Review Article

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. Thence, 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 ($La_{1-x}Sr_xMnO_3$). 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

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 interme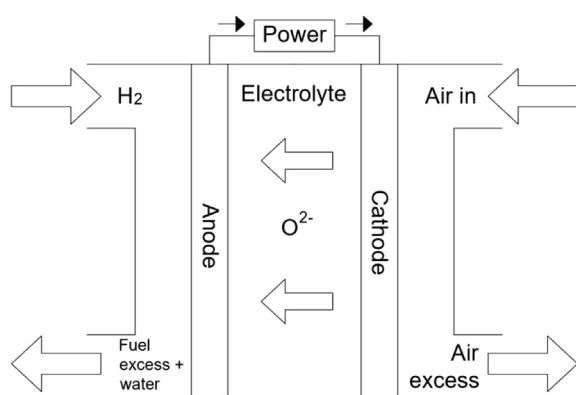diate or even high temperatures simultaneously. Thereby, the present work aims to review some literary studies in which novel SOFC electrode and electrolyte materials have been introduced by focusing on enhancing fuel cell performance and/or reducing operating temperatures in order to provide a nice and simple access point and show some progresses by introducing novel compounds, along with briefly summarizing the present results.

Materials

Current SOFC models make use of 8 mol%Y_2O_3 and stabilized ZrO_2 (8-YSZ)/Ni as anodes, YSZ (yttria-stabilized zirconia) as electrolytes and $La_{0.8}Sr_{0.2}MnO_3$ (LSM) as cathodes [12]. Ordinary solid oxide fuel cells must work at temperatures of over 800 °C in order to provide optimal electrolyte and electrode 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)):

$$H_2 + O^{2-} = H_2O + 2e^- \tag{1}$$

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

Fig. 1 – Working principle of a solid oxide fuel cell.

Anode

Hydrocarbon
fuel + H_2S →

Ni-YSZ

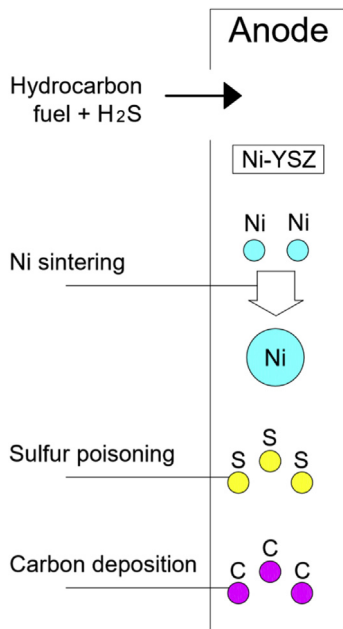Ni sintering

Sulfur poisoning

Carbon deposition

Fig. 2 – Scheme of Ni-YSZ anode issues.

conductivity, structural stability and compatibility with other materials in SOFCs [22]. However, once in contact with hydrocarbon fuels, either combined with steam or CO_2, Ni-YSZ cermet becomes susceptible to carbon deposition and contaminant poisoning, mainly by hydrogen sulfide (H_2S) [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 (Al_2O_3) 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. Al_2O_3–NiO (0, 0.36, 0.72 and 3.6 wt% of Al_2O_3) and Al_2O_3-YSZ (0, 0.44, 0.88, 4.4 wt% of Al_2O_3) 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 Al_2O_3 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 Al_2O_3, it was noted an acceptable amount of $NiAl_2O_4$ 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 H_2 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 Al_2O_3 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 H_2, CH_4 and C_2H_6. 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 H_2, 251.3 mW cm^{-2} for those fueled by dry CH_4 and 379 mW cm^{-2} for the ones fueled by dry C_2H_6. Thence, 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 $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZXYYb) into the starting material, due to being known as a high conductivity material [27]. BZCYYb was obtained by the citrate method, in which $Ba(NO_3)_2$, $ZrO(NO_3)_2$, $Ce(NO_3)$, Y_2O_3 and Yb_2O_3 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 H_2 and containing 30 ppm H_2S. 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 (Nb_2O_5) to a Ni-YSZ anode so as to assess sulfur tolerance through reactive sputtering. Nb_2O_5, which was obtained by evaporating the $Nb(HC_2O_4)_4$ solution, was deposited on the top of the Ni-YSZ surface. The tests were carried out when cells were fueled by H_2 at temperatures below 700 °C until it reached performance stabilization. Then, H_2S (50 ppm) was added together with H_2 in order to assess surface sulfur tolerance. Nb_2O_5 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 H_2S 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 H_2S atmosphere showed that Nb_2O_5 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 CeO_2 compounds increases both the material's

