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Chapter 21

Perovskites Used in Fuel Cells

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Additional information is available at the end of the chapter

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Abstract

Fuel cells are devices for energy generation with very high theoretical efficiency. Many researches were been carried out in the last few decades in order to develop reliable fuel cells. Solid oxide fuel cells (SOFC) and polymeric exchange membrane fuel cells (PEMFC) are those with more potential for commercial use. Specially for SOFC cathodes, many perovskites have been proposed as potential materials for this application. Nevertheless, other components of SOFC, such as the electrolytes, anodes and interconnects, have also been targeted with potential perovskites. More recently, the use of perovskites in PEMFC has also been proposed and studied. As many perovskite compositions can be used in SOFC components, some of the most important are discussed in this chapter and some recent works in perovskites for PEMFC are also referred. As a whole, in this chapter, the reader will find the relationship between the properties of perovskites with their compositions and the main effects of dopant agents regarding the utilization of these materials in different components of SOFC and in electrodes of PEMFC.

Keywords: SOFC, IT-SOFC, PEMFC, Nonstoichiometric compounds

1. Introduction

Fuel cells are devices that convert the chemical energy of a fuel directly into electrical energy and heat. The most common fuel is H_2, but other hydrocarbon compounds such as methanol, methane, natural gas, ethanol or others can also be used. A single cell is composed of three main components: anode, cathode and electrolyte. For the effective use of fuel cells, single cells must be interconnected to increase the power production, which requires the use of two more components: interconnects, for the serial electrical connection, and sealants, for the hermetic sealing of the set. The electrodes are permeated by the gases, fuel in the anode and oxygen (air) in the cathode, and they catalyse electrochemical reactions through electron capitation or

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conduction from or to the reactive sites; the electrolyte, an electrical insulator, promotes ionic conductivity. Figure 1 shows a general schematic drawing of a fuel cell operation. The residual water (if pure H_2 is used) can be produced in the anode or in the cathode and it will depend of the nature of the electrolyte. If the electrolyte is a cationic conductor, the water will form in the cathode and, conversely, if it is an anionic conductor, the water will be formed in the anode.

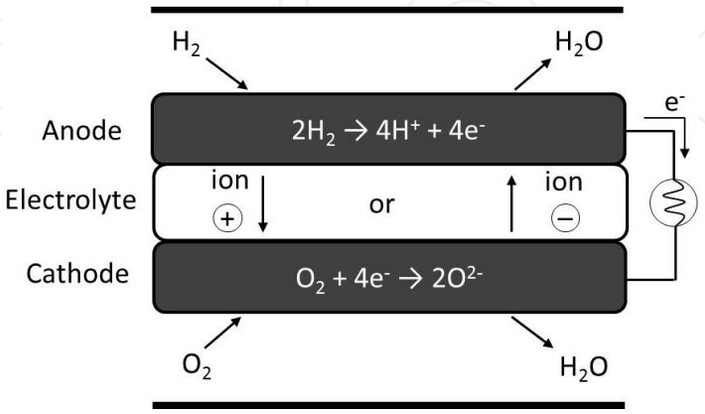


Figure 1. General operation scheme of a fuel cell running with H_2.

In general, a fuel cell works similarly to a battery; however, its energy is not stored in its electrodes, so there is no need for recharging because there is a continuous supply of fuel in the anode and oxidants (air) in the cathode. The electrical work provided by the electrochemical reactions does not consume the cell's components, which keeps on converting the chemical energy into electricity and heat while its electrodes are supplied with the gases.

There are different types of fuel cells and they are named according to the material used in the electrolyte. Besides the materials used in their components, the fuel cells also differ in other important aspects such as efficiency and operation temperature. In Table 1, the main characteristics of fuel cells are summarized.

