



Review Article

Reduction of operation temperature in SOFCs utilizing perovskites: Review**Nagihan Caylak Delibas^{a,*} , Soudabeh Bahrami Gharamaleki^b , Masrour Mansouri^c**
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ABSTRACT

Fuel cells are electrochemical devices utilized for converting chemical energy to electrical energy. Solid Oxide Fuel Cells (SOFCs) have several advantages over other kinds. For instance, high energy efficiency expanded fuel flexibility, low environmental pollutant emission are the properties of SOFCs that make them superior to other fuel cell types. Due to these special characteristics, SOFCs are gained a great deal of attraction. These fuel cells consist of different main operating parts, a cathode, an anode, and electrolyte which each of them demands special materials to operate with the most efficiency. SOFCs mostly operate in high temperatures (800-1000 °C). Reducing the operating temperature to lower than 600 °C or intermediate temperatures 600-800 °C is one of the methods that can make them more practical devices. Perovskite oxides can be used effectively as all main parts of SOFCs because of their excellent properties like electrical and ionic conductivities, oxygen ion vacancies, great catalytic properties, thermal durability, and chemical stability to decrease the operating temperature. In this review, numerous perovskite-based materials utilized in the anode and the cathode electrodes of SOFCs are investigated in the most recent, advanced, and novel works. The perovskite materials, their properties, and their influence on the fuel cell's performance, and in some cases the sulfur tolerance of the materials when H₂S co-exists in the fuel of the fuel cell are reviewed in this paper. Adding different dopants in A-site and B-site of the perovskite oxides is the most effective way to modify the characteristics of the materials. This review can provide great data on the possible perovskite oxides with the capability of enhancing the efficiency of SOFCs by reducing the operating temperature, and their most decisive and significant characteristics, like composition, structure, electrical conductivity, electrochemical and mechanical properties for research groups working on solid oxide fuel cells.

1. Introduction

Fuel cells are efficient devices for conversion of chemical energy to electrical through electrochemical reactions, and among different fuel cells, like polymer electrolyte membrane, molten carbonate, and alkaline fuel cells (Table 1) solid oxide fuel cells (SOFCs) are the promising energy convertor with high efficiency, great fuel flexibility, they can use hydrocarbons, coal syngas, ammonia, and hydrogen, and low pollutant emission [1-4]. SOFCs consist of different parts like

anode, cathode, electrolyte, current collectors, interconnectors, and sealants. Nonetheless, all parts are effective on the performance of the fuel cells, three main elements that determine the efficiency of the cell are the porous anode, electrolyte, and porous cathode. Oxidant gas flows into the cathode and the fuel available in the anode electrode, and the reactions happen at the three-phase boundary (TBP) of electrolyte, gas, and electrode interface [5].

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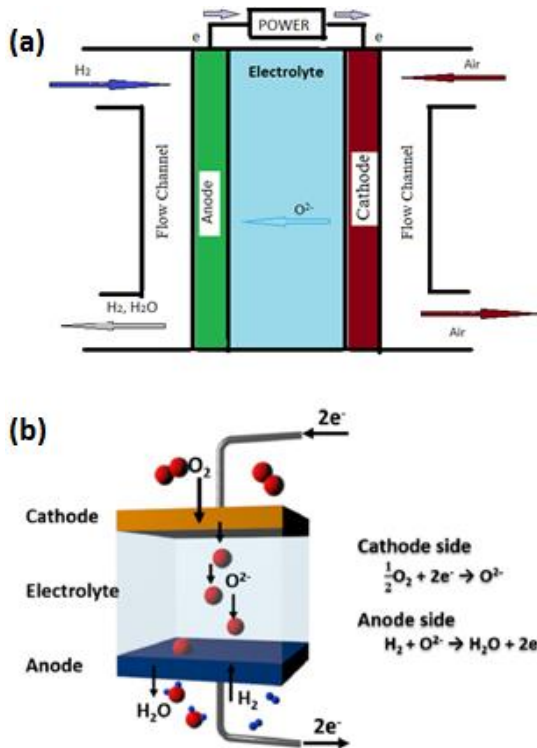


Figure 1. (a) : A schematic picture of SOFC with H₂ as fuel, (b) electrochemical reactions inside the cell [6]

In this process, the oxygen anions travel from the cathode to the anode through the electrolyte and react with the fuel in the anode electrode. As a result, electrons release in anode and go through the outer path to the cathode electrode. This way, chemical energy of the electrochemical reactions turn to electricity. A schematic picture of a solid oxide fuel cell is demonstrated in Figure 1 [6]. Although SOFCs have several advantages which make them excellent devices for electrical energy production, they have some drawbacks. One of the most problematic features of these fuel cells is their operating temperature. SOFCs mostly work at 800-1000 °C. Operating in such high temperatures could result in a decreased lifetime of the cell, low compatibility between the components, high thermal degradation of cell's materials, a long time of start-up, and higher costs. Thus, lowering the operating temperature to low temperatures like < 600 °C or to intermediate temperatures 600-800 °C is essential to address these problems to have the possibility to choose among various materials, with different characteristics, that can work in lower temperatures without having the problems mentioned above for fuel cell's components used in high temperatures [7-9].