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 $Ce_xZr_{1-x}O_2$ 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 $Ce_xZr_{1-x}O_2$ with x = 0.10, Zimicz et al. [32] have studied the effect of a different synthesization method to produce a Ce—Zr—O system with $Ce_{0.9}Zr_{0.1}O_2$ 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 $Ce_xZr_{1-x}O_2$ composition with x = 0.5. Stoichiometric amounts of $Ce(NO_3)_3$ and $ZrO(NO_3)_2$ 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 H_2 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: $La_{0.5}Sr_{0.5}Ti_{0.5}Mn_{0.5}O_{3\pm d}$ (LSTM), $Nd_{0.5}Sr_{0.5}Ti_{0.5}Mn_{0.5}O_{3\pm d}$ (NSTM) and $Sm_{0.5}Sr_{0.5}Ti_{0.5}Mn_{0.5}O_{3\pm d}$ (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

$Sr(NO_3)_2$, $Mn(NO_3)_2$, $[CH_3CH(O^-)CO_2NH_4]2Ti(OH)_2$ and $Ln(NO_3)_3$ (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 $Ln_{0.5}Sr_{0.5}Ti_{0.5}Mn_{0.5}O_{3\pm d}$ oxide systems. As regards electrical properties, the results indicated that NSTM 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 NSTM has the highest electrical conductivity, once Nd addition leads to a metallic behavior in some Ti molecules. It was noted better operation performance in NSTM 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: $Sr_2FeNb_{0.2}Mo_{0.8}O_{6-\delta}$ (SFNM20). A solid state reaction with stoichiometric ratio among $SrCO_3$, Fe_2O_3, Nb_2O_5 and MoO_3 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% H_2 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 $Pr_{0.5}Ba_{0.5}MnO_{3-\delta}$ (PBMO3) and $PrBaMn_2O_{5+\delta}$ (PBMO5), respectively. PBMO3 was produced both in its pure and doped form with 10 mol% Mo (Mo-PBMO3) by the sol-gel method. The doped material had the following composition: $Pr_{0.5}Ba_{0.5}Mn_{0.9}Mo_{0.1}O_{3-\delta}$. PBMO5 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 PBMO3 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 PBMO3, although being less than

those for the doped material. PBMO5 exhibited high performance stability up to 850 °C, with conductivity values of 8.16 and 91.5 S cm^{-1} in 5% H$_2$ and air, respectively. A peak power density value of 570 mW cm^{-2} was reached, both without any catalysts and 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 H$_2$S [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. Ce$_{0.85}$Sm$_{0.15}$O$_{1.925}$ (SDC) powders were produced by the Ethylenediaminetetra-acetic acid (EDTA) − citrate method, by using Sm(NO$_3$)$_3$ and Ce(NO$_3$)$_3$ as starting materials. Mn$_{1.5}$Co$_{1.5}$O$_4$ (MCO) powders were synthesized by using Mn(NO$_3$)$_2$ and Co(NO$_3$)$_2$ 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 La$_2$O$_3$ 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 introduction 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(NO$_3$)$_3$ and Sm$_2$O$_3$ as starting materials, while Ni$_{1-x}$Cu$_x$O powders were synthesized, also by the GNP method, with Ni(NO$_3$)$_2$ and Cu(NO$_3$)$_2$ as starting materials. The reaction produces Ni$_{1-x}$Cu$_x$-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)):

$$½O_2 + 2e^- = O^{2-} \tag{2}$$

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 perovskite (La$_{1-x}$Sr$_x$MnO$_3$) 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 (La$_{0.8}$Sr$_{0.2}$)$_{0.95}$MnO$_{3-\delta}$ (LSM)−Gd$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ (gadolinium-doped ceria, GDC) were investigated. The same compound (GDC) was added by Liu et al. [49] to a La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) perovskite, also focusing on increased operational performance.
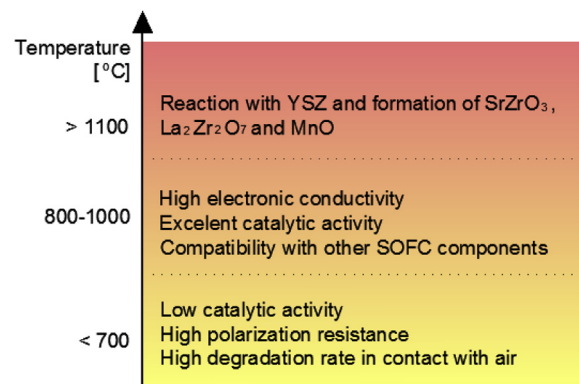