Fuel cell type	**Alkaline (AFC)**	**Phosphoric Acid (PAFC)**	**Polymeric Exchange Membrane (PEMFC)**	**Molten Carbonate (MCFC)**	**Solid Oxide (SOFC)**
Electrolyte	Potassium hydroxide	Phosphoric acid	Polymer	Molten carbonates	Dense ceramics
Operation Temperature	50-120°C	180-210°C	60-100°C	550-650°C	550-1000°C
Transported ion	OH^-	H^+	H^+	CO_3^{2-}	O^{2-}
Expected efficiency	35-55%	35-45%	35-45%	45-55%	40-60%

Table 1. Fuel cell types and their characteristics

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Among all the fuel cells, the SOFC is the one where materials with a perovskite structure are the most applied and studied. Except for the sealant, all other components of the SOFC can potentially consist of perovskite ceramics. The most common materials found in the single SOFC configuration are yttria-stabilized zirconia (YSZ) in the electrolyte, Ni/YSZ cermet in the anode and strontium-doped lanthanum manganite (LSM) in the cathode. As can be seen, only the cathode is composed of a perovskite material. However, several scientific researchers have attempted to substitute the materials of the electrolyte and the anode with perovskites. In the case of the electrolyte, their main goal is to increase the ionic conductivity at lower temperatures and, for the anode, the aim is to include hydrocarbons as potential fuels, since Ni is often poisoned by fuels containing carbon. For the interconnects, the perovskite materials used in this component were gradually substituted with stainless steel, a much cheaper material that is capable of supporting the cell; recently, perovskite-coated stainless steel has arisen as a potential interconnect material. Also, a new group of perovskites has received attention for proton-conducting SOFC, where the electrolyte works with cationic conduction, although these cells have not yet achieved a performance similar to the conventional oxygen-conducting cells.

As can be seen, the materials used in SOFC must fit many requirements in terms of electrochemical properties. Besides, chemical and physical compatibility must exist between the materials for each component. As SOFC runs in high temperature, a chemical decomposition or a chemical reaction cannot occur during its operation and the chosen materials must have a similar thermal expansion coefficient in order to avoid the formation of cracks during thermal cycling. The high operation temperature of SOFC brings some advantages: increasing the activity of the electrodes and the conductivity of the components and favours ing the kinetics of the electrochemical reactions and gaseous exchange. However, reducing their operation temperature also has its advantages: decreased densification and thermal stress and, more importantly, diversifying the materials used in their components, since many perovskites are unstable at high temperatures. SOFCs that work below 800°C can be referred to as intermediate temperature SOFC (IT-SOFC).

Recent researches indicate that besides SOFC components, perovskite materials also have potential for application in PEMFC electrodes. However, this study still is very incipient. In the coming sessions, perovskites used in the SOFC components have been addressed separately and according to the components where it can be applied. Then, in one session, perovskites for use in PEMFC electrodes were discussed.

2. Cathodes for SOFC

The cathode, in an SOFC, is the interface between the electrolyte and the oxygen, its main functions are conduct electrons to the reactive sites and catalyze the reduction of the O_2 molecules. Therefore, the material applied in this component must have specific properties in the operation temperature such as electronic conductivity, catalytic activity, chemical and physical compatibility with the electrolyte and interconnect, as well as a porous and stable

microstructure. The choice of material depends mainly on the chemical composition of the electrolyte and the operating temperature.

As said, LSM is the most common material used in SOFC cathode due to its properties and compatibility with YSZ at high temperatures. Pure lanthanum manganite ($LaMnO_3$), with $A^{3+}B^{3+}O_3$ stoichiometry, is an intrinsic p-type semiconductor where the presence of cationic vacancies, primarily in the A sites, induces an oxygen nonstoichiometry. These vacancies are occupied by oxygen anions which lead to an oxygen excess that, in turn, causes the appearance of Mn^{4+} species in order to maintain the overall neutrality. The Mn^{4+}/Mn^{3+} ratio can be increased by doping both A and B sites, adding electronic holes in the structure and, hence, increasing the electronic conductivity. The most common is to dope the A site with bivalent cations such as Sr^{2+}, establishing the general formula $La_{1-x}Sr_xMnO_{3-\delta}$, according to the molar amount of strontium occupying lanthanum sites.

It is important to note that by doping the perovskites, different properties are influenced at the same time and, for application in SOFC, some of them can be disadvantageous. According to Shuk et al., doping A sites of lanthanum manganite improves its electronic conductivity and reaches its maximum at the composition $La_{0.45}Sr_{0.55}MnO_{3-\delta}$, Sr^{2+} is at 55% mol or $x = 55$, although this property also depends on the oxygen partial pressure. However, at this amount, the thermal expansion coefficient is too high, as observed by Florio et al., causing a physical mismatch with YSZ electrolytes. In amounts until 15% of strontium, there is a stabilization of the perovskite against YSZ, as reported by Yokokawa et al. but, despite this, the most common composition found in the literature is $La_{0.7}Sr_{0.3}MnO_{3-\delta}$. Doping the B sites increases the electronic conductivity and also the ionic conductivity, which is positive for the cathode performance; however, Tai et al. observed negative effects on the thermal expansion coefficient, derailing its use with YSZ electrolytes.