This way, the chance to find the most suitable material for three main parts of the SOFC can enhance and as a result, the efficiency of the fuel cell can increase. However, cathodic polarization increases at lower temperatures, which leads to reduced cell output.

Table 1. Different fuel cells' properties [12]

Fuel Cell	T (°C)	Electrolyte	Transported Ion	Efficiency
Solid Oxide	550-1000	Dense Ceramics	O ²⁻	40-60%
Polymeric Exchange Membrane	60-100	Polymer	H ⁺	35-45%
Alkaline	50-120	Potassium Hydroxide	OH ⁻	35-55%
Molten Carbonate	550-650	Molten Carbonates	CO ₃ ²⁻	45-55%
Phosphoric Acid	180-210	Phosphoric Acid	H ⁺	35-45%

Due to this issue, the selection of materials for the electrodes is a vital decision and can significantly affect the cell's efficiency [10]. Perovskite-based materials are one of the most appropriate anode and cathode materials for SOFCs because of their excellent characteristics such as super electrical conductivity, catalytic activity, Ferro and piezoelectric, thermal stability, magnetoresistance, mechanical durability, and low cost [11]. In this review, we focused on the perovskite-based materials utilized in the anode and the cathode of SOFCs operating mostly in low or intermediate temperatures. In other words, the perovskite materials, their characteristics, performance, and weaknesses when used as SOFCs' anode and cathode are elaborated in this review paper and the most efficient way to improve the electrochemical properties of the perovskite oxides is introduced. All in all, this paper could be used as a source to review the features of the perovskites used in SOFCs electrodes to enhance their performances, how to make those perovskite materials, and how to measure the properties of the oxides by the researchers and students working on improving intermediate temperature solid oxide fuel cells.

2. Perovskites

Perovskites have ABO₃ composition formula, but there are other perovskite-based materials such as double perovskites, layered perovskites, and perovskite-like materials. [13,14]. Perovskites have a cubic structure in which the A-site cation's (mostly alkaline earth or rare earth metal cation) coordination number is 12 and the B-site cation's (transition metal cation) coordination number is 6. The B-site cation is often smaller than the A-site cation.

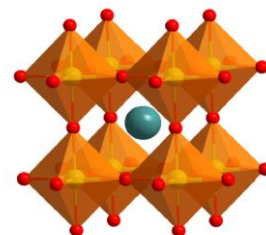


Figure 2. Schematic of perovskite structure [7]

A single perovskite's structure is illustrated in Figure 2 [15, 16]. Mixed ionic and electric-conducting perovskites have excellent oxygen ionic and electric conductivity with larger TBP areas that result in enhanced performance of the cell [17, 18]. Numerous studies have been done on the investigation of the synthesis method's effect, the performance of the perovskite-based materials, and their characteristics. . Because of their electrochemical, catalytic properties and various structures, perovskites have numerous applications like being solid oxide fuel cells' components, gas sensors, and high temperature superconductors, magnetic and dielectric materials. Perovskite materials can have different morphologies (Figure 3) [19]. The structure of perovskites can elongate, tilt or rotate due to the decrease of a coordination number, doping, pressure and temperature. Moreover, the distortion from cubic to one of lower symmetry can result in various morphologies such as orthorhombic, tetragonal, and monoclinic structures.

Composition, structure, and chemical bonds in the perovskite explain the features of the oxides. For instance, the thermal expansion coefficient and catalytic activity of the perovskite materials depend on strength of chemical bonds and band structure. Figure 4 demonstrates the dependence of the electronic conductivity to temperature of various SrTiFeO_3 (STF) and SrTiNbO_3 (STN) perovskites. One can see from this picture that STN perovskites have better conductivity than STFs and temperature does not have significant effect on the electronic conductivity of all perovskites [20].