Fig. 3 − LSM cathode behavior at different temperatures [44−46].

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_2O_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.

$A_2BO_{4+\delta}$ *composites*. Materials with an $A_2BO_{4+\delta}$ 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_2CuO_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_2CuO_4-based composites were studied by Li et al. [50] and Chiu et al. [51].

Ferkhi and Yahia [53] proposed lanthanum nickelates $La_{2-x}NiO_{4\pm\delta}$ (LXNO) with x varying between 0.01 and 0.05 as cathode materials for SOFC. LXNO powders were sintered by mixing La_2O_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 $La_{1.99}NiO_{4+\delta}$ is a promising material for lowering SOFCs operating temperature, thus leading to less material degradation and longer lifetime.

$La_{2-x}Ca_xNiO_{4+\delta}$ (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_2O_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 $La_{2-x}Pr_xNiO_{4+\delta}$ (x = 0, 0.5, 1 and 2) structure has been prepared through material deposition on CGO ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$) 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 $PrNiO_{3-\delta}$, $Pr_4Ni_3O_{10+\delta}$ and Pr_6O_{11}, 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, $La_{2-x}Pr_xNiO_{4+\delta}$ with x = 1 presented optimal features.

Perovskite materials with Ni and Fe in the A-site structure have been proposed by Konysheva and Irvine [56] as possible replacements for SOFC electrode applications. Their studied composition was $(100 - x)\ La_{0.95}Ni_{0.6}Fe_{0.4}O_3 - xCeO_2$ (LNFCx) which was added to CeO_2 in order to enhance the material's ionic conductivity. $La_{0.95}Ni_{0.6}Fe_{0.4}O_3$ and CeO_2 were added and further blended by mechanical 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_2CuO_4 (PCO) material with the addition of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (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 synthetize PCO powders. However, the authors have mixed PCO with several wt% of samarium doped ceria, $Cm_{0.2}Ce_{0.8}O_{1.9}$ (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$_{5+\delta}$ double perovskite. Cobalt-based materials with LnBaCo$_2$O$_{5+\delta}$ (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$_{5+\delta}$ 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$_{5+\delta}$ (SBCNx) with x varying from 0 to 0.5 at intervals of 0.1, has been investigated by Xia et al. [57]. Cathode material powders were synthesized by an adapted EDTA-glycine method mentioned therein. Starting materials were Sm(NO$_3$)$_2$, Ba(NO$_3$)$_2$, Co(NO$_3$)$_3$ and Ni(NO$_3$)$_3$. All compounds presented single-phase structures. Up to 1000 °C, the material presented chemical stability with SDC electrolytes, which is an excellent material for electrolytes operating at intermediate temperatures [59]. The electronic conductivity decreases with an increase in Ni content. However, SBCNx with maximum Ni content presented satisfactory conductivity values (approximately 300 S cm^{-1} at 700 °C), as well as high catalytic activity. The thermal expansion coefficient value decreased as Ni content increased, thus achieving 15.59·10^{-6} K^{-1} which is higher than those of common electrolyte materials. Due to its great electrical performance, SBCNx is rather promising for being used as SOFC cathode, although it still shows undesirable thermal expansion properties.