In the case of IT-SOFC, the temperature decrease impairs the performance of LSM, mostly because of the loss in catalytic activity. One alternative is to mix LSM with a fraction of YSZ, forming a composite cathode which can lead to better cathode/electrolyte adhesion and to an increase in the reactive sites. Mogensen et al. tested LSM/YSZ composite cathodes and showed an improvement in the catalytic activity. However, yet more promising is the use of mixed ionic electronic conductor (MIEC) perovskites. The use of this kind of material increases the amount of reactive sites, compensating the kinetic losses at temperatures below 800°C.

Doped lanthanum ferrites MIEC perovskites are a common example where the kinetic losses in the cathode, due to the low temperature, are compensated by an increase in the active reduction area. In the LSM perovskite, the B site doping with Co ions significantly increases the oxygen diffusion, and the substitution of Mn by Fe can enhance surface exchange processes. Based on this improvement, strontium- and cobalt-doped lanthanum ferrites (LSCF), with a general formula of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, have excellent electrochemical properties for use in IT-SOFC. However, the thermal expansion coefficient of LSCF is not compatible with YSZ electrolytes, hence these perovskites can only be used with compatibility layers or with other compounds as electrolytes. In an attempt to overcome the thermal expansion incompatibility with YSZ electrolytes, Ko et al. used a composite cathode consisting of LSCF and GDC (gadolinea-doped ceria), another common electrolyte material, and achieved good overall

performance, with a decrease of cathode polarization, for many hours of cell operation. However, other authors who tested cells with LSCF cathodes showed voltage loss with time, probably due to the thermal decomposition of this perovskite. Different amounts of dopants can be found in the literature and they report the high electronic and ionic conductivity of these compounds; they also show high activity for the O_2 reduction reaction.

Other compounds such as layered or double perovskites are also MIECs and potential materials for SOFC cathodes. These perovskites can have a structure coordinated by 4 or 5 oxygen atoms, and are typically $A_2BO_{4+\delta}$ or $AA'B_2O_{5\pm\delta}$. Some typical compositions of layered perovskites are $La_2NiO_{4+\delta}$ and $La_2CoO_{4+\delta}$, or with three cations $GdBaCo_2O_{5\pm\delta}$ and $PrBaCo_2O_{5\pm\delta}$. An interesting aspect of these materials is that they do not need to be heavily substituted to promote high oxygen diffusion. This characteristic is owed to its structure, where oxygen vacancies are concentrated in a plan between layers formed by cations, leading to anisotropic ion conduction due to a decrease in the activation energy for vacancy migration. Tarancón et al. compiled some values and showed that the oxygen self-diffusion coefficient at 500°C of $La_2NiO_{4+\delta}$ is 3.3×10^{-9} cm²/s, which is one order of magnitude higher than a typical LSCF/GDC composite cathode. The cation-ordered structure also plays a role in the oxygen surface exchange, which becomes a very important factor in cathodes with good oxygen diffusion, such as these.

Studies have also been carried out in order to determine the doping in layered perovskites; however, an undesirable increase in the thermal expansion coefficient was also observed. According to Kim et al., partial substitution with strontium to form $NdBa_{1-x}Sr_xCo_2O_{5+\delta}$ increases the specific area resistance of the cathodes and, relatively with pure layered perovskite, the doped layered perovskites showed a higher cathodic polarization due to the oxygen disorder introduced by dopant cations.