3. Perovskites Utilized in The Cathode

In the cathodic part of the fuel cell, oxygen enters the fuel cell and turns into oxygen ions through oxygen reduction reaction (ORR) [22, 23]. There are various perovskite-based materials that can make great cathodes. Perovskites with cobalt at the B-site of the perovskite structure have properties like reducing polarization resistance, and high conductivity that make them suitable materials for the cathode electrodes Figure 5 demonstrates the conductivity of a La-based perovskite. For instance, Meng et al investigated the conductivities and CTEs of $\text{Pr}_{1-x}\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($x=0.2, 0.4, 0.6$) perovskites and they reported that the sample with $x=0.4$ has the highest conductivity (1040 Sm^{-1}) among all perovskites. However, the CTEs of the samples were higher than the CTEs of standard electrolytes, thus, they cannot be used without further modifications in fuel cells to reduce CTEs [24].

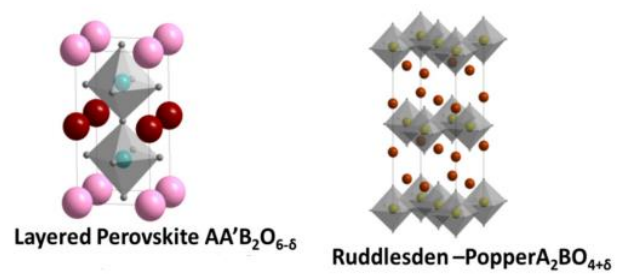


Figure 3. Different perovskite materials' structure [19]

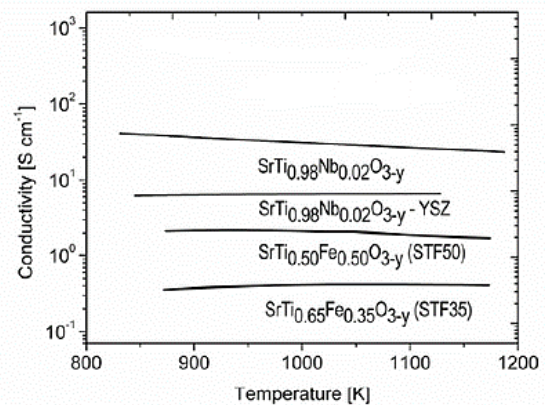


Figure 4. Electronic conductivity of STN and STF perovskites [20]

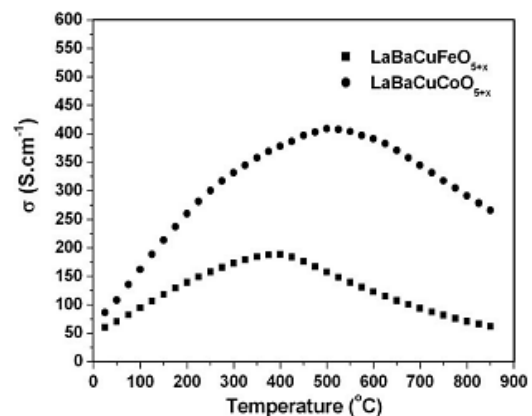


Figure 5. La-based perovskite showed better conductivity with Co rather than Fe in B-site [21]

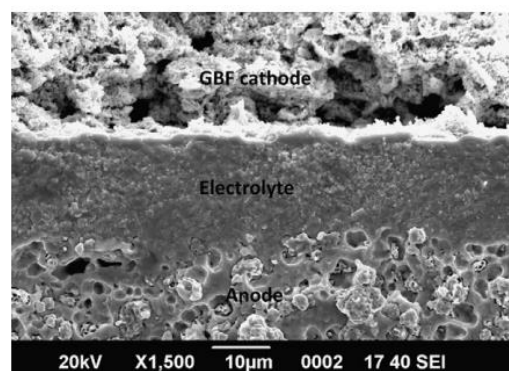


Figure 6. GBF cathode layer in a tri-layer cell [25]

Moreover, perovskites with Lanthanum at A-site with a transition metal at B-site because of high MIEC are one of the most promising cathode materials. Also, it is reported that at low temperatures, La-based perovskite materials have good porosity and ionic and electrical conductivity that make them a good choice for SOFC's electrodes [10].

GdBaFe₂O_{5+δ} (GBF) perovskites were synthesized using modified Pechini process and characterized by Ding et al [25] and the sample showed good catalytic activity for oxygen reduction. It also demonstrated the lowest polarization resistance 0.08 Ωcm² and the highest power density 861 mWcm⁻² at 700 °C. GBF cathode layer is demonstrated in Figure 6. Bebels et al investigated the electrochemical properties of La_{0.58}Sr_{0.44}Co_{0.2}Fe_{0.8}O_{3-δ}, La_{0.78}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-δ} and composite La_{0.65}Sr_{0.3}MnO_{3-δ} – 8 mol% Y₂O₃ stabilized ZrO₂ as cathode electrodes for SOFCs with Ce_{0.8}Gd_{0.2}O_{2-δ} (CGO) and YSZ as electrolyte at 600–850 °C using impedance spectroscopy and current-overpotential measurements. The perovskite materials were prepared by the spray-drying technique. Tests have demonstrated that the L₇₈SCF perovskite exhibits the lowest area specific polarization resistance RF (0.4 W cm² at 800 °C and PO₂ = 21 kPa) which means that this perovskite has the highest electrocatalytic activity among all other samples. [26].