Ca doped on the A site in Pr$_{1-x}$Ca$_x$BaCo$_2$O$_{5+\delta}$ (PCBCO) with x varying from 0.1 to 0.4 has been studied by Fu et al. [58]. The conventional solid state reaction method was used to synthesize the material, being Pr$_6$O$_{11}$, CaCO$_3$, BaCO$_3$ and Co$_3$O$_4$ the starting materials. The compounds with x = 0.1 and x = 0.2 presented a highly dense single-phase structure, while x = 3 and x = 4 compounds exhibited impurity phases. PCBCO results with the SDC electrolyte showed chemical compatibility. Thermal expansion coefficient (TEC) decreases with increased Ca content with a minimum value of 19.1·10^{-6} K^{-1}, which is still higher than those of other cathode materials. As regards electrical performance, Ca doping decreased the electrical conductivity, due to an increase in oxygen vacancy concentration in its structure. Electrochemical performance and power density, which varies from 645.5 to 620.6 mW cm^{-2} for x = 0.1–0.2 at 800 °C, were also affected by the reduction with increased Ca content. Ca-doped PCBCO exhibited lower TEC values if compared to the compound without Ca. However, electrochemical performance decreased, which is not a good feature for its use as cathode.

The performance of LaBa$_{0.5}$Sr$_{0.5}$Co$_2$O$_{5+\delta}$ (LBSCO) has been investigated by Choi et al. [60] as cathode material. Sr was introduced into the perovskite A-site. The Pechini method was used to produce LBSCO by using La(NO$_3$)$_3$, Ba(NO$_3$)$_2$, Sr(NO$_3$)$_2$ and Co(NO$_3$)$_2$ as starting materials. To improve the composite's electrochemical properties, GDC was added to LBSCO in the ration of 0, 20, 30, 40, 50 and 60 wt%. The resulting material (LBSCO-xGDC) showed no reactions between the elements at temperatures of up to 1000 °C. The area specific resistance decreases by increasing x in up to 40 wt%, and then it increases. If compared to the same material, but Sr-free with 40 wt% of GDC, the power density of LBSCO-40GDC was almost 28% higher at 650 °C, thus reaching 1267 mW cm^{-2} and indicating that Sr enhanced cell performance. It was concluded that LBSCO-40GDC is a promising cathode material under intermediate operation temperatures.

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$_{5+\delta}$ (NBCO) and NdBa$_{0.5}$Sr$_{0.5}$Cu$_2$O$_{5+\delta}$ (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$_2$(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 NBSCO has greater features for such application.

A novel cobalt-free compound NdBaFe$_{2-x}$Mn$_x$O$_{5+\delta}$ (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 BZCY electrolyte. The compound with x = 0.1 showed good power density values (453 mW cm^{-1}), 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 $Sr_4Fe_6O_{13-\delta}$ 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 $Sr_4Fe_6O_{13-\delta}$ solid precursor under an oxygen deficient atmosphere at 900 °C, the ORR activity was increased by 4–8 times if compared to single-phase $Sr_4Fe_6O_{13-\delta}$, 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 $PrNi_{0.4}Fe_{0.6}O_{3-\delta}$ composition has been investigated by Rebello et al. [72]. The material powders were synthesized by the solid state reaction method, being Pr_6O_{11}, NiO and Fe_2O_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, $PrNi_{0.4}Fe_{0.6}O_{3-\delta}$ exhibited a TEC value close to those of conventional electrolyte materials, which makes it a good candidate for being used as SOFC cathode.

La_2ZnMnO_6 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_2O_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}), which are satisfactory values for SOFC application. However, the overall performance is relatively lower than other materials cited herein.

Four perovskite oxides with partial Ni substitution for Mo have been investigated by Hou et al. [74]. $LaNi_{1-x}Mo_xO_3$ (LNMO) (x = 0.10, 0.15, 0.20, and 0.25) were prepared by the citrate method with La_2O_3, $Ni(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$. Although all compounds exhibited phased perovskite, a La_2MoO_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 = 015 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 oxide ion conductivity in order to enable the migration of oxide 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 oxide 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
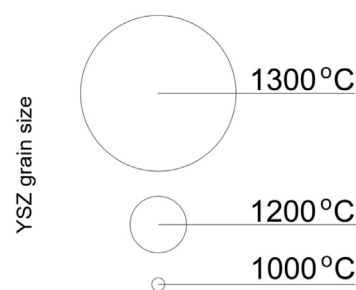
Fig. 4 – Proportional YSZ grain sizes when calcined at different temperatures [77].

