Novel materials for solid oxide fuel cell technologies: A literature review

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Abstract
This study aims to review novel materials for solid oxide fuel cell (SOFC) applications covered in literature. Hence, it was found that current SOFC operating conditions lead to issues, such as carbon surface deposition, sulfur poisoning and quick component degradation at high temperatures, which make it unsuitable for a few applications. Therefore, many researches are focused on cell performance enhancement through replacing the materials being used in order to improve properties and/or reduce operating temperatures. Most modifications in the anode aim to avoid some issues concerning conventionally used Ni-based materials, such as carbon deposition and sulfur poisoning, besides enhancing catalytic activity, once this component is directly exposed to the fuel. It was also found literature about the cathode with the aim of developing a material with enhanced properties in a wider temperature range, which has been compared to the currently used one: LSM perovskite (La$_{0.6}$Sr$_{0.4}$MnO$_3$). Novel electrolyte materials can have ionic or protonic conductivity, thus performance degradation must be avoided at several operating conditions. In order to enhance its electrochemical performance, different materials for electrodes (cathode and anode) and electrolytes have been assessed herein.

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Contents

Introduction ............................................................................................................................................. 26021
Materials ............................................................................................................................................... 26021
Electrode materials .............................................................................................................................. 26021
Anode ................................................................................................................................................. 26021
Cathode ................................................................................................................................................ 26024
Electrolyte .......................................................................................................................................... 26027
Oxygen ionic conductivity .................................................................................................................... 26027
Protonic conductors ............................................................................................................................... 26028
Discussions .......................................................................................................................................... 26030
Anode .................................................................................................................................................. 26030

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Introduction

Fuel cells are electrochemical devices that convert chemical energy into electrical energy with high efficiency from fuel oxidation, while at the same time reducing the amount of oxidant [1,2]. Chemical energy conversion into electricity is completely electrochemical, i.e. it occurs without any movement [3]. Among the various types of fuel cell, solid oxide fuel cells (SOFC) stand out on account of several aspects, such as having high energy conversion efficiency, fuel flexibility, high-quality exhaust heat, all-solid-state structure, high power density, low greenhouse gas emissions, reduced noise and environmental impact [1,4–6]. A SOFC consists of electrodes (anode and cathode) and an electrolyte. The anode receives the fuel and the cathode receives an oxidant, while the electrolyte allows oxide ions or protons to pass through it. Fig. 1 illustrates a general SOFC performance with an oxygen-conducting electrolyte fueled by hydrogen.

The first SOFC model was developed by Baur and Preis in 1937, which operates at 1000 °C. Ever since, most commonly used SOFC models operate at high temperatures (close to 1000 °C) [7]. This fact leads to material degradation at great speed and incurs high maintenance costs, thus hindering their economic feasibility [8], which can be overcome by lowering operating temperatures to an intermediate range (500–800 °C), once it can reduce their cost and improve stability [9].

A considerable hindrance to SOFCs operation temperature reduction is the low performance of traditional electrode materials working within this temperature range [10]. As regards electrolyte membrane materials, they may exhibit a pattern of behavior which is inappropriate to fuel cell application [11]. Studies have focused on seeking novel electrode and electrolyte materials that can withstand SOFCs operating conditions, while showing great performance at intermediate or even high temperatures simultaneously. Therefore, the present work aims to review some literary studies in which novel SOFC electrode and electrolyte materials have been introduced by focusing on enhancing fuel cell performance and/or reducing operating temperatures in order to provide a nice and simple access point and show some progresses by introducing novel SOFC electrode and electrolyte performance [13]. In order to make the equipment more commercially feasible, it is necessary to develop novel electrode materials that exhibit high electrocatalytic activity [14] and electrolyte materials that prevent detrimental reactions which lead to performance degradation [15] at lower operation temperatures. Its components should also have similar thermal expansion coefficients (TEC) in order to minimize thermal stress [16].

Electrode materials

Anode

Anode is the component which directly exposes the catalyst to fuels [5], therefore being one of the most important components of SOFCs [17], once it must catalyze the following oxidation reaction (Eq. (1)):

$$\text{H}_2 + \text{O}^{2-} = \text{H}_2\text{O} + 2e^- \quad (1)$$

Although conventional Ni-based anodes in SOFCs serve their fuel catalysis role due to excellent electrochemical properties and low cost [18], there are a few problems yet to be circumvented, such as nickel sintering, carbon surface deposition and sulfur poisoning when impure hydrocarbon fuels are used, thus leading to component degradation [5,19,20]. Fig. 2 illustrates these issues related to NI-YSZ anode behavior. Therefore, it is imperative to invest in the development of new materials with increased tolerance to sulfur poisoning and carbon deposition in order to produce SOFCs with more robustness and fuel flexibility [21]. Materials to be used for anode production must have a few important properties, such as high electrical conductivity, thermal expansion compatibility with the electrolyte material and high porosity [17].

Modified nickel-zirconia. Ni-YSZ cermet has been commonly used as SOFC anode due to its great features, such as high
conductivity, structural stability and compatibility with other materials in SOFCs [22]. However, once in contact with hydrocarbon fuels, either combined with steam or CO₂, Ni-YSZ cermet becomes susceptible to carbon deposition and contaminant poisoning, mainly by hydrogen sulfide (H₂S) [24,25]. The addition of other materials to it can circumvent these undesirable properties and enhance fuel cell stability [23]. Therefore, these modifications have been investigated by several authors in literature.

Song et al. [22] studied the effects of adding alumina (Al₂O₃) to Ni-YSZ anodes. The compounds were produced by a two-step sintering method, which has been detailed by the authors. Commercial YSZ and NiO powders were used as starting materials, being alumina the process additive. Al₂O₃–NiO (0, 0.36, 0.72 and 3.6 wt% of Al₂O₃) and Al₂O₃–YSZ (0, 0.44, 0.88, 4.4 wt% of Al₂O₃) were prepared with the same volume fractions of alumina. A three-layer anode was produced by both materials besides the NiO-YSZ layer.

The synthesized materials were analyzed, whose results were satisfactory as regards increased SOFC performance. It was observed that the addition of Al₂O₃ to NiO prevented an overgrowth of NiO grains, which increased electrical conductivity and decreased anode activation polarization. With respect to the reaction between NiO and Al₂O₃, it was noted an acceptable amount of NiAl₂O₄ when approximately 0.2 wt% of alumina was used. These properties enhance both the stability and conductivity (about 39% higher than the one with no alumina) of anodes, thus leading to SOFC performance enhancement. It was found that an optimum value for alumina wt% was 0.2 when electronic conductivity reaches approximately 1300 S cm⁻¹ in a humidified H₂ atmosphere, and open circuit power density should be 321 mW cm⁻². These results were also noted in an investigation conducted by Wang et al. [26], in which the addition of alumina to a Ni-YSZ anode increased cell performance and coking resistance. However, a large amount of Al₂O₃ sharply reduced conductivity (17.3% of reduction for 2.68 wt% alumina), thus indicating that it is an optimum wt% value. In addition, the equipment has stably operated for 130 h at 750 °C.

The addition of silver (Ag) to a Ni-YSZ anode has been studied by Wu et al. [23]. Commercial NiO and YSZ were adopted to produce the anode by the co-tape casting method, while the electroless silver plating (ESP) method was used to introduce Ag into the anodes, with Ag(NH₃)₂OH as starting material. Their SOFC was fueled by H₂, CH₄ and C₂H₆. A single phase structure was formed, thus indicating structural stability in its application. The addition of Ag showed no effect on open circuit voltages and it enhanced anode electrochemical performance due to its higher ion conductivity, greater power density values and sharp decline in carbon deposition when using a hydrocarbon fuel. A material with 0.20 wt% of silver content achieved better results on account of enhancing maximum power density to 463 mW cm⁻² for cells fueled by H₂, 251.3 mW cm⁻² for those fueled by dry CH₄ and 379 mW cm⁻² for the ones fueled by dry C₂H₆. Hence, it can be concluded that Ag is a promising material to improve SOFCs performance at high operating temperatures.

By focusing on enhancing the Ni-YSZ anode tolerance to sulfur, Sengodan et al. [24] infiltrated a BaZrₓCe₀.₇Y₀.₁Yb₀.₂O₃₋ₓ (BZCYYb) into the starting material, due to being known as a high conductivity material [27]. BZCYYb was obtained by the citrate method, in which Ba(NO₃)ₓ, ZrO(NO₃)₂, Ce(NO₃)₃, Y₂O₃ and Yb₂O₃ are the starting materials. The analyses showed good material stability and no reaction between BZCYYb and YSZ at up to 950 °C. The anode presented no performance degradation at 700 °C while operating over 500 h, being fueled by H₂ and containing 30 ppm H₂S. The material was manufactured by a simple and economic method, which enabled operation under both oxidizing and reducing conditions, thereby making it feasible for SOFC anode applications.