Zhou et al [27] investigate LaSrMnCoO_{5+δ}'s CTE and conductivity between 30-1000 °C and reported that the perovskite has higher CTE compared to YSZ, and Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) which are standard electrolytes, and lower conductivity than the LnBaCo₂O_{5+δ} perovskite. Nevertheless, it exhibited good thermal compatibility with SDC at 600-850 °C. Irshad et al studied the performance of a solid oxide fuel cell with a cobalt doped LaNiO₃ perovskite (LaNi_{1-x}Co_xO_{3-δ} (x = 0.4, 0.6, 0.8) as cathode electrode. The perovskite oxides were synthesized by high temperature decomposition in a furnace approach. Measurements reveal that LaNi_{1-x}Co_xO_{3-δ} (x =0.6) showed the highest value of conductivity (Figure 7) because of its porous and networked structure of sub micrometric grains. The maximum power density for the cell with LaNi_{1-x}Co_xO_{3-δ} (x = 0.6) as cathode was 0.45 Wcm²[28]. Ling et al [29] observed the performance of cubic perovskite oxide Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-δ} (SSFCu) prepared by the modified Pechini method. They stated that the oxygen (O₂) vacancies enhanced which led to the improved electrochemical activity of the sample and the conductivity of the sample is about 72-82 S Cm⁻¹ between 400-600 °C. They also mentioned that the CTEs of SSFC and SDC (as electrolyte) are about the same. The temperature dependence of the conductivity of the SSFC is depicted in Figure 8. Three cathode materials La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃, Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O₃, and Sm_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O₃ were studied by Shen et al [30] at various temperatures and it was understood that La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ had the highest conductivity (176 S cm⁻¹) at 300 °C. Mostafavi et al compared the properties of two

different types of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF) powders (one prepared by co-precipitation method and the other one purchased from a commercial source) as cathode materials.

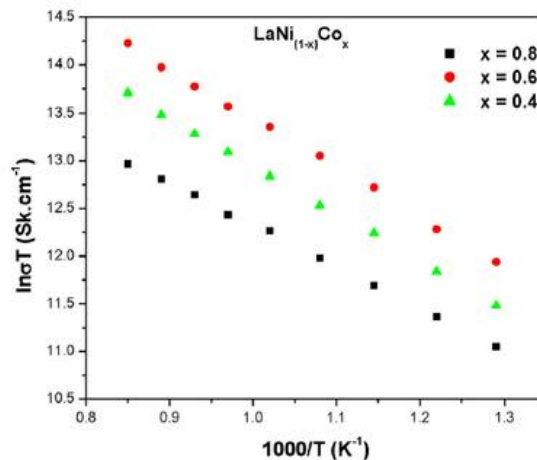


Figure 7. Comparison of electronic conductivity of LaNi_{1-x}Co_x (x= 0.4, 0.6, and 0.8) [28]

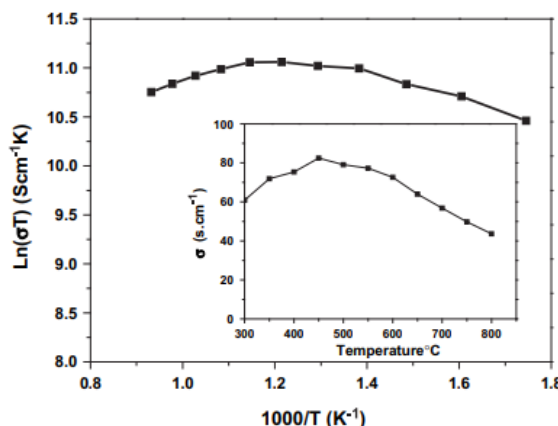


Figure 8. Electrical conductivities of SSFCu samples at different temperatures [29]