and In co-doped ceria $Ce_{0.80}Sm_{0.20-x}In_xO_{1.90}$ [x = 0 (SDC), 0.075 (SDCI75), 0.10 (SDCI100), 0.15 (SDCI150)] have been studied by Tao et al. [86]; Dy and Ca co-doped ceria $Ce_{1-x-y}Dy_xCa_yO_2$-$_\delta$ {(x = 0.20, y = 0.00), (x = 0.16, y = 0.02), (x = 0.14, y = 0.03), (x = 0.13, y = 0.035)} have been investigated by Tanwar et al. [75]; and Nd and Y co-doped ceria $Ce_{0.80}Nd_{0.20-x}Y_xO_{1.90}$ (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 In^{3+} ions were introduced into its structure in order to substitute Sm^{3+} ions. As regards its performance, SDCI presented great ohmic 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 In^{3+} doping (SDCI75 and SDCI100) improved the SOFC overall performance.

Tanwar et al. [75] synthesized $Ce_{1-x-y}Dy_xCa_yO_{2-\delta}$ {(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 route using Dy_2O_3 and $CaCO_3$ 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 $1.45 \cdot 10^{-2}$ 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 $Ce_{0.80}Nd_{0.20-x}Y_xO_{1.90}$ (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 $(NH_4)_2Ce(NO_3)_6$, Nd_2O_3, Y_2O_3 and $C_6H_8O_7$ 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 ($1.28 \cdot 10^{-2}$ 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. Lathanum apatites with $A_{10-x}M_6O_{26\pm\delta}$ 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 $La_{10-x}Ba_xSi_6O_{27-x/2}$ 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 ($La_{9.5}Ba_{0.5}Si_{5.5}Al_{0.5}O_{26.5}$) and compared the results to those presented by the undoped material ($La_{10}Si_5AlO_{26.5}$). La_2O_3, SiO_2, Al_2O_3 and $BaCO_3$ 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 ($2.21 \cdot 10^{-2}$ 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 $La_{10}Si_5AlO_{26.5}$ apatite can enhance its properties to be used as SOFCs electrolyte.

The effect of iron- and aluminium-doped lanthanum apatites with $La_{9.83}Si_{6-x-y}Al_xFe_yO_{26\pm\delta}$ (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's (PE). The starting materials were SiO_2, La_2O_3, $Al(OH)_3$ and Fe_2O_3. 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 $2.04 \cdot 10^{-2}$ 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 $La_{10}Si_{6-x}Cu_xO_{27-\delta}$ (x = 0–2), synthesized with $La(NO_3)_3$ and $Cu(NO_3)_2$ by the sol-gel method. Its structure presented reasonable stability and no impurities. The compound exhibited maximum conductivity of $4.8 \cdot 10^{-2}$ 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 RE_6MoO_{12} (RE = rare earth) a compound that forms a fluorite structure during crystallization processes. Since doped rare earth Ce_6MoO_{15} has presented excellent conductivity, these authors have investigated RE_6MoO_{12} (RE = Er, Yb) by using Ce^{4+} and Zr^{4+} as stabilizing agents to obtain $Er_5CeMoO_{12.5}$, $Yb_5CeMoO_{12.5}$ and $Yb_5ZrMoO_{12.5}$ with a cubic structure. The materials were synthesized by the solution combustion method using $Yb(NO_3)_3$, $Er(NO_3)_3$, $Ce(NO_3)_3$, $ZrO(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ as starting materials.

Tests indicated single-phase products with a cubic fluorite structure. At 1000 °C, $Er_5CeMoO_{12.5}$ and presented a conductivity value of $1.03 \cdot 10^{-4}$ 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 Zr^{4+} was used as stabilizing agent, it was observed a lower conductivity value than that of 8-YSZ, thus indicating that Ce^{4+} 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, Yushi et al. [93] have synthesized a $BaZr_{1-x}Y_xO_{3-\alpha}$ (x = 0, 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_2O_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 x = 0.2 and is $1.07 \cdot 10^{-3}$ 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 $BaZr_{0.8-x}In_{0.2}Bi_xO_{3-\delta}$ (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. $9.93 \cdot 10^{-4}$ 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 $BaCe0._{90-x}Y_{0.10}M_xO_{3-\delta}$ (M = Mn, Co and Fe; $0 \leq x \leq 0.10$) structure. They also tested a Mn- and Fe-doped compound $BaCe_{0.80}Y_{0.10}Mn_{0.05}Fe_{0.05}O_{3-\delta}$. All samples were synthesized by the solid state reaction method, being $BaCO_3$, CeO_2, Y_2O_3, Sc_2O_3, MnO, Fe_2O_3 and Co_3O_4 the starting materials. No impurities were detected in their structures, except for $BaCe_{0.80}Y_{0.10}Fe_{0.10}O_{3-\delta}$ which presented a BaY_2O_4 phase. Under air atmosphere, metal doping decreases conductivity. Mn-doped compounds presented the highest decrease, and Co-doped the lowest. This value does not depend on x concentration. In hydrogen, a Co-doped material with x = 0.075 presented the highest conductivity. The authors concluded that the transition-metal doping does not change the conduction mechanism of materials in hydrogen, nor conductivity values under such atmosphere.