Choi et al. [28] studied the addition of niobium oxide (Nb₂O₅) to a Ni-YSZ anode so as to assess sulfur tolerance through reactive sputtering. Nb₂O₅, which was obtained by evaporating the Nb(HC₂O₄)₅ solution, was deposited on the top of the Ni-YSZ surface. The tests were carried out when cells were fueled by H₂ at temperatures below 700 °C until it reached performance stabilization. Then, H₂S (50 ppm) was added together with H₂ in order to assess surface sulfur tolerance. Nb₂O₅ coating rendered a power density peak increase of 113% (23–49 mW cm⁻²) and conductivity of 50 S cm⁻¹ due to its stable catalytic activity and conductivity under these operating conditions. Under a 50 ppm H₂S atmosphere, the cell current density has remained stable for over 12 h, even with an initial drop. Enhanced cell conductivity, power density and stability under a H₂S atmosphere showed that Nb₂O₅ might be a good replacement as anode material, although its performance needs to be enhanced.

Ce–Zr–O systems. Among several types of materials, there has been an increased use of ceria-derived catalysts due to their desirable features, such as high oxygen storage capacity, morphology stability and redox properties [19,29]. Under reduction conditions, ceria-based anodes present properties that contribute to fuel cell electrochemical reactions [30]. The addition of Zr to CeO₂ compounds increases both the materials...
catalytic activity and thermal stability [31]. Ce−Zr−O systems have been investigated as SOFC anode due to these properties. Redox and catalytic properties of Ce0.8Zr0.2O2−δ with x = 0.10, 0.25, 0.50, 0.75 and 0.90 (CZ10, CZ25, CZ50, CZ75 and CZ90, respectively) were investigated by Kearney et al. [31]. The powders were synthesized by a citrate complexation method. The samples showed a single-phase structure. Test results have revealed that CZ75 has the highest catalytic activity and CZ90 has the lowest, which indicates that x = 0.75 is the optimal value for this feature. The CZ75 reduction occurred within 666−690 °C, which is a suitable property for an intermediate temperature SOFC. For future works, it would be interesting to evaluate electrochemical performance parameters.

Based on Ce0.8Zr1.2O2 with x = 0.10, Zimicz et al. [32] have studied the effect of a different synthesis method to produce a Ce−Zr−O system with Ce0.8Zr0.1O2 nominal composition, which has been obtained through a gel-combustion method and following stoichiometric routes with glycine, lysine and alanine as fuels. It was noted that the stoichiometric synthesis process produces solids with smaller particle sizes, lower agglomeration and higher oxidation activity. These are better properties if compared to non-stoichiometric processes studied in their previous work [29]. In addition, the glycine combustion method presented higher performance when operating at intermediate temperatures, which makes it suitable for IT-SOFC applications. The process to obtain the material and the used fuel directly influences its features, such as morphology and catalytic performance.

Furthermore, Feng et al. [19] studied Ce0.8Zr1.2O2 composition with x = 0.5. Stoichiometric amounts of Ce(NO3)3 and ZrO(NO3)2 were mixed with other elements through a modified microwave-induced method. No secondary phases were found in their structure. As regarding electrochemical performance, the material presented acceptable power densities with H2 as fuel, reaching a maximum value of 508 mW cm−2 at 800 °C, but it decreased to 218 mW cm−2 at 700 °C. It also exhibited lower polarization resistance and higher resistance to carbon deposition if compared to conventional Ni-based materials. Therefore, it presented good properties to be used as SOFC anode, especially at temperatures close to 800 °C.

LnSTM (Ln: La, Nd and Sm) perovskites. It is known that Ti has excellent behavior under reduced atmosphere [20]. According to Jeong et al. [33], the addition of Ti or Cr and Mn or Fe to the B-site of complex perovskites increases both their structural stability and catalytic activity, respectively. Once B-site composition is consolidated, it becomes interesting to investigate the material’s behavior with different elements in its A-site. Therefore, several perovskite oxides have been investigated with regard to elements replacement as SOFC anode [34].

LnSTM perovskites were studied by Jeong et al. [33] and Kim et al. [34] with three different chemical compositions: La0.5Sr0.5Ti1−xMnxO3−δ (LSTM), Nd0.5Sr0.5Ti0.8Mn0.2O3−δ (NSTM) and Sm0.5Sr0.5Ti0.8Mn0.2O3−δ (SSTM). Each composition has been synthesized and investigated as potential anode materials for SOFC application. Both authors synthesized the compounds by the glycine nitrate process (GNP) by using Sr(NO3)2, Mn(NO3)2, [CH3CH(OH)CO2NH4]2Ti(OH)2 and Ln(NO3)3 (Ln = La, Nd and Sm) as starting materials. Single-phase structures were observed in both works.

By testing the chemical behavior of compounds in the same atmosphere and weight ratios, Jeong et al. [33] observed no chemical reactions between these materials and commonly used electrolyte materials, such as 8-YSZ and CGO91 at up to 1500 °C, which indicates that they are suitable to be used as anodes in high temperature SOFCs. Sm smaller ionic radius in comparison with those of Nd and La leads to changes in SSTM, such as a more distorted structure and higher onset temperature in Ln0.5Sr0.5Ti0.8Mn0.2O3−δ oxide systems. As regards electrical properties, the results indicated that LSM reaches conductivity values of 4.20 and 2.19 S cm−1 in air at 900 and 650 °C, respectively. Kim et al. [34] also indicated that LSM has the highest electrical conductivity, once Nd addition leads to a metallic behavior in some Ti molecules. It was noted better operation performance in LSM and SSTM, while LSTM retained a considerable amount of oxygen, i.e. an undesirable feature for anodes.

Nickel-free double perovskite. Although Ni-based composites have excellent performance as SOFC anodes, they are hardly affected by carbon surface deposition and sulfur poisoning [5,35]. Consequently, several studies have been conducted with the aim of developing nickel-free compounds for being used as SOFC anodes.

Ding et al. [5] proposed a new material with a nickel-free double perovskite structure: Sr2FeNb2O9−δ (SFNM20). A solid state reaction with stoichiometric ratio among SrCO3, Fe2O3, Nb2O5 and MoO3 powders mixed with acetone has been produced in order to synthesize the compound. It was observed a single-phase double perovskite structure. Under reduced atmosphere, the material presented chemical stability. The electrical conductivity test showed satisfactory results at an intermediate temperature, reaching 5.3 and 2.5 S cm−1 in 5% H2 at 800 and 600 °C, respectively. As regards cell performance, SFNM20 presented high coking resistance, high performance, redox stability and high catalytic activity. These are great features for the presently proposed application, thus leading to the assumption that SFNM20 is an alternative material as a nickel-free anode in SOFCs.

By investigating another option of nickel-free double perovskite, Sun et al. [35] and Sengodan et al. [36] synthesized Pr0.5Ba0.5Mn1−xMo2O6−δ (PBM03) and PrBaMn2O6−δ (PBM05), respectively. PBM03 was produced both in its pure and doped form with 10 mol% Mo (Mo-PBM03) by the sol-gel method. The doped material had the following composition: Pr0.5Ba0.5Mn1−xMo2O6−δ. PBM05 was synthesized by a two-step sintering method explained by the authors in their work. Both materials presented single-phased structures.

The addition of Mo to PBM03 enhanced the material’s performance as anode, once Mo increased maximum power density, reaching 600 mW cm−2 (22% higher than that of the undoped material), catalytic activity and electrical conductivity (101 S cm−1 in air at 800 °C), by reducing its area specific resistance (ASR) by 33% and 23% at 800 and 850 °C, respectively, and increasing the number of oxygen vacancies in material’s structure. The performance parameters were also satisfactory for undoped PBM03, although being less than
those for the doped material. PBMeOS exhibited high performance stability up to 850 °C, with conductivity values of 8.16 and 9.15 S cm⁻¹ in 5% H₂ and air, respectively. A peak power density value of 570 mW cm⁻² was reached, both without any catalysts and with no degradations due to carbon surface deposition in up to 500 h operation. Consequently, both doped and undoped materials are desirable for SOFC anode applications.

Modified Ni-SDC. Nickel-samaria doped ceria (Ni-SDC) has been investigated as SOFC anode due to its high power densities, moreover, ceria is a good sulfur sorbent at high temperatures given that it reacts with H₂S [37,38]. Therefore, this element can soften the undesirable properties of Ni in this application, which has been studied in order to modify Ni-SDC composition and enhance SOFC performance.