Cathodes for proton-conducting SOFC are MIEC perovskites based mainly on barium and iron and a very common general composition is $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$. The ideal cathode for this kind of SOFC should conduct protons simultaneously with oxygen and electrons. Cathodes with Co dopant cations exhibit excellent performance; however, it was found that these cobalt-containing perovskites usually have problems with thermal expansion, undesired reduction and evaporation of Co. Hence, other cations are proposed, such as Ni or Nb, in order to eliminate the Co from these compositions. Another approach, as proposed by Zhang et al., is to modify the proton-conducting electrolytes, such as $BaCe_{0.8}Sm_{0.2}O_{3-\delta}$, introducing transitional elements, such as Fe. However, despite of good cationic and anionic conduction, these modified cathodes present low electrical conduction and poor catalytic activity, and need to be further improved. All compositions of cathodes for proton conducting SOFC are commonly applied with electrolytes based on cerium oxide or even with other perovskites composition, that were addressed in the Electrolytes session.

Besides the composition, the final microstructure of the cathode is of great importance. It has been demonstrated that modifications in the microstructure of the cathode can have great impact on the overall fuel cell performance. The optimum cathode porous microstructure should enhance the gas flow and have a high surface area. It also must own a minimal mechanical resistance in order to prevent cracking and collapsing of the component.

3. Interconnects for SOFC

Interconnects provide an electrical connection between cathode of one individual cell to the anode of the adjacent cell in a SOFC stack and ensure a physical barrier between the reducing atmosphere (at the anode) and the oxidizing atmospheres (at the cathode). Therefore, the material to be used as interconnect has to present a series of important characteristics, which considerably reduces the candidate material for this component. High electrical conductivity, with values higher than 1 S/cm or, in terms of area-specific resistance, values below 0.1 $\Omega.cm^2$ are required with no ionic conductivity. Chemical stability at the operation temperatures and in reducing and oxidant atmospheres, considering that atomic interdiffusion can be a recurrent problem and reaction with sealant materials can also destabilize the perovskite. Thermal expansion compatible with anode and cathode. Enough mechanical strength to bear the load of the stack and support other components. Finally, in the case of the utilization of the heat generated by the SOFC in cogeneration, a thermal conductivity of at least 5 W/mK is necessary.

The most common perovskite compositions for interconnects are based on lanthanum chromite ($LaCrO_3$). In its structure, larger-sized cations, such as Ca^{2+} and Sr^{2+}, can substitute for La^{3+} while smaller cations, such as Ni^{2+}, Cu^{2+} or Al^{3+}, can replace Cr^{3+}. Mahato et al. demonstrated that the divalent cations, such as Ca^{2+} or Sr^{2+}, increase the conductivity of $LaCrO_3$. The divalent cations will act as acceptor dopants when residing at the trivalent (La^{3+} or Cr^{3+}) sites. Thus, in order to maintain charge neutrality, holes are created as a charge compensating defect, which consequently leads to p-type conductivity. Similarly, Fergus et al. attributed the addition of trivalent cations, such as Al^{3+}, to an increase in the p-type conductivity, but in this case, occurring mainly due to an increase in carrier mobility. It may be noted that the solubility of the divalent cations decreases upon increasing pO_2.

As with other perovskites, the dopant type and amount must be carefully chosen, because they often modify thermal expansion and chemical stability at the same time as electrical conductivity. For example, pure $LaCrO_3$ has a thermal expansion coefficient of 9.5e-6 K^{-1} and an electrical conductivity of 1 S/cm at 1000°C. With the addition of 20% of cobalt in the B sites, these values increase to 14.6e-6 K^{-1} and 15 S/cm, respectively. Whereas the addition of 10% of magnesium in the A sites keeps the thermal expansion stable with an increase in the conductivity of up to 3 S/cm. Another issue related to doped $LaCrO_3$ is its poor sinterability in air, which Anderson et al. attributed to the high vapor pressure of volatile chromium components. Hence, the use of CaO, for example, creates a liquid phase during sintering and enhances the sinterability of the $(La,Ca)CrO_3$ compound.

In the case of cells operating below 700°C, there is the possibility of using metallic interconnects, which brings great advantages. With metallic interconnects, the other components can be deposited as thin films layers which can diminish costs with raw material. Besides, it can lead to better mechanical strength with more efficient accommodation of thermal tensions during heating and cooling. However, even alloys with high antioxidant capacity are proven to suffer in extreme conditions where interconnects are employed, so a ceramic coating with conventional high-temperature interconnect materials is necessary. Brylewski et al. coated a ferritic stainless steel with a $La_{0.8}Sr_{0.2}CrO_3$ ceramic film and compared the oxidation rate with

an uncoated sample in wet atmosphere. In this study, it was shown that oxidation rates could be decreased with the use of conducting films; however, the authors also observed that chromium oxide could segregate from the perovskite to form undesired phases. Usually, the coating materials are perovskites, but recently, some spinel compositions have also been proposed.