$BaCeO_3$ doped with Sm have been studied by Gorbova et al. [95]. $BaCe_{1-x}Sm_xO_{3-\delta}$ ($0 \leq x \leq 0.2$) powders were prepared by the solid state method using CeO_2, Sm_2O_3 and $BaCO_3$ as starting materials. A cubic perovskite phase was observed. In air, conductivity increases as x does. At 900 °C, the material with x = 0.15 showed a maximum value of $78 \cdot 10^{-3}$ S cm^{-1}, i.e. 1460% higher than that of the undoped compound. The thermal expansion coefficient was significantly lower than that of $BaCeO_3$, being this value the same as that for YSZ, therefore it can be a possible electrolyte replacement in proton-conducting SOFCs.

Oxides containing both Ce and Zr are also present in literature. Basbus et al. [92] reported a study on $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ (BCZY) which was synthesized by a solid state reaction with amounts of $BaCO_3$, CeO_2, ZrO_2 and Y_2O_3. A crystal structure with cubic symmetry was observed. The material presented a thermal expansion coefficient which is similar to those of some anode materials, but lower than commonly used cathode materials. Its protonic conductivity showed high values at wet oxidation or reducing atmosphere, approximately $1 \cdot 10^{-4}$ S cm^{-1} and it exhibited good carbon tolerance. The authors concluded that the compound is an option as electrolyte for SOFCs or to cover an electrolyte material with less carbon tolerance.

The replacement of Ba for Sr at the A-site of Y- and Sm-doped Ce- and Zr-oxides has been investigated by Radenahmad et al. [96]. $Ba_{1-x}Sr_xCe_{0.5}Zr_{0.35}Y_{0.1}Sm_{0.05}O_{3-\delta}$ (x = 0.5, 0.7, 0.9, 1.0) (BSCZYSm) was produced by a solid state reaction through stoichiometric amounts of $BaCO_3$, SrO, CeO_2, ZrO_2, Y_2O_3 and Sm_2O_3. A crystal structure with cubic symmetry was observed. Compositions with x = 0.5 and x = 1.0 exhibited the highest ($2.39 \cdot 10^{-3}$ 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 ($La_{28-y}W_{4+y}O_{54+\delta}$) are promising candidates as protonic conductors for SOFCs [97].

Nb-doped lanthanum tungstate $La_{27}W_4NbO_{55-\delta}$ (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_2O_3, WO_3 and $Nb(HC_2O_4)_5$ 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-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 $(La_{1-x}K_x)_{27.08}W_{4.92}O_{55.38-\theta}$ (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_2O_3 and fluorite $La_{28-y}W_{4+y}O_{54+\delta}$. 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 tungstates are good candidates for SOFC.

Discussions

It is evident that, once efficiency reaches 60%, CO_2 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 components due to their great properties and doping flexibility [20,104,105], and studies tend to keep introducing new elements to attenuate some drawbacks [66]. Current problems of conventional materials are gradually being alleviated, and commercial intermediate temperatures SOFCs are imminent.

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.

Cathode

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.