MnO and Co were selected by Zhao et al. [37] to modify Ni-SDC composition. Ce₀.₈₅Sm₀.₁₅O₁.₉₂₅ (SDC) powders were produced by the Ethylenediaminetetra-acetic acid (EDTA) – citrate method, by using Sm(NO₃)₃ and Ce(NO₃)₃ as starting materials. MnₓCo₁ₓO₄ (MCO) powders were synthesized by using Mn(NO₃)₂ and Co(NO₃)₂ as starting materials, also by EDTA-citrate method. As regards their properties, MCO-modified anodes registered an increase in up to 55% of peak power densities (1756 mW cm⁻² at 700 °C), as well as higher porosity and better electrochemical performance. However, the modified anode presented worse stability than Ni-SDC, which is mainly due to a higher carbon deposition rate that can be assigned to its higher catalytic activity. Up until recently, this material is a great alternative to intermediate temperature SOFCs, although it was stated that its properties could be optimized if the proportion of MCO in the modified Ni-SDC anode were changed.

Other options of oxides have been investigated by Qu et al. [39], with the aim of modifying Ni-SDC anodes. In their study, CaO, BaO, SrO, MgO and La₂O₃ were added to the Ni-SDC compound. The material was produced by mixing SDC, NiO and the oxide powders with ethanol, with subsequent drying at 80 °C. The anodes with the addition of Ba, Sr, Mg and La showed secondary phases in their structure, even in reduced atmosphere. Ni-SDC mixed with Ca, however, presented chemical stability. SrO- and MgO-modified anodes showed increased carbon deposition rates if compared to conventional Ni-SDC. CaO- and BaO-compounds, however, exhibited reduced carbon deposition rates. Although the oxides introduced reduced conductivity (1936 and 1600 S cm⁻¹ for CaO- and BaO-compounds at 500 °C, respectively), power density was the highest (1009 mW cm⁻²) for CaO-modified anode at 700 °C. Under the same conditions, CaO-modified anode has operated stably for 70 h at 650 °C, while it lasted 1.2 h for unmodified Ni-SDC anode. Once great cell performance and CaO low cost have been achieved, Ni-SDC-Ca is a promising material for intermediate temperature SOFC applications.

The effects of Cu addition to Ni-SDC were investigated by Zhu et al. [40]. SDC powders were obtained by the glycine nitrate process (GNP) by using Ce(NO₃)₃ and Sm₂O₃ as starting materials, while Ni₁₋ₓCuₓO powders were synthesized, also by the GNP method, with Ni(NO₃)₂ and Cu(NO₃)₂ as starting materials. The reaction produces Ni₁₋ₓCuₓ-SDC with x ranging from 0 to 0.15. The materials exhibited no impurity phases in their structure. Electrical conductivity and porosity increased with higher x. However, conductivity started to decrease when x = 0.15 due to the material’s porosity. When x = 0.10, the compound exhibited maximum power density (483 mW cm⁻²) and conductivity (approximately 6000 S cm⁻¹ in reduced atmosphere at 700 °C), which makes it a promising anode material for intermediate temperature SOFCs.

Cathode
When it comes to SOFC technology, cathodes are of great importance due to their catalytic role in the following oxygen reduction reaction (Eq. (2)):

\[
\frac{1}{2}O_2 + 2e^- = O^{2-}
\]  

(2)

Cathode materials must improve fuel cell performance by reducing power losses and providing great electrical contact between interconnected components and the electrode [41]. Therefore, they must present features such as good catalytic activity, high electrical conductivity, porosity and stability, while at the same time being unreactive with the electrolyte material [41,42]. Currently, a commonly cathode material that can be used at high temperatures is LSM (La₀.₈Sr₀.₂MnO₃) along with YSZ electrolyte. However, due to its high activation energy and increased polarization resistance in lower temperatures, LSM can decrease SOFC performance at lower operation temperatures [14,43]. In addition, the material can react with YSZ electrolyte at temperatures over than 1100 °C [44]. LSM behavior is illustrated at Fig. 3. For the development of commercially-viable SOFCs, it is necessary to produce new cathode materials with greater electrochemical performance and robustness [9].

LaSr perovskites with GDC. The currently used LSM/YSZ composite cathode material has been conventionally sintered at low temperatures, which can lead to structural problems when exposed to high temperatures required to obtain a dense electrolyte layer [47]. The use of an inhibitor in the cathode material’s composition has been studied by the same authors for direct carbon fuel cells [48], in which (La₀.₇Sr₀.₃)₀.₉₅MnO₃₋ₓ (LSM) – Gd₀.₆Ce₀.₄O₂₋ₓ (gadolinium-doped ceria, GDC) were investigated. The same compound (GDC) was added by Liu et al. [49] to a La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃ (LSCF) perovskite, also focusing on increased operational performance.

![Fig. 3 – LSM cathode behavior at different temperatures](image_url)

LaSr perovskites with GDC.
For SOFC technology development, Rehman et al. [47] have studied a LSM/YSZ composite with GDC as sintering inhibition agent. LSM was sintered by a solid state reaction between La$_2$O$_3$, SrCO$_3$ and MnO$_2$, which exhibited single phase. Thereafter, the compound was mixed with YSZ and GDC, which is the product of a mixture of Gd(NO$_3$)$_3$ and Ce(NO$_3$)$_3$. The GDC-coated LSM/YSZ material presented much better porosity if compared to LSM/YSZ. As regards thermal expansion, there were no significant changes. At lower temperatures, the cell’s electrochemical performance decreased, which indicated capability of high temperature operation. 215 mW cm$^{-2}$ maximum power density was reached. In a nutshell, GDC addition to LSM/YSZ resulted in better features for SOFC technology application, although its performance should be improved.

Important properties of LSCF-GDC cathodes have been investigated by Liu et al. [49]. LSCF was synthesized by dissolving La(NO$_3$)$_3$, Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ in distilled water, and then impregnated onto the GDC. A single phase structure indicated stability between LSCF and GDC in temperatures of up to 750 °C. However, tests have revealed a coarsening of LSCF particles, thus leading to ohmic losses and agglomeration, which affect electrical contacts between particles. To avoid performance degradation, the authors impregnated MgO and LaNi$_{0.6}$Fe$_{0.4}$O$_3$ (LNF) as additive to improve structural stability. The additive inhibited the growth of LSCF particles, thence enhancing electrochemical activity and stability.

A$_2$BO$_{4+d}$ composites. Materials with an A$_2$BO$_{4+d}$ structure (A = rare earth; B = Cu, Fe and Ni) have been investigated due to their potential use as cathodes in fuel cells. Among these compositions, lanthanum nickelates exhibit extremely high oxygen surface exchange coefficient [52], while Pr$_7$CuO$_4$-based composites present compatibility with commercial electrolyte materials [50], which makes them feasible for commercial applications. Lanthanum nickelates with several La contents have been studied by Ferkhi and Yahia [53], while Kolchugin et al. [52] and Sharma et al. [54] have investigated calcium- and praseodymium-doped lanthanum nickelates, respectively, with different content. Pr$_7$CuO$_4$-based composites were studied by Li et al. [50] and Chiu et al. [51].

Ferkhi and Yahia [53] proposed lanthanum nickelates La$_2$$_{x}$NiO$_{4+d}$ (LXNO) with $x$ varying between 0.01 and 0.05 as cathode materials for SOFC. LXNO powders were sintered by mixing La$_2$O$_3$ and Ni(NO$_3$)$_2$ by the citrate method. It could be noted that L3NO and L5NO cathodes reacted with YSZ electrolyte at 900 °C, which is an undesirable feature for such application. Although an increase in lanthanum percentage decreases the material’s pore diameter, the four configurations presented excellent porosity. The L1NO showed the lowest activation energy and highest porosity, which makes it suitable for intermediate temperature SOFC. The authors have concluded that La$_2$$_{0.99}$NiO$_{4+d}$ is a promising material for lowering SOFCs operating temperature, thus leading to less material degradation and longer lifetime.

La$_2$_xCa$_3$Ni$_{0.4+d}$ (LCNOx), a lanthanum nickelate doped with Ca, has been investigated by Kolchugin et al. [52], with $x$ varying from 0 to 0.4. The powders were produced by the two-step solid state reaction method in which La$_2$O$_3$, NiO, CaCO$_3$ and SrCO$_3$ were the starting materials. A single-phase structure was observed. Increased Ca content led to both higher electrical conductivity values and lower electrochemical electrode activity. LCNO4 presented the highest conductivity at 700 °C, reaching approximately 110 S cm$^{-1}$ and becoming stable in up to 900 °C. All compounds exhibited chemical stability at up to 800 °C. Future works should focus on enhancing electrode activity so as to make the material suitable for SOFC cathode application.