4. Anodes for SOFC

The efficient use of hydrocarbons as fuels for SOFC is one of the most relevant issues concerning its current development, and their utilization depends mainly on the characteristics of the anode. Conventional SOFC anodes work only when pure H_2 is used as fuel; otherwise, the deposition of carbon in the catalyst surface poisons the cell and rapidly compromises its performance. Therefore, new materials are proposed in order to promote the direct oxidation of hydrocarbons, or even an internal reforming, considering the longevity of the SOFC lifespan. Many of these new materials are perovskites.

One potential perovskite for use in anodes is based on lanthanum chromite, a typical interconnect composition. Doping this compound on A and B sites enhances its activity towards methane oxidation. The presence of chromium at the B sites also improves redox stability and tolerance to sulphur; however, it costs the compound a decrease in the total conductivity. The use of strontium and manganese dopants helps to maintain the compound's stability and a typical composition is $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM). These dopant cations also enhance ionic/electronic conductivity and catalytic activity. The conductivity of LSCM can reach 38 S/cm at 900°C in air, but in the presence of H_2, this value can decrease to 1.5 S/cm at the same temperature.

The overall performance of LSCM anodes are compatible with the conventional Ni/YSZ cermets, showing better performance when methane is used as fuel. Also, if the fuel has sulphur impurities (H_2S), LSCM is more tolerant than the conventional cermet anodes. However, Zha et al. demonstrated the formation of sulphides within a few days when LSCM anodes operate with a 10%H_2S containing H_2 fuel. The authors also demonstrate that an increase in the Cr content on the perovskite lattice increases the number of impurity phases.

The use of cerium cations in the A sites of the LSCM lattice is also studied, with an expectation that increasing the catalytic activity would also increase the open circuit voltage (OCV) in cells fuelled with methane. The substitution with Ru in the B sites was studied due to its high catalytic activity in the steam reforming reaction with very good stability, but its application is limited by its very high cost.

Another proposed perovskite anode is based on lanthanum-doped strontium titanate, which shows good electrical conductivity in reducing atmospheres and reliable dimensional and chemical stability. Besides, it has good capacity at high temperatures to operate with CH_4 fuel without the detecting of carbon deposits formation and with high OCV, this can be a key factor in the SOFC fuel flexibility. According to Ruiz-Morales et al., anodes with the substitution of

Ti by Mn and Ga cations can put strontium titanates on par with conventional Ni-YSZ cermets when the cells are operating with H_2 fuel.

In order to enhance its electrocatalytic performance, a B site doping must be carried out and the choice of dopant must influence the redox properties and the conductivity. A potential B site dopant is chromium, for example, $La_{0.3}Sr_{0.7}Ti_{0.8}Cr_{0.2}O_{3-\delta}$ (LSTC). This composition has excellent stability and electrical conductivity; however, its catalytic activity is still very low, in order to be used as an SOFC anode, it is necessary to incorporate some catalytic materials.

5. Electrolytes for SOFC

In recent years, most of the efforts in SOFC development have been focussed on intermediate temperature solid oxide fuel cells (IT-SOFCs). The majority of them use a fluorite-structured oxide, CGO and/or YSZ in the electrolyte. In 1971, Takahashi et al. discovered that perovskite-structured materials possessed oxide ion conductivity; in 1992, Goodenough et al. reported that $LaGaO_3$ exhibited important ionic conductivity that was improved with different dopants being modified with strontium and magnesium in La and Ga sites (LSGM), respectively, showed higher oxide ion conductivity. However, these kinds of perovskites can only work under certain operating conditions, as they are not stable at low oxygen pressures. In CO and CO_2 atmosphere, they form carbonates; in reducing atmospheres, there is a Ga depletion along the grain boundaries degrading the material; and at high temperatures, they show an important solubility of Al, Ni, Co oxides. Therefore, this material (LSGM) is considered a good candidate as electrolyte for intermediate temperature SOFCs (IT-SOFCs). Since the 1970s, $LnAlO_3$ perovskites have been studied mainly taking into account their lower cost and high reduction and volatilization stability with respect to ceria and lanthanum galates; however, they exhibit problems of high electronic conductivity at high oxygen partial pressures and poor sinterability why they are constrained as an additive to composite solid electrolytes.