Table 1 − Features of reviewed materials for anodes.			
Material	Features	Sintering method	Operating temperature [°C]
Modified Ni-YSZ	Addition of Al_2O_3 on Ni-YSZ increased both the electrical conductivity and chemical stability	Two-step method	750
	Addition of Ag decreased the carbon deposition, enhancing the electrochemical performance	Co-tape casting method	750
	$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3−δ}$ (BZXYYb) infiltration into Ni-YSZ presented no reaction with YSZ electrolyte and no performance degradation in contact with H_2S	Citrate method	700
	Nb_2O_5-coated Ni-YSZ exhibited a power density 113% higher than undoped material and stability in contact with H_2S	Reactive sputtering	700
$Ce_xZr_{1-x}O_2$	Addition of Zr into CeO_2 compounds enhanced the conductivity, with maximum value at $x = 0.75$	Citrate complexation method	up to 690
LnSTM (Ln: La, Nd and Sm) perovskites	Addition of Ti−Mn to b-site perovskites increased anode chemical performance, as well as conductivity. $Nd_{0.5}Sr_{0.5}Ti_{0.5}Mn_{0.5}O_{3±d}$ (NSTM) indicated better results	Glycine nitrate process (GNP)	up to 900
Nickel-free double perovskite	$Sr_2FeNb_{0.2}Mo_{0.8}O_{6−δ}$ (SFNM20) presented higher coking resistance and redox stability, as well as satisfactory conductivity	Solid state reaction	up to 800
	Pure $Pr_{0.5}Ba_{0.5}MnO_{3−δ}$ exhibited great performance, which was enhanced by Mo doping. PBMO5 presented great performance	Combustion method	800
Modified Ni-SDC	$Mn_{1.5}Co_{1.5}O_4$ (MCO) modified anodes exhibited higher carbon deposition rate, an undesirable feature	Ethylenediaminetetra-acetic acid (EDTA) − citrate method	up to 700
	CaO-modified Ni-SDC increased the power density and stability under reduction atmosphere	Mechanical mixing	up to 700
	The addition of Cu indicated both high power density and conductivity	Glycine nitrate process (GNP)	600−800

Table 2 — Features of reviewed materials for cathodes.

Material	Features	Sintering method	Operating temperature [°C]
LaSr perovskites with GDC	GDC-coated LSM/YSZ exhibited both greater porosity and conductivity if compared to LSM/YSZ	Solid state reaction	up to 850
	LSCF-GDC with LNF as an additive improved chemical stability and electrochemical performance	GDC − citrate method LSCF − Solid state reaction	up to 750
$A_2BO_{4+\delta}$ composites	$La_{2-x}NiO_{4\pm\delta}$ (LXNO) exhibited greater performance at x = 0.01	Citrate method	lower than 900
	$La_{2-x}Ca_xNiO_{4+\delta}$ (LCNOx) presented chemical stability and great conductivity. However, the Ca doping decreased electrochemical activity	Two-step solid state reaction method	up to 800
	$La_{2-x}Pr_xNiO_{4+\delta}$ for x = 1 exhibited no decomposition at 700 °C after 30 days, operation stability and high power density	Electrostatic spray deposition method (ESD)	up to 700
	$(100 − x) La_{0.95}Ni_{0.6}Fe_{0.4}O_{3 − x}CeO_2$ (LNFCx) showed great features for 2 mol% $\leq$ x $\leq$ 50 mol%	Mechanical mixing	up to 900
	PCO-40CGO showed great stability and thermal compatibility with CGO electrolyte	Glycine nitrate process (GNP)	700
	PCO mixed with SDC20 presented chemical stability and high power density	Glycine nitrate process (GNP)	up to 1000
LnBaCo$_2$O$_{5+\delta}$ double perovskite	Ni-doped $SmBaCo_{2-x}Ni_xO_{5+\delta}$ (SBCNx) exhibited chemical stability, no reaction with SDC electrolytes and high catalytic activity	Modified EDTA-glycine method	up to 1000
	Ca-doped $Pr_{1-x}Ca_xBaCo_2O_{5+\delta}$ (PCBCO) showed compatibility with SDC electrolyte. Ca increase led to electrochemical performance decrease	Solid state reaction	up to 850
	$LaBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}.xGDC$ (LBSCO-xGDC) (x = 0, 20, 30, 40, 50, 60 wt%) with x = 40 wt% presented power density 28% higher than Sr-free material	Pechini method	650
Cobalt-free perovskite	$NdBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ (NBSCO) exhibited compatibility with SDC electrolyte, high electrochemical activity and electrical conductivity	Citrate-EDTA sol-gel method	up to 1000
	$NdBaFe_{2-x}Mn_xO_{5+\delta}$ exhibited great power density and highest conductivity at x = 0.1	Citric acid-nitrate process	500−700
	$Sr_4Fe_6O_{13-\delta}$ showed satisfactory oxygen reduction reaction activity and lower resistance than other $SrFeO_3$-based compounds	Citrate-EDTA method	900
Alkaline earth metal free perovskites	$PrNi_{0.4}Fe_{0.6}O_{3-\delta}$ exhibited high electrical conductivity and feasible TEC value	Solid state reaction	up to 1000
	La_2ZnMnO_6 presented low conductivity values, satisfactory power densities and conventional TEC value	Citrate method	up to 700
	$LaNi_{1-x}Mo_xO_3$ with x = 0.25 showed increasing conductivity with higher temperatures, as well as low overpotential losses and high power densities	Citrate method	up to 850