Another option for doped lanthanum nickelates have been investigated by Sharma et al. [54]. A La$_{2-x}$Pr$_x$NiO$_{4+d}$ ($x = 0, 0.5, 1$ and $2$) structure has been prepared through material deposition on CGO (Ce$_{0.9}$Gd$_{0.1}$O$_{2-δ}$) by the electrostatic spray deposition method (ESD), being La(NO$_3$)$_3$, Pr(NO$_3$)$_3$ and Ni(NO$_3$)$_2$ the starting materials. The replacement of La for Pr resulted in a single-phased solid solution with no impurities, thus showing initial chemical stability.

Unlike Vibhu et al. [55], who had investigated the same structure and noted a completely dissociation of the material into PrNiO$_{2.5}$, Pr$_4$NiO$_{4+d}$, and Pr$_2$O$_3$, the authors found no secondary phase under 700 °C after 30 days for $x$ ranging between 0 and 1. However, a decomposition was noted when temperature was increased to 800 °C for $x = 1$ and $x = 2$ for both temperatures. Regarding electrochemical performance, their cell exhibited maximum power density value of 438 mW cm$^{-2}$ and low degradation in up to 500 h operation. The polarization resistance decreased by increasing Pr content. In conclusion, La$_{2-x}$Pr$_x$NiO$_{4+d}$ with $x = 1$ presented optimal features.

Perovskite materials with Ni and Fe in the A-site structure have been proposed by Kornyshova and Irvine [56] as possible replacements for SOFC electrode applications. Their studied composition was (100 - $x$) La$_{0.95}$Ni$_{0.2}$Fe$_{0.8}$O$_{3-x}$CeO$_2$ (LNFCx) which was added to CeO$_2$ in order to enhance the material’s ionic conductivity. La$_{0.95}$Ni$_{0.2}$Fe$_{0.8}$O$_{3}$ and CeO$_2$ were added and further blended by chemical mixing, followed by a calcination process. The obtained ratios were $x = 2, 5, 8, 10, 25, 50$ and $75$ mol%. The material’s structure exhibited three phases with $x$ being up to $10$ mol%, in which the NiO phase is very small in comparison with the two other ones. These compositions also presented great conductivity at temperatures of over 300–350 °C up to 900 °C. When $x ≥ 25$ mol%, the structures were more complex, i.e. they had at least 5 different phases. However, LNFC25 exhibited a metallic conductivity behavior at temperatures above 550 °C, while LNFC50 and LNFC75 exhibited a semiconducting behavior at high temperatures. By the data analysis, the authors concluded that the materials can be used as SOFC cathodes, once they are in the range of 2 mol% ≤ $x$ < 50 mol%.

Li et al. [50] studied a Pr$_x$CuO$_4$ (PCO) material with the addition of Ce$_{0.5}$Gd$_{0.5}$O$_{1.95}$ (CGO) in order to increase cathode electrochemical performance. PCO powders were obtained by the glycine nitrate process (GNP) by using Pr(NO$_3$)$_3$ and Cu(NO$_3$)$_2$ as starting materials. The PCO was then mixed with CGO, which resulted in PCO-xCGO, where $x$ represents the wt % of mixed CGO. By using 10, 20, 30, 40 and 50 wt% CGO, the authors tested the materials as cathodes in SOFC. The addition of CGO to the PCO cathode has significantly improved its electrochemical performance. It was noted that cathode polarization resistance varied at 700 °C, being the lowest value...
when CGO content was 40 wt%. In addition, PCO-40CGO exhibited good porosity, thermal compatibility and no reaction with CGO electrolyte, which makes it suitable for SOFC cathode application.

The same method has been used by Chiu et al. [51] to synthesize PCO powders. However, the authors have mixed PCO with several wt% of samarium doped ceria, Sm$_{2}$CO$_{3}$O$_{1.9}$ (SDC20). The material exhibited chemical stability at temperatures of up to 1000 °C, which is suitable for high temperature SOFC application. As regards cathode performance, the 10 wt% compound presented the lowest polarization resistance, 18% lower than pure PCO cathode, and the highest power density value, i.e. 347.5 mW cm$^{-2}$, which is 22% higher than PCO with 30 wt% SDC. For this study, 10 wt% of SDC20 was selected as optimal value.

LnBaCo$_{2}$O$_{4.4}$ double perovskite. Cobalt-based materials with LnBaCo$_{2}$O$_{4.8}$ (Ln = La, Pr, Nd, Sm, Gd and Y) composition have interesting features as cathode materials, such as high oxygen surface exchange coefficient and high electrical conductivities. However, cobalt-based compounds also present high thermal expansion coefficient if compared to commonly used electrode materials [57,58]. The addition of elements to their structure can attenuate this property and enhance cathode performance, therefore it has been studied by several works, e.g. Xia et al. [57] and Fu et al. [58] studied LnBaCo$_{2}$O$_{4.8}$ with Ln = Sm and Ln = Pr, respectively, to be used as intermediate temperature SOFC cathode.

Ni doping on the Co site in SmBaCo$_{2-x}$Ni$_x$O$_{5.1}$ (SBCNx) with x varying from 0 to 0.5 at intervals of 0.1, has been investigated by Fu et al. [58]. The material presented chemical stability with Ca doping decreased the electrical performance, Ca doping decreased the electrical conductivity, thus reaching 51.92 S cm$^{-2}$. Ni doping on the Co site in SmBaCo$_{2-x}$Ni$_x$O$_{5.1}$ (SBCNx) with x varying from 0.1 to 0.4 has been studied by Fu et al. [58]. The material presented a highly dense single-phase structure, while x = 0.1 showed good power density values (453 mW cm$^{-2}$), which indicated that it is a promising candidate as cathode for intermediate temperature SOFCs application.

Cobalt-free perovskite compounds. As mentioned previously, there are some disadvantages of cobalt-based compounds, such as high thermal expansion coefficients, which leads to an incompatibility with other SOFC components, and elevated cost [43,61]. Therefore, cobalt-free compounds should be developed with greater performance as cathode material. Kong et al. [62] investigated cobalt-free perovskite oxides NdBaCu$_{2}$O$_{5.8}$ (NBCO) and NdBa$_{2}$Sr$_{2}$Cu$_{2}$O$_{8.8}$ (NBSCO) as cathode materials for intermediate temperature SOFCs. Both material powders were synthesized by the citrate-EDTA sol-gel method, in which Cu(NO$_3$)$_{2}$, Ba(NO$_3$)$_{2}$, Sr(NO$_3$)$_{2}$ and Nd(NO$_3$)$_{3}$ were mixed with Nd$_2$O$_3$, which had been previously dissolved in nitric acid. The compounds showed no impurities in their structures. In contact with SDC electrolyte, both materials exhibited no chemical reactions at temperatures of up to 1000 °C, as well as a satisfactory thermal expansion coefficient. However, the Sr-doped NBCO presented higher electrochemical activity of oxygen reduction reaction and higher electrical conductivity, thus reaching 51.92 S cm$^{-1}$ at 545 °C. This work has indicated that both NBCO and NBSCO can be used as SOFC cathode materials at intermediate temperatures, although NBCO has greater features for such application.

A novel cobalt-free compound NdBaFe$_{2-y}$Mn$_y$O$_{5.8}$ (x = 0.0–0.3) has been studied by Mao et al. [61]. The materials were produced by the citric acid-nitrate process which used MnO, Nd$_2$O$_3$, Ba(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ as starting materials. The compounds presented double-perovskite phases with no impurity. Conductivity increased with increased Mn content in up to x = 0.1, reaching 114 S cm$^{-1}$ at 550 °C, and then it suffered a reduction of up to x = 0.3. Tests indicated a chemical compatibility between the material and the BZY electrolyte. The compound with x = 0.1 showed good power density values (453 mW cm$^{-2}$), which indicated that it is a promising candidate as cathode for intermediate temperature SOFCs application.
Among cobalt-free perovskites, SrFeO\(_3\)-based systems present high oxygen reduction reaction activity and low cost. Thence, Jiang et al. [63] has investigated Sr\(_2\)FeO\(_3\) as cathode for intermediate temperature SOFCs. The material was synthesized by the citrate-EDTA method using stoichiometric amounts of Sr(NO\(_3\))\(_2\) and Fe(NO\(_3\))\(_3\), and no impurities were detected in its structure. The thermal expansion coefficient showed great values if compared to other SrFeO\(_3\)-based perovskites found in literature. As regards electrochemical performance, the ASR values were higher than those of other SrFeO\(_3\)-based perovskites, although they are still lower than those of conventional cathode materials. The material presented low oxygen reduction reaction (ORR) activity due to its crystal structure. By calcining the Sr\(_2\)FeO\(_3\)-based solid precursor under an oxygen deficient atmosphere at 900 °C, the ORR activity was increased by 4–8 times if compared to single-phase Sr\(_2\)FeO\(_3\), thus indicating that it is an attractive SOFC cathode.