Most recently, there have been studies about ceramic materials that present protonic conductivity, and they are being employed as electrolytes in SOFC. In this respect, the first studies were presented by Iwahara et al. about $SrCeO_3$ materials. Some years later, the studies were directed mainly towards $BaCeO_3$ and $BaZrO_3$ perovskites due to of their higher proton conductivity, which was improved by Y doping (BCY and BZY, respectively). It is known that these barium cerate electrolytes exhibit both oxide ion and protonic conduction depending on the working temperature, changing from protonic to oxide ion transport when temperature are varied from 600°C to 1,000°C, whereas this behaviour has not been observed in strontium cerates. However, against this high conductivity is the very low chemical stability of $BaCeO_3$ materials, while Y-doped BaZrO3 with a little lower proton conductivity exhibit a great chemical stability, with the problem of resistive grain boundaries. Nevertheless, Y-doped $BaZrO_3$ could be more appropriate for its application in SOFCs.

For SOFC development, relatively high ionic conductivity of solid electrolytes is not the only requirement; an enhancement of durability is also needed. To improve both aspects, many

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works have been carried out, some propose to decrease the thickness of the electrolyte or using the named composite electrolytes (e.g., BCY and a molten salt phase).

6. Perovskites used in PEMFC

From a catalytic point of view, the use of perovskites has been principally reserved for high-temperature fuel cells due to the improved kinetics of reactions in electrodes with temperature. Nevertheless, the possible use of ABO_3 structures as catalysts in the replacement of noble metals is an idea that has been proposed in the early 1990s, based on the mixed oxide-ion/electronic conductivity and the low cost of these materials.

These structures are a potential alternative to Pt or Au in different air cathode-electrochemical cells, where the main drawbacks to the commercial viability of those devices are the low activity of oxygen-reduction and oxygen-evolution reactions (ORR and OER), respectively. In the proton exchange fuel cell field, most of the published materials with ABO_3 structures are directed towards the ORR. In alkaline solutions, they should exhibit comparable activities to those platinum-based metal catalysts, and this activity is supposed to be directly related with the electronic configuration of their surface cations. Among the different materials studied, lanthanum is the most common A cation because, combined with other transition metals, it has demonstrated ORR activity. B site substitutions with certain transition-metal elements should impact ORR rates (e.g., with Mn, Co and Ni) and should enhance the chemical and electrochemical stability of the perovskites (e.g., Cr and Fe) in alkaline solutions. Among lanthanum-based perovskites, $LaCoO_3$ has revealed itself to be interesting due to its large ORR current density and the positive shift shown in the onset potential. In addition, $LaNiO_3$-based oxides with B cation substitution, such as $LaNi_{1-x}Fe_xO_3$ (x = 0–0.2) are promising materials in alkaline media, with an improved catalytic activity related with the increase in the valence state of Ni with the B site substitution. On this basis, perovskites have been proposed to work in temperature ranging from 60°C to 200°C, such as cathodes in alkaline fuel cells. In this media, a 2-electron pathway mechanism has been described where the HO^{2-} created is further reduced. Good performance has been reported with different compositions in the $La_{1-x}A'_xBO_3$ system with A' = Ca, Sr and B = Co, Ni and Mn.

ABO_3 oxides are also an alternative to platinum in high temperature protonic exchange fuel cells (HT-PEMFC); in these devices, new membranes based on polybenzimidazole (PBI) impregnated by H_3PO_4 allows for an increase in the operation temperature to 130°C–200°C. The increase in the operation temperature gives a chance to Pt-free catalysts, where perovskites show improved chemical resistance under these temperatures. With this aim, $LaMnO_3$ and $LaSrMnO_3$ have been prepared by combustion synthesis with high electrical conductivity at 200°C and improved resistance towards H_3PO_4 corrosion.