Table 3 − Features of reviewed materials for electrolytes.

Material	Feature	Sintering method	Operating temperature [°C]
Ionic conductivity			
Co-doped ceria	Sm and In co-doped ceria $Ce_{0.80}Sm_{0.20-x}In_xO_{1.90}$ conductivity increased as x did. The material showed great power density	Pechini method	up to 650
	The Ca content in $Ce_{1-x-y}Dy_xCa_yO_{2-\delta}$ increased the electrical conductivity	Citrate-nitrate auto-combustion method	up to 600
	$Ce_{0.80}Nd_{0.20-x}Y_xO_{1.90}$ presented satisfactory electrical conductivity, which was optimal at x = 0.2	Citrate-nitrate auto-combustion method	up to 600
Doped lanthanum silicate apatite	Ba-doped $La_{9.5}Ba_{0.5}Si_{5.5}Al_{0.5}O_{26.5}$ presented higher porosity and greater conductivity if compared to the undoped material	Solid state reaction	up to 800
	Fe- and Al-doped $La_{9.83}Si_{6-x-y}Al_xFe_yO_{26\pm\delta}$ exhibited better conductivity with increased x and decreased y	Mechanochemical activation (MA), sol-gel (SG), solid state reaction (SSR) and Pechini (PE)	600−850
	Cu-doped $La_{10}Si_{6-x}Cu_xO_{27-\delta}$ showed maximal conductivity at x = 1.5, with high electrochemical performance. However, it exhibited high thermal expansion	Sol-gel method	up to 800
Molybdenum oxides	RE_6MoO_{12} (RE = Er, Yb) presented conductivity that was 161% higher than that of 8-YSZ electrolyte	Solution combustion method	up to 1000
Protonic conductivity			
BaZr- or/and BaCe-based oxides	$BaZr_{1-x}Y_xO_{3-z}$ (x = 0, 0.05, 0.1, 0.15, 0.20, 0.25, 0.30) exhibited high conductivity with increased x and low operating temperatures	Solid state reaction	300−900
	$BaZr_{0.8-x}In_{0.2}Bi_xO_{3-\delta}$ (x = 0, 0,05, 0.1, 0.2) showed high conductivity and power density at x = 0.05	Citric acid − EDTA method	600
	$BaCe0._{90-x}Y_{0.10}M_xO_{3-\delta}$ (M = Mn, Co and Fe; $0 \leq x \leq 0.10$) had its conductivity decreased with metal doping	Solid state reaction	600−1000
	$BaCe_{1-x}Sm_xO_{3-\delta}$ ($0 \leq x \leq 0.2$) showed the highest conductivity with x = 0.15 and thermal expansion coefficient compatible with commercial electrode materials	Solid state reaction	up to 900
	$BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ exhibited thermal expansion coefficient lower than that of commercial cathode materials, good carbon tolerance and high conductivity	Solid state reaction	up to 900
	Increased Sr content in $Ba_{1-x}Sr_xCe_{0.5}Zr_{0.35}Y_{0.1}Sm_{0.05}O_{3-\delta}$ (x = 0.5, 0.7, 0.9, 1.0) decreased conductivity	Solid state reaction	300−700
Lanthanum tungstates	$La_{27}W_4NbO_{55-\delta}$ (LWNO) showed no reactions with common electrode materials and relatively low power density	Freeze-drying method	750−1000
	$(La_{1-x}K_x)_{27.08}W_{4.92}O_{55.38-\theta}$ (x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10) (LWx) exhibited the highest conductivity at x = 0.02	Solid state reaction	up to 1500

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 it 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 $BaCeO_3$-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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