Alkaline earth metal free perovskites. Materials with perovskite structure derived mainly from LnFeO\(_3\), LnCoO\(_3\), LnNiO\(_3\), LnMnO\(_3\) and LnCrO\(_3\) [64]. The addition of alkaline earth metals to their structure increases the number of oxygen vacancies, thus improving their initial performance [65]. However, in addition to cobalt drawbacks, alkaline earth metal elements have also some disadvantages that should be taken into account. These materials may undergo Cr-poisoning (especially Sr) and surface segregation in contact with other elements, which reduce their long-term performance [64,66–71]. Then, perovskites should be studied without alkaline earth metals.

A double B mixed perovskite structure with Pr\(_2\)Ni\(_4\)Fe\(_6\)O\(_{15}\)-based composition has been investigated by Rebello et al. [72]. The material powders were synthesized by the solid state reaction method, being Pr\(_2\)O\(_3\), NiO and Fe\(_2\)O\(_3\) as the starting compounds. Afterwards, it presented a single phase structure. The electrical conductivity of the material was enhanced at intermediate temperatures (between 600 and 800 °C), than there was a little decrease until it stabilized in up to 1000 °C. Regarding thermal expansion, Pr\(_2\)Ni\(_4\)Fe\(_6\)O\(_{15}\)-based exhibited a TEC value close to those of conventional electrolyte materials, which makes it a good candidate for being used as SOFC cathode.

La\(_2\)ZnMnO\(_4\) has been studied by Coronado et al. [73] as a candidate for SOFC cathode, once double perovskite oxides have shown great properties such as high conductivity and permeability. The compound was produced by the citrate method, with La\(_2\)O\(_3\), ZnO and MnCO\(_3\) as precursors. Until 600 °C, it presented a stable structure, while a partially reduction of Mn\(_4^+\) to Mn\(_3^+\) could be noted for temperatures of over 600 °C. The material exhibited no abrupt TEC changes in up to 700 °C, being its maximum value for the reduced phase. However, both phases presented TEC values within the range of conventional SOFC components. Although the electrical conductivity values were not satisfactory (lower than 0.06 S cm\(^{-1}\)), the maximum power density (155 mW cm\(^{-2}\)) were prepared by the citrate method with La\(_2\)O\(_3\), Ni(NO\(_3\))\(_2\) and (NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\). Although all compounds exhibited phased perovskite, a La\(_2\)MoO\(_6\) impurity could be found in LNMO with x = 0.20 and 0.25. Regarding cell performance, the material with x = 0.10, 0.15 and 0.20 exhibited excellent conductivity at 120 °C, but it decreased as temperature increased, thus reaching 40 S cm\(^{-1}\) for x = 0.15 and 30 S cm\(^{-1}\) for x = 0.20 at 800 °C. The other compound had an opposite behavior, in which conductivity values increased along with higher temperatures, being x = 0.15 the optimum value. For x = 0.10 and 0.15, power densities were not satisfactory. However, with increased x, they increased slightly, reaching 660 and 565 mW cm\(^{-2}\) for x = 0.25 at 850 and 800 °C, respectively. Moreover, LNMO with x = 0.25 exhibited low overpotential losses and high operation stability, which makes it a promise candidate for being used as SOFC cathode.

Electrolyte

As an electrode, electrolyte has important roles during SOFC operation. The material must have high oxygen ion conductivity in order to enable the migration of oxygen ions via oxygen vacancies, as well as high density so as to prevent gas mixing and low electronic conductivity [75,76]. Currently, YSZ is the most commonly used material as SOFC electrolyte [76]. However, it has undesirable features at high temperatures, such as substantial grain sizes after calcination [77], as illustrated in Fig. 4. As electrolyte layer thickness should not be broad, in order to minimize the losses, YSZ grain size is an important feature [78]. Moreover, it is relatively expensive [79,80]. These facts have motivated many researches about novel materials with enhanced properties, most of them being aimed at lowering SOFCs operating temperatures.

Although oxygen ion conductivity is still the most researched subject in literature, studies on novel compounds for protonic conductors in solid oxide fuel cells have been conducted since Iwahara et al. [81,82] had first released their investigation on the theme, in which perovskite ABO\(_3\) materials were analyzed. Once in contact with water, they exhibit a proton-conduction behavior, and since water generation occurs inside the SOFC, it becomes a great alternative as electrolyte [83]. The reduced activation energy of protons during transport allows operation at lower temperatures and the possibility of being able to operate by using materials with higher conductivity are among their attractive features [84,85].

Oxygen ionic conductivity

Co-doped ceria. Ceria-doped materials have been developed and investigated as electrolyte for intermediate temperature SOFCs due to their great features for such application [75]. Sm

![Fig. 4 – Proportional YSZ grain sizes when calcined at different temperatures [77].](image-url)
and In co-doped ceria Ce0.80Sm0.20-xInxO2.80 (x = 0 (SDC), 0.075 (SDC175), 0.10 (SDC100), 0.15 (SDC150)) have been studied by Tao et al. [86]; Dy and Ca co-doped ceria Ce1-x-yDyxCayO2-δ (x = 0.20, y = 0.00) have been investigated by Tanwar et al. [75]; and Nd and Y co-doped ceria Ce0.80Nd0.20-Y2O3.90 (x = 0.0, 0.02, 0.03, 0.04 and 0.06) have been studied by Kobi et al. [87].

Tao et al. [86] successfully produced an SDCI series by the Pechini method, which is detailed in their work. The material's electrical conductivity increased as x did, i.e. as more In3+ ions were introduced into its structure in order to substitute Sm3+ ions. As regards its performance, SDCI presented great ionic resistances and maximum power density values (444 and 341 mW cm⁻² for SDCI75 and SDCI100, respectively) under temperatures of up to 650 °C. However, SDCI150 quickly decreased its performance due to having high electronic conductivity, which reduces the open-circuit voltage. It was observed an activation energy decrease with increased x. Thereby, it was concluded that SDCI with higher In3+ doping (SDC175 and SDCI100) improved the SOFC overall performance.

Tanwar et al. [75] synthesized Ce1-x-yDyxCayO2-δ (x = 0.20, y = 0.00), (x = 0.16, y = 0.02), (x = 0.14, y = 0.03), (x = 0.13, y = 0.035) by the citrate-nitrate auto-combustion method using Dy2O3 and CaCO3 dissolved in dilute nitric acid. The material’s electrical conductivity presented an increase with the presence of Ca in its structure on account of being a boundary scavenger, where 3 mol% was the optimized value, when conductivity reached 1.45 × 10⁻² S cm⁻¹. Co-doping leads to a change in the ordering of oxygen vacancies, which increase its conductivity. When x = 0.14, the material presented the highest conductivity at temperatures of up to 600 °C, which makes it feasible for SOFC application.

Co-doped materials Ce0.80Nd0.20-Y2O3.90 (x = 0.0, 0.02, 0.03, 0.04 and 0.06) were produced by Kobi et al. [87] by the citrate-nitrate gel auto-combustion method at low temperatures by using (NH₄)₂Ce(NO₃)₆, Nd₂O₃, Y₂O₃ and Ca(H₂O)₆ as starting materials. All compounds presented a single phase and high density values (>92% of theoretical density). As regards electrical conductivity, the material with x = 0.02 showed the highest value (1.28 × 10⁻² S cm⁻¹ at 600 °C), although the others have feasible values for being used as SOFC electrolytes. Despite their stability, it is necessary to verify the compounds compatibility with cell components and thermal expansion, which is suggested as future study.

Doped lanthanum silicate apatite. Lanthanum apatites with A₁₀₋₇₈MoO₄₈₋₇₈ phases (A = rare-earth and alkaline-earth metal cations, M = Si, Ge, P, V, Zn ...) were found in literature, once these compounds have high oxide ion conductivity and work at intermediate temperatures. Their structures allow doping, which supports the production of high performance lanthanum silicate apatite [80,88].