Although perovskites have been proposed for noble metal replacement mainly on the cathode side of fuel cells, there are strong proposals that consider its use for the oxidation of alcohols in the anode of direct methanol fuel cells (DMFCs) working at 60°C–80°C. White y Sammells proposed, in a pioneer work, perovskite electrocatalysts in, among others, $SrMO_3$ (M = Ru,Pd),

$SmCoO_3$ and $SrRuMO_3$ (M = Pt, Pd) systems. They demonstrated activity towards direct methanol oxidation during cyclic voltammetry measurements that gave methanol oxidation currents up to 28 mA/cm² at 0.45 V vs. SCE. Following these results, $SrRuO_3$ was prepared by the combustion method as a high specific surface area catalyst with performance comparable to PtRu towards MeOH oxidation at potentials ranging from 0.25 to 0.35 V; nevertheless, the authors proposed the addition of Pt to enhance its catalytic activity. Similarly, strontium-substituted lanthanum cobaltite and copper-based perovskite nanoparticles were synthesized by the sol–gel method. Although the methanol oxidation onset potential was 0.03 V lower for LSCo than that for LSCu, an improved electrocatalytic activity for LSCu was found. This was attributed to the higher methanol adsorption capability of Cu ions and to the oxygen ion (O^{2-}) transport into the proximity of adsorbed methanol oxidation that facilitates the formation of intermediates at the reaction site.

Finally, perovskites are being reconsidered as anode catalysts in alkaline DMFC. In contrast to acid electrolytes, the use of an alkaline media improves the kinetics of the reaction while much less expensive catalysts, particularly oxides, could potentially be used. With this idea, $La_{2-x}SrxNiO_4$ ($0 \leq x \leq 1$) was prepared using the citric acid sol–gel route producing higher current densities and negligible poisoning by the methanol oxidation products than those already reported on other perovskite oxides.

7. Synthesis and processing of perovskites for fuel cells

There are several different methods to synthetize perovskites with suitable properties and morphology for use in fuel cells and the method chosen to obtain these materials can influence the final performance of the cell. The mixture of oxides through reaction-sintering was used in the beginnings of the obtaining of oxides with multiple cations, such as perovskites for application in fuel cells and. In some cases, it is investigated until nowadays. However, some disadvantages like compositional heterogeneity, grain growth and, in the case of electrodes, low specific surface area, led to the development and utilization of new methods.

Many of these novel methods were based on a chemical route, where a solution containing the desired cations is used in order to obtain the final multiple oxide. The use of the coprecipitation method can enhance the oxidation catalysis of cathode materials; however, it can be more difficult to carry out because of external influences during the precipitation reaction. Sol–gel is a very common method to synthesize perovskites and it has a relative ease of control and requires lower temperatures of crystallization, allowing the obtaining of a single-phase homogeneous microstructure.

Drip pyrolysis can produce electrode materials with a high concentration of surface reaction sites, but with a poor surface area. One of the most applied methods is the solution combustion synthesis, due to its simplicity and quickness to produce fine powders and the possibility to vary some parameters in order to modify the final morphology.

The processing of materials is one of the great challenges in the fabrication of SOFC devices and many different processing methods were applied and reported in order to fabricate SOFC

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components. The use of expensive methods such as RF sputtering were carried out at the end of the last century; however, more recently, researchers and industries in this field have a great tendency of choosing simpler and less expensive techniques. Methods like screen printing, tape casting and dip coating, which are based on the preparation of a suspension containing a previously synthesized powder, are common methods to fabricate electrodes and electrolytes for SOFC and allow the control of the microstructure, which is a very important factor since electrodes must be porous and electrolytes, dense.

Figure 2 shows two scanning electron micrographs of porous thin LSM films fabricated on YSZ substrates by dip coating. The LSM powders were obtained by combustion synthesis and different solvents (a and b) were used to prepare the dispersions. Even with sintering at the same temperature, it is possible to observe that slightly different microstructures were obtained, but a strong influence on the thickness of films can be seen.

