Rouanet A. Stability and thermodynamic properties of rare earth perovskites. *High Temp. Sci*. 1979;13: 331–336.
- [142] Lee HC, Kang BK, Lee JH, Heo YW, Kim JY, Kim JJ. Adhesion behavior between yttrium-stabilized zirconia added $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$ interconnector and yttrium-stabilized zirconia-based substrate. *Ceram. Int*. 2013;39:8737–8741.
- [143] Ruiz-Morales JC, Canales-Vázquez J, Marrero-López D, Peña-Martínez J, Pérez-Coll D, Núñez P, Rodríguez-Placeres JC, Ballesteros-Pérez B, Dorta-Martín VI, Savaniu C. *Pilas de Combustible de Óxidos Sólidos (SOFC)* Ed. Centro de la Cultura Popular Canaria. ISBN: 978-84-7926-567-0, 2008.
- [144] Choi J, Kim B, Shin D. Fibrous mixed conducting cathode with embedded ionic conducting particles for solid oxide fuel cells. *Int. J. Hydrogen Energ*. 2014;39:14460–14465.
- [145] Hueso L, Mathur N. Dreams of a hollow future. *Nature*. 2004;427:301–304.
- [146] Ruiz-Morales JC, Marrero-López D, Gálvez-Sánchez M, Canales-Vázquez J, Savaniu C, Savvina SN. Engineering of materials for solid oxide fuel cells and other energy and environmental applications. *Energy Environ. Sci*. 2010;3:1670–1681.
- [147] Pinedo R, Ruiz de Larramendi I, Ortiz-Vitoriano N, Jimenez de Aberasturi D, Rojo T. Nanotechnology for improving solid oxide fuel cells. *Materials and processes for energy: communicating current research and technological developments* (A. Méndez-Vilas, Ed.). 512–522. 2013.

- [148] Jimenez de Aberasturi D, Serrano-Montes AB, Liz-Marzán LM. Modern applications of plasmonic nanoparticles: from energy to health. *Adv. Optical Mater.* 2015;3:602–617.
- [149] Jiang SP. A review of wet impregnation—An alternative method for the fabrication of high performance and nano-structured electrodes of solid oxide fuel cells. *Mater. Sci. Eng. A.* 2006;418:199–210.
- [150] Liu Z, Liu B, Ding D, Liu M, Chen F, Xia C. Fabrication and modification of solid oxide fuel cell anodes via wet impregnation/infiltration technique. *J. Power Sources.* 2013;237:243–259.
- [151] Marrero-López D, Ruiz-Morales JC, Peña-Martínez J, Canales-Vázquez J, Núñez P. Preparation of thin layer materials with macroporous microstructure for SOFC applications. *J. Solid State Chem.* 2008;181:685–692.
- [152] Pinedo R, Ruiz de Larramendi I, Gil de Muro I, Insausti M, Ruiz de Larramendi JI, Arriortua MI, Rojo T. Influence of colloidal templates on the impedance spectroscopic behaviour of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.8}\text{Ni}_{0.2}$ or solid oxide fuel cell applications. *Solid State Ionics.* 2011;192:235–240.
- [153] Pinedo R, Ruiz de Larramendi I, Jimenez de Aberasturi D, Gil de Muro I, Aguayo AT, Ruiz de Larramendi JI, Rojo T. A straightforward synthesis of carbon nanotube–perovskite composites for solid oxide fuel cells. *J. Mater. Chem.* 2011;21:10273–10276.
- [154] Pinedo R, Ruiz de Larramendi I, Khavrus VO, Jimenez de Aberasturi D, Ruiz de Larramendi JI, Ritscheld M, Leonhardt A, Rojo T. Microstructural improvements of the gradient composite material $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ by employing vertically aligned carbon nanotubes. *Int. J. Hydrogen Energ.* 2014;39:4074–4080.
- [155] Bellino MG, Sacanell JG, Lamas DG, Leyva AG, Walsöe de Reca NE. High-performance solid-oxide fuel cell cathodes based on cobaltite nanotubes. *J. Am. Chem. Soc.* 2007;129:3066–3067.
- [156] Liu J, Wang X, Peng Q, Li Y. Vanadium pentoxide nanobelts: highly selective and stable ethanol sensor materials. *Adv. Mater.* 2005;17:764–767.
- [157] Kuo TJ, Huang MH. Gold-catalyzed low-temperature growth of cadmium oxide nanowires by vapor transport. *J. Phys. Chem. B* 2006;110:13717–13721.
- [158] Ostermann R, Li D, Yin Y, McCann JT, Xia Y. V_2O_5 Nanorods on TiO_2 Nanofibers: A new class of hierarchical nanostructures enabled by electrospinning and calcination. *Nano Lett.* 2006;6:1297–1302.
- [159] Kwon CW, Son JW, Lee JH, Kim HM, Lee HW, Kim KB. High-performance micro-solid oxide fuel cells fabricated on nanoporous anodic aluminum oxide templates. *Adv. Funct. Mater.* 2011;21:1154–1159.

- [160] Boehme M, Ionescu E, Fu G, Ensinger W. Room temperature synthesis of indium tin oxide nanotubes with high precision wall thickness by electroless deposition. *J. Nanotech.* 2011;2:119–126.
- [161] Pinedo R, Ruiz de Larramendi I, Jimenez de Aberasturi D, Gil de Muro I, Ruiz de Larramendi JI, Arriortua MI, Rojo T. Synthesis of highly ordered three-dimensional nanostructures and the influence of the temperature on their application as solid oxide fuel cells cathodes. *J. Power Sources.* 2011;196:4174–4180.
- [162] Zhi M, Lee S, Miller N, Menzler NH, Wu N. An intermediate-temperature solid oxide fuel cell with electrospun nanofiber cathode. *Energy Environ. Sci.* 2012;5:7066–7071.
- [163] Huang YY, Vohs JM, Gorte RJ. Characterization of LSM-YSZ composites prepared by impregnation methods. *J. Electrochem. Soc.* 2005;152:A1347–A1353.
- [164] Zhi MJ, Mariani N, Gemmen R, Gerdes K, Wu NQ. Nanofiber scaffold for cathode of solid oxide fuel cell. *Energy Environ. Sci.* 2011;4:417–420.
- [165] Zhang N, Li J, Li W, Ni D, Sun K. High performance three-dimensionally ordered macroporous composite cathodes for intermediate temperature solid oxide fuel cells. *RSC Adv.* 2012;2:802–804.
- [166] Zhang X, Liu L, Zhao Z, Tu B, Ou D, Cui D, Wei X, Chen X, Cheng M. Enhanced oxygen reduction activity and solid oxide fuel cell performance with a nanoparticles-loaded cathode. *NanoLett.* 2015;15:1703–1709.
- [167] Park BH, Choi GM. Ex-solution of Ni nanoparticles in a $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ alternative anode for solid oxide fuel cell. *Solid State Ionics.* 2014;262:345–348.
- [168] Vohs JM, Gorte RJ. High-performance SOFC cathodes prepared by infiltration. *Adv. Mater.* 2009;21:943–956.
- [169] Pinedo R, Ruiz de Larramendi I, Ortiz-Vitoriano N, Gil de Muro I, Rojo T. Novel $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3\text{:Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ composite nanotubes for energy conversion and storage. *J. Power Sources.* 2012;201:332–339.
- [170] Fan L, Wang C, Zhu B. Low temperature ceramic fuel cells using all nanocomposite materials. *NanoEnergy.* 2012;1:631–639.