As in a previous work, Nojiri et al. [89] stated that the optimized conductivity of La₁₀₋₇₈Ba₃Si₆O₂₇₋₇₈ occurs with x ranging between 0.5 and 0.6, Cao and Jiang [88] investigated a Ba-doped aluminium lanthanum apatite with x = 0.5 (La₉₈₋₇₈Ba₂₋₇₈Si₅₋₇₈Al₅₋₇₈O₂₆₋₇₈) and compared the results to those presented by the un-doped material (La₁₀₋₇₈Si₆Al₂O₂₆₃). La₂O₃, SiO₂, Al₂O₃ and BaCO₃ were used as starting materials to synthesize the compounds under identical conditions. The Ba-doped material exhibited a lower sintering temperature and porosity due to its structure having higher density if compared to undoped apatite. It also presented significantly higher conductivity (2.21 × 10⁻² S cm⁻¹ at 800 °C), as well as a slightly higher range of activation energy. It could be concluded that doping Ba on the La site for La10Si₆Al₂O₂₆.₅ a apatite can enhance its properties to be used as SOFCs electrolyte.

The effect of iron- and aluminium-doped lanthanum apatites with La₉₋₇₈Si₆₋₇₈Al₅₋₇₈O₂₆₋₇₈ (x = 0, 0.25, 0.75, and 1.5), y = 0, 0.25, 0.75, and 1.5) has been investigated by Gasparyan et al. [80]. The authors synthesized the compounds by several methods, such as mechanochemical activation (MA), sol-gel (SG), solid state reaction (SSR) and Pechini (PE). The starting materials were SiO₂, La₂O₃, Al(OH)₃ and Fe₂O₃. Tests indicated a conductivity increase with increased Al and decreased Fe contents by the MA method, which seemed to be the one through which compounds presented better conductivities, being x = 0.75 and y = 0.25 optimal values for this property, when it reached 2.04 × 10⁻² S cm⁻¹ at 700 °C. The results showed that the synthesis process has great influence on the material’s features.

Ding et al. [90] investigated a Cu-doped lanthanum apatite La₁₀₋₇₈Si₆₋₇₈CuO₂₇₋₇₈ (x = 0–2), synthesized with La(NO₃)₃ and Cu(NO₃)₂ by the sol-gel method. Its structure presented reasonable stability and no impurities. The compound exhibited maximum conductivity of 4.8 × 10⁻² S cm⁻¹ at 800 °C with x = 1.5. Cu doping has increased the TEC value of the material, although it is still acceptable if compared to other commonly used electrolytes. The enhanced performance of Cu-doped lanthanum apatite indicated that it is a promising candidate as SOFC electrolyte.

Molybdenum oxides. According to Schildhammer et al. [91], rare earth molybdenum oxides are acknowledged as materials with several composition types and structural characteristics, being RE₄MoO₁₂ (RE = rare earth) a compound that forms a fluorite structure during crystallization processes. Since doped rare earth Ce₄MoO₁₂ has presented excellent conductivity, these authors have investigated RE₄MoO₁₂ (RE = Er, Yb) by using Ce⁴⁺ and Zr⁴⁺ as stabilizing agents to obtain Er₄Ce₂MoO₁₂₅, Yb₄Ce₂MoO₁₂₅ and Yb₂ZrMoO₁₂₅ with a cubic structure. The materials were synthesized by the solution combustion method using Yb(NO₃)₃, Er(NO₃)₃, Ce(NO₃)₃, ZrO(NO₃)₂, and (NH₄)₆Mo₇O₂₄ as starting materials.

Tests indicated single-phase products with a cubic fluorite structure. At 1000 °C, Er₄Ce₂MoO₁₂₅ and presented a conductivity value of 1.03 × 10⁻⁴ S cm⁻¹, i.e. 161% higher than those of 8-YSZ, which is a commonly used material as SOFC electrolyte. For temperatures ranging between 500 and 900 °C, both compounds resistance decreased as temperature increased. When Zr⁴⁺ was used as stabilizing agent, it was observed a lower conductivity value than that of 8-YSZ, thus indicating that Ce⁴⁺ plays an important role in features of materials.

Protonic conductors BaZr- or/and BaCe-based oxides. BaCe- and BaZr-based oxides have structures that allow transporting protons through their crystal lattice, which makes them attractive protonic
conductor electrolytes [92]. While BaCeO$_3$-based compounds present high conductivity and low chemical stability, BaZrO$_3$-based ones exhibit the exact opposite [93,94].

By focusing on enhancing BaZrO$_3$-based compounds conductivity, given their great chemical stability, Yushii et al. [93] have synthesized a BaZr$_{0.80}$Y$_{0.10}$O$_{3-δ}$ ($x = 0.05, 0.1, 0.15, 0.20, 0.25, 0.30$) material, which operated within a temperature range of 300–900 °C. The material was produced by the solid state reaction method that made use of BaCO$_3$, ZrO$_2$ and Y$_2$O$_3$ as starting materials, and its structure presented no impurities after being calcined at 1500 °C. Tests showed that Y doping could enhance BaZrO$_3$ conductivity, being $x = 0.2, 0.25$ and $0.3$ the material’s highest values at 900 °C, 600 °C and 300 °C, respectively. The highest value was found to be $x = 0.2$ and is $1.07 \times 10^{-3}$ S cm$^{-1}$. Therefore, Y-doped concentration is useful to decrease operating temperature along with high conductivity. These features make it an attractive alternative for intermediate temperature SOFCs.

The properties of BaZr$_{0.80}$In$_{0.20}$Bi$_2$O$_{5.6}$ ($x = 0, 0.05, 0.1, 0.2$) have been investigated by Ling et al. [85]. The material powders were produced by the citric acid EDTA method with Ba(NO$_3$)$_2$, Zr(NO$_3$)$_4$, In(NO$_3$)$_3$ and Bi(NO$_3$)$_3$ being the starting materials. The resulting structure exhibited single-phase cubic perovskite, even when exposed to boiling water or calcined in 10% CO$_2$–N$_2$, thus proving its chemical stability. As regards electrochemical features, the material with $x = 0.05$ showed the highest conductivity, i.e. $9.93 \times 10^{-3}$ S cm$^{-1}$ at 600 °C, and the highest performance and power density among the studied compositions. Therefore, it is a good candidate for being used as SOFC electrolyte.

In order to analyze a BaCeO$_3$ compound behavior under air and hydrogen atmosphere, Shimura et al. [83] doped the material with Mn, Fe and Co and produced a BaCe$_{0.90-x}$Y$_{0.10}$M$_x$O$_3$ ($x = 0, 0.05, 0.1, 0.2$) structure. They also tested a Mn- and Fe-doped compound BaCe$_{0.80}$Y$_{0.10}$Fe$_{0.05}$O$_{3-δ}$ which was synthesized by the solid state reaction method with amounts of BaCO$_3$, CeO$_2$, ZrO$_2$ and Y$_2$O$_3$. Crystal structure with cubic symmetry was observed. Compositions with $x = 0.5$ and $x = 1.0$ exhibited the highest ($2.39 \times 10^{-3}$ S cm$^{-1}$) and lowest conductivity at 500 °C in wet argon atmosphere, respectively, which demonstrates that increased Sr content decreases conductivity. Through operating at temperatures ranging between 300 and 700 °C, it was possible to note that conductivity increases with higher temperatures. For SOFC application, BSCZYSm with $x = 0.5$ presented chemical stability and satisfactory conductivity values within an atmosphere intermediate temperature range.

Lanthanum tungstate. Given high carbon and sulfur resistance over 650 °C, great conductivity and lower sintering temperatures, lanthanum tungstates (La$_{28-y}$W$_{4+y}$O$_{54+α}$) are promising candidates as protonic conductors for SOFCs [97].

Nb-doped lanthanum tungstate La$_{27}$W$_{14}$Nb$_{0.5}$O$_{55.3}$ (LWNO) has been produced and evaluated through being used with different electrodes by Rey et al. [98]. It was produced by a freeze-drying method described by the authors in Ref. [99], being La$_{27}$O$_{54}$, WO$_3$ and Nb(H$_2$O)$_6$ the starting materials. In contact with LSM and LSCM electrodes, LWNO showed no reactions at up to 1400 °C, and there were no reactions with LSCF at up to 1000 °C as well. Power density values (140 and 18 mW cm$^{-2}$ at 900 and 650 °C, respectively) for LWNO electrolyte are similar to those found for BaZr$_2$-oxides doped with Y, but they are quite lower than oxides containing both Zr and Ce. The material is an interesting option for SOFCs, as long as operation temperatures are higher than 750 °C in order to obtain optimal LWNO performance.