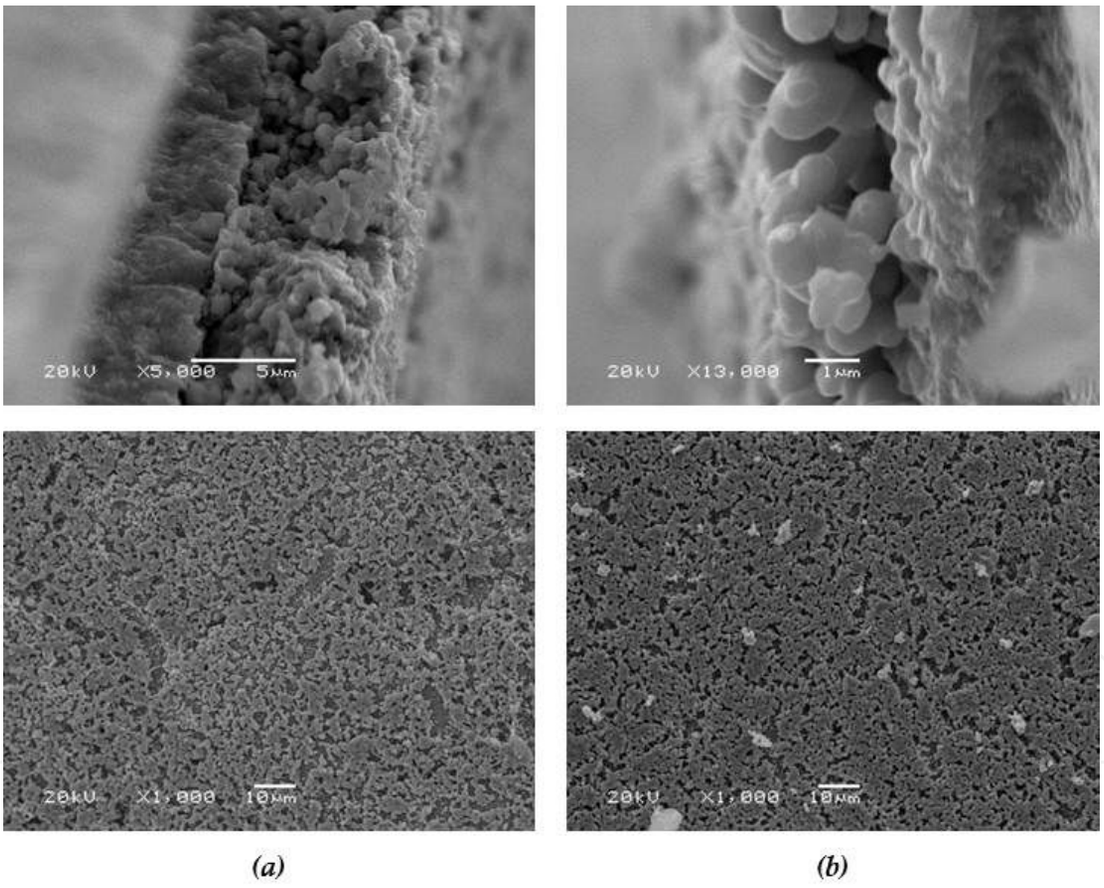


Figure 2. LSM films obtained on YSZ substrates by dip coating with different solutions.

Another approach to fabricate SOFC components is based on wet chemical techniques, where a solution is prepared and the perovskite crystallization reaction takes place on another SOFC component. The adaptation of sol–gel with dip coating or spray pyrolysis, for example, makes it possible to obtain the perovskite *in situ*. That is, already in a form of a final SOFC component

instead of obtaining the powder and then coating another surface with it. These are very promising techniques because they can also reduce the processing temperature in some cases.

8. Final considerations

Ceramic perovskite-type oxides have great potential for utilization in efficient energy conversion devices such as fuel cells, especially in SOFC and PEMFC. The research and development on PEMFC is more recent and, until now, has been restricted to electrodes whereas in SOFC it has been shown that the perovskites, together with processing, will definitely play a key role towards its commercialization. The vast variety of compositions obtained with doping elements in nonstoichiometric amounts allows the modification of properties in a wide range. Very often, the use of such elements interferes in more than one property and it is common to have deleterious effects in the overall component performance.

In SOFCs, many perovskite compositions have already been tested, particularly for cathodes, and the majority are based on one or more of these cations: La, Mn, Fe, Sr Cr, Co, Ni, among others. The catalytic activity and the mixed ionic and electronic conduction are the most sought characteristics for use in the electrodes while for electrolytes only the ionic conduction is desirable, whereas for interconnects, electronic conduction is the one. Of course, besides electrochemical properties, the compositions must have chemical and physical compatibility with each other when used in a fuel cell. This means that they should not react or decompose to form undesirable phases and the thermal expansion coefficient of all components must be similar in order to avoid the formation or propagation of cracks during operation and/or thermal cycling.

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