A partial replacement of La for K (potassium) has been studied by Liu et al. [97]. Their work focused on (La$_{1.0}$-$x$K$_{x}$)$_{27}$O$_{4}$W$_{4+y}$O$_{55.3-α}$ ($x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10$) (LWx) which were prepared by the solid state reaction method. It was observed that calcination temperatures below 1150 °C contributed to the formation of phases, such as La$_2$O$_3$ and fluorite La$_{28-y}$W$_{4+y}$O$_{54+α}$. By doping K$^+$, oxygen vacancies are introduced into the material’s structure, thus enhancing protonic conductivity. However, it reaches the highest value at $x = 0.02$, and then conductivity decreases. It was also noted that under wet conditions, K$^+$ has not influenced the conduction mechanism, thus increasing activation energy. Although calcination temperature was relatively high, slightly K-doped lanthanum tungstate is good candidates for SOFC.
Discussions

It is evident that, once efficiency reaches 60%, CO2 emission becomes 60% lower than those of coal-fired power [100], and by considering wide application possibilities, since portable devices (20 W) in plants generate some MWs [101], SOFC is one of the most promising candidates for power generation in the near future. The efforts are now focused on reducing some operation issues concerning degradation of conventional materials and reducing production and maintenance costs, in order to make SOFCs feasible for commercialization [102].

The progress of materials for SOFC components is remarkable, mainly in the latest decades. Although no material does not have any operational drawbacks for each component [103], researches have been conducted by focusing on modifying conventional SOFC materials or introducing new ones. Perovskites have been hardly explored to all SOFC materials and reducing production and maintenance costs, in order to make SOFCs feasible for commercialization [102].

Materials with a perovskite structure have been very widely studied for SOFC cathode technology, due to their great properties and chemical stability at intermediate temperatures [104,111]. Cobalt and alkaline earth metals are elements that are widely used in order to enhance cell performance, but also have drawbacks. Therefore, there are studies that already propose their removal or substitution. However, most cathode materials still have these elements. Most items of research aim to reduce SOFCs operating temperatures, although there are some materials that work at temperatures of up to 1000 °C. Table 2 describes features of the reviewed materials for cathodes herein.

### Anode

In SOFC anode technology, several works using both Ni and Ce as catalyst materials could be found. In addition, Ni also improves the equipment mechanical strength [3] and is still the best choice as anode [106,107]. However, Ni-based compounds have undesirable features such as redox instability, carbon deposition and sulfur poisoning. Although there was no research that solved these three issues simultaneously up until recently [25], the compounds have been commonly modified in order to circumvent them. Ceria-based compounds have gained more attention because of their activity and stability and are present in many different compositions, mainly with SDC. However, anode reaction atmosphere conditions can cover ceria with carbonate species, thus leading to a reduction in the reaction rate [108–110]. It is appropriate to carry out more researches about Ce-based materials in the long-term operation.

It can be noted that, as conventionally used materials, most novel proposed anodes have transition metals in their compositions, due to their high catalytic activity and stability under anode atmospheres [111]. Most researches focus on lowering operating temperatures. Table 1 describes features of the reviewed materials for anodes herein.

### Table 1 – Features of reviewed materials for anodes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Features</th>
<th>Sintering method</th>
<th>Operating temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Ni-YSZ</td>
<td>Addition of Al2O3 on Ni-YSZ increased both the electrical conductivity and chemical stability</td>
<td>Two-step method</td>
<td>750</td>
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<td></td>
<td>Addition of Ag decreased the carbon deposition, enhancing the electrochemical performance</td>
<td>Co-tape casting method</td>
<td>750</td>
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<td></td>
<td>BaZr0.1Ce0.9O2-Y2O3-Yb2O3-δ (BZY) infiltration into Ni-YSZ presented no reaction with YSZ electrolyte and no performance degradation in contact with H2S</td>
<td>Citrate method</td>
<td>700</td>
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<tr>
<td></td>
<td>Nb2O5-coated Ni-YSZ exhibited a power density 113% higher than undoped material and stability in contact with H2S</td>
<td>Reactive sputtering</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>Addition of Zr into CeO2 compounds enhanced the conductivity, with maximum value at x = 0.75</td>
<td>Citrate complexation method</td>
<td>up to 690</td>
</tr>
<tr>
<td>LnSTM (Ln: La, Nd and Sm) perovskites</td>
<td>Addition of Ti-Mn to b-site perovskites increased anode chemical performance, as well as conductivity. Nd0.5Sr0.5Ti0.5Mn0.5O3 (NSTM) indicated better results</td>
<td>Glycine nitrate process (GNP)</td>
<td>up to 900</td>
</tr>
<tr>
<td>Nickel-free double perovskite</td>
<td>SrFeNb2O8-MnO2 (SFNM20) presented higher coking resistance and redox stability, as well as satisfactory conductivity</td>
<td>Solid state reaction</td>
<td>up to 800</td>
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<td></td>
<td>Pure Pr2O3-BaO-MnO2, exhibited great performance, which was enhanced by Mo doping. PBMO5 presented great performance</td>
<td>Combustion method</td>
<td>800</td>
</tr>
<tr>
<td>Modified Ni-SDC</td>
<td>Mn1.5Co1.5O4 (MCO) modified anodes exhibited higher carbon deposition rate, an undesirable feature</td>
<td>Ethylenediaminetetra-acetic acid (EDTA) – citrate method</td>
<td>up to 700</td>
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<td>CaO-modified Ni-SDC increased the power density and stability under reduction atmosphere</td>
<td>Mechanical mixing</td>
<td>up to 700</td>
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<tr>
<td></td>
<td>The addition of Cu indicated both high power density and conductivity</td>
<td>Glycine nitrate process (GNP)</td>
<td>600–800</td>
</tr>
<tr>
<td>Material</td>
<td>Features</td>
<td>Sintering method</td>
<td>Operating temperature [°C]</td>
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<tr>
<td>LaSr perovskites with GDC</td>
<td>GDC-coated LSM/YSZ exhibited both greater porosity and conductivity if compared to LSM/YSZ LSCF-GDC with LNF as an additive improved chemical stability and electrochemical performance</td>
<td>Solid state reaction</td>
<td>up to 850</td>
</tr>
<tr>
<td>A₂BO₄₋ₓ composites</td>
<td>La₂₋ₓNiO₄₊ₓ (LXNO) exhibited greater performance at x = 0.01 LₐpₓCaₓNiO₄₋ₓ (LCNOx) presented chemical stability and great conductivity. However, the Ca doping decreased electrochemical activity</td>
<td>Electrostatic spray deposition method (ESD)</td>
<td>up to 700</td>
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<td>La₂₋ₓPrₓNiO₄₋ₓ for x = 1 exhibited no decomposition at 700 °C after 30 days, operation stability and high power density</td>
<td>Mechanical mixing</td>
<td>up to 900</td>
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<td>(100 – x) La₀.₉₅Ni₀.₆Fe₀.₄O₃₋ₓCeO₂ (LNFCx) showed great features for 2 mol% ≤ x ≤ 50 mol%</td>
<td>Glycine nitrate process (GNP)</td>
<td>700</td>
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<td>PCO-4CGO showed great stability and thermal compatibility with CGO electrolyte</td>
<td>Glycine nitrate process (GNP)</td>
<td>up to 1000</td>
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<tr>
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<td>PCO mixed with SDC20 presented chemical stability and high power density</td>
<td>Modified EDTA-glycine method</td>
<td>up to 1000</td>
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<tr>
<td>LnBaCo₂₋ₓO₃₋ₓ double perovskite</td>
<td>Ca-doped Prₓ₋ₓCaₓBaCo₂₋ₓ₋ₓ (PCBCO) showed compatibility with SDC electrolyte. Ca increase led to electrochemical performance decrease</td>
<td>Solid state reaction</td>
<td>up to 850</td>
</tr>
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<td>LaBaₓSr₁₋ₓCo₂₋ₓ₋ₓGDC (LBSCOₓ₋ₓGDC) (x = 0, 20, 30, 40, 50 wt%) with x = 40 wt% presented power density 28% higher than Sr-free material</td>
<td>Pechini method</td>
<td>650</td>
</tr>
<tr>
<td>Cobalt-free perovskite</td>
<td>NdBaₓSr₁₋ₓCaₓO₃₋ₓ (NBSCO) exhibited compatibility with SDC electrolyte, high electrochemical activity and electrical conductivity</td>
<td>Citrate-EDTA sol-gel method</td>
<td>up to 1000</td>
</tr>
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<td></td>
<td>NdBaₓ₋ₓMnₓ₋ₓO₃₋ₓ (NBMx) exhibited great power density and highest conductivity at x = 0.1</td>
<td>Citric acid-nitrate method</td>
<td>500–700</td>
</tr>
<tr>
<td></td>
<td>SrₓFe₂O₆₋ₓ exhibited satisfactory oxygen reduction reaction activity and lower resistance than other SrFeOₓ-based compounds</td>
<td>Citrate-EDTA method</td>
<td>900</td>
</tr>
<tr>
<td>Alkaline earth metal free perovskites</td>
<td>PrNiₓ₋ₓFeₓ₋ₓO₃₋ₓ exhibited high electrical conductivity and feasible TEC value</td>
<td>Solid state reaction</td>
<td>up to 1000</td>
</tr>
<tr>
<td></td>
<td>LaₓZnMnO₃ presented low conductivity values, satisfactory power densities and conventional TEC value</td>
<td>Citrate method</td>
<td>up to 700</td>
</tr>
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<td>LaNiₓ₋ₓMoₓO₃ with x = 0.25 showed increasing conductivity with higher temperatures, as well as low overpotential losses and high power densities</td>
<td>Citrate method</td>
<td>up to 850</td>
</tr>
<tr>
<td>Material</td>
<td>Feature</td>
<td>Sintering method</td>
<td>Operating temperature [°C]</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
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<td>---------------------------</td>
</tr>
<tr>
<td>Ionic conductivity</td>
<td><strong>Sm and In co-doped ceria Ce_{0.80}Sm_{0.20-x}In_xO_{1.90}</strong> conductivity increased as x did. The material showed great power density. <strong>The Ca content in Ce_{1-x-y}Dy_xCa_yO_{2.5} increased the electrical conductivity, which was optimal at x = 0.2.</strong> <strong>Ce_{0.80}Nd_{0.20}Y_{0.10}O_{1.90}</strong> presented satisfactory electrical conductivity. <strong>Ba-doped La_{9.83}Ba_{0.17}Al_{5.83}O_{26.55}</strong> presented higher porosity and greater conductivity if compared to the undoped material. <strong>Fe- and Al-doped La_{9.83}Si_{6.83}Fe_{0.17}O_{26.55}</strong> exhibited better conductivity with increased x and decreased y. <strong>Cu-doped La_{9.83}Si_{6.83}Cu_{0.17}O_{27.55}</strong> showed maximal conductivity at x = 1.5, with high electrochemical performance. However, it exhibited high thermal expansion.</td>
<td>Pechini method</td>
<td>up to 650</td>
</tr>
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<td><strong>RE_{6}MoO_{12} (RE = Er, Yb)</strong> presented conductivity that was 161% higher than that of 8-YSZ electrolyte. <strong>Cu-doped La_{9.83}Si_{6.83}Cu_{0.17}O_{27.55}</strong> showed maximal conductivity at x = 1.5, with high electrochemical performance. However, it exhibited high thermal expansion.</td>
<td></td>
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</tr>
<tr>
<td>Doped lanthanum silicate apatite</td>
<td><strong>Ba-doped La_{9.83}Ba_{0.17}Al_{5.83}O_{26.55}</strong> presented higher porosity and greater conductivity if compared to the undoped material. <strong>Fe- and Al-doped La_{9.83}Si_{6.83}Fe_{0.17}O_{26.55}</strong> exhibited better conductivity with increased x and decreased y.**</td>
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<td></td>
<td><strong>Cu-doped La_{9.83}Si_{6.83}Cu_{0.17}O_{27.55}</strong> showed maximal conductivity at x = 1.5, with high electrochemical performance. However, it exhibited high thermal expansion.</td>
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<tr>
<td>Molybdenum oxides</td>
<td><strong>BaZr_{1-x}Y_{x}O_{3.9} (x = 0, 0.05, 0.1, 0.15, 0.20, 0.25, 0.30) exhibited high conductivity with increased x and low operating temperatures.</strong> <strong>BaZr_{0.8-x}In_{x}Zr_{0.2}O_{3.5} (x = 0, 0.05, 0.1, 0.2) showed high conductivity and power density at x = 0.05.</strong> <strong>BaCeO_{0.98-x}Y_{0.02}M_{0.02}O_{3.5} (M = Mn, Co and Fe; 0 ≤ x ≤ 0.10) had its conductivity decreased with metal doping.</strong> <strong>BaCe_{0.8}Sm_{0.2}O_{3.5} (0 ≤ x ≤ 0.2) showed the highest conductivity with x = 0.15 and thermal expansion coefficient compatible with commercial electrode materials.</strong> <strong>BaCe_{0.6-0.2}Zr_{0.4}Y_{0.2}O_{3.4}</strong> exhibited thermal expansion coefficient lower than that of commercial cathode materials, good carbon tolerance and high conductivity.</td>
<td>Solid state reaction</td>
<td>300–900</td>
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<td><strong>Increased Sr content in Ba_{1-x}Sr_xCe_{0.5}Zr_{0.5}Y_{0.1}Sm_{0.05}O_{3.1} (x = 0.5, 0.7, 0.9, 1.0) decreased conductivity.</strong> <strong>La_{27}W_{4.8}Nb_{0.8}O_{55.38} (LWNO) showed no reactions with common electrode materials and relatively low power density.</strong> (<strong>La_{1-x}K_{x}La_{1/2}W_{4.92}O_{55.38-x} (k = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10)</strong> exhibited the highest conductivity at x = 0.02.</td>
<td>Citric acid — EDTA method</td>
<td>600</td>
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<td><strong>Lanthanum tungstates</strong></td>
<td>Solid state reaction</td>
<td>600–1000</td>
</tr>
<tr>
<td></td>
<td><strong>Increased Sr content in Ba_{1-x}Sr_xCe_{0.5}Zr_{0.5}Y_{0.1}Sm_{0.05}O_{3.1} (x = 0.5, 0.7, 0.9, 1.0) decreased conductivity.</strong> <strong>La_{27}W_{4.8}Nb_{0.8}O_{55.38} (LWNO) showed no reactions with common electrode materials and relatively low power density.</strong> (<strong>La_{1-x}K_{x}La_{1/2}W_{4.92}O_{55.38-x} (k = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10)</strong> exhibited the highest conductivity at x = 0.02.</td>
<td>Solid state reaction</td>
<td>750–1000</td>
</tr>
<tr>
<td></td>
<td><strong>Lanthanum tungstates</strong></td>
<td>Freeze-drying method</td>
<td>300–700</td>
</tr>
<tr>
<td></td>
<td><strong>Lanthanum tungstate</strong></td>
<td>Solid state reaction</td>
<td>up to 1500</td>
</tr>
</tbody>
</table>
Electrolyte

Materials with open lattice structures are still the most widely used as SOFC electrolytes [103]. Ce- and La-based materials are those which have been most extensively investigated as novel materials for SOFC electrolytes, as can be seen in Table 3. Rare earth molybdenum oxides were studied as a different option for such application. With respect to protonic conductors, BaZr- and BaCe-based oxides are still the most widely studied compounds, although lanthanum tungstates are also interesting options. Proton-conducting SOFC allows large decrease in operating temperatures [94]. In this review, two works were cited [93,96], which have investigated SOFC under temperatures as low as 300 °C. In general, these investigations focus on materials that can operate at intermediate temperatures.

Conclusions

Several novel materials have been presented as SOFC components herein by focusing on cell performance enhancement.

In conclusion, as nickel-based materials suffer from carbon deposition on their surface, they need modifications to operate in a SOFC. Ni/YSZ is the most commonly used material as anode, which can be modified with the addition of other elements or compounds, such as Ag, alumina, niobium and BaCeO3-based compounds. Ni/SDC materials can be added with Co and Mn and Co or Cu. These procedures might enhance the cell’s electrochemical performance and lower its operating temperature. Other compounds such as Ce–Zr–O systems and nickel-free perovskites are also promising SOFC anodes.

La-based compounds have been widely investigated as SOFC cathodes. LSM perovskite is a commonly used material, and the addition of GDC to its structure enhances cell performance. Lanthanum nickelates are also La-based materials used for such application, while double perovskite and perovskite oxides can use La or other elements, such as Pr and Nd. Cobalt-free perovskites seemed to lower the production price, while alkaline earth metal free perovskites seemed to enhance the material resistance to surface deposition. In a nutshell, compounds with a perovskite structure are largely used for such a propose.

YSZ material has been replaced with Ce- and La-based compounds through using several doped elements that increase electrolyte performance. Rare earth molybdenum oxides were recently introduced and need further studies with the aim of establishing themselves as viable alternatives. For protonic conductors, BaZr- and BaCe-based oxides are the most widely studied compounds with several modifications in their composition. However, lanthanum tungstates are also interesting options to be investigated.

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