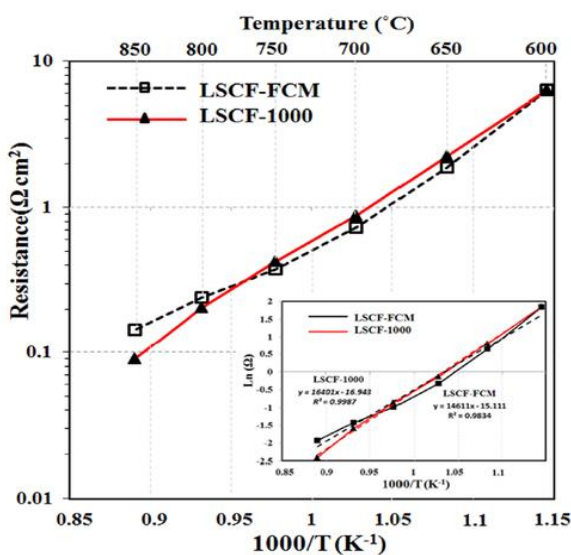


Figure 9. Comparison of resistance of two types of LSCF perovskites [31]

They studied various features of these perovskites such as electrochemical characteristics, morphology, phase composition and particle size and reported that polarization resistance and activation energy are almost the same for both powders and as it is illustrated in Figure 9 polarization resistance decreases when temperature increases. [31].

Choi et al [32] studied electrical conductivity of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (NSC) with ($x=0.3, 0.4, 0.5, 0.6,$ and 0.7) and stated that the conductivity of the samples improved with the increase of Sr content up to 0.5 , but when the Sr content surpassed 0.5 , due to more dominant ionic compensation, the electrical conductivity decreases.

The electrical conductivities of NSC perovskites are demonstrated in Figure 10.

Wu et al [33] investigated the characteristics of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x=0-0.6$) perovskites. The conductivities of the samples were dependent on the structure of the materials, the amount of dopants, and the temperature. The results showed the transferring semiconductor to a metallic behavior and among all the compositions the sample with $x=0.4$ demonstrated the best conductivity (2583 S Cm^{-1}) at 500°C . However, the CTE of the sample was quite high in comparison with the standard electrolytes that could lead to the reduction of mechanical durability and the sample should be modified to have lower CTE. Hammouche et al [34] tested the thermal expansion coefficient and conductivities of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system ($x=0-0.5$) and reported that all the samples CTEs are close to the standard electrolyte YSZ, nevertheless, the weakly doped compositions demonstrated the highest thermal compatibility with YSZ and the electrochemical activity of the samples increased with the increasing of dopant content. Ullmann et al measured the electrochemical (electrical conductivity and ionic transport) and other important properties (thermal expansion and oxygen deficiency) of $\text{A}_{1-a}\text{A}'_a\text{BO}_3$ perovskite-type materials ($\text{A}=\text{La}, \text{Pr}, \text{Ce}; \text{A}=\text{Sr}; \text{B}=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Ga}, \text{Mg}$) as cathode. They stated that lanthanum manganite has the lowest thermal expansion coefficient and highest thermodynamic stability among all other perovskite-type oxides. They also found that the electronic conductivity is affected by Fe and Co in the b-site of the perovskite and ionic conductivity is related to the concentration of Sr in the A-site of the structure [35].

The crystal structure, electrical conductivity, and CTE of $\text{NdBaCu}_2\text{O}_{5+\delta}$ and $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Cu}_2\text{O}_{5+\delta}$ were investigated by Kong et al [36] and they observed that the electrical conductivity of samples at 560°C (16.87 S Cm^{-1}) and 545°C (51.92 S Cm^{-1}) are higher than conductivities at other temperatures due to some phase transitions. Also, it was reported that the CTE values of the samples were compatible with $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ electrolyte.

The reduction in CTE values for these cobalt-free Nd-based perovskites is related to the spin-state transition of Cu and the absence of Co.

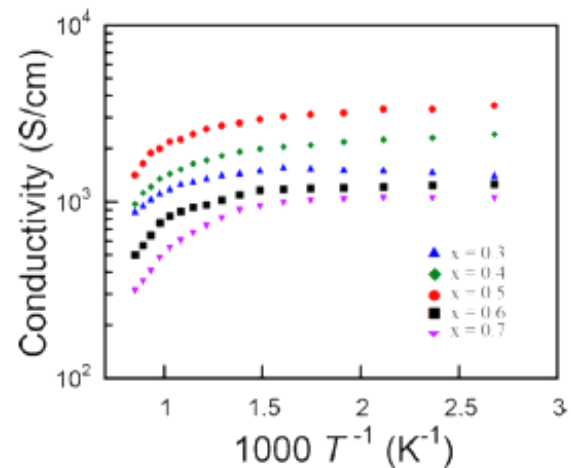


Figure 10. Electrical conductivities of NSC samples at different temperatures [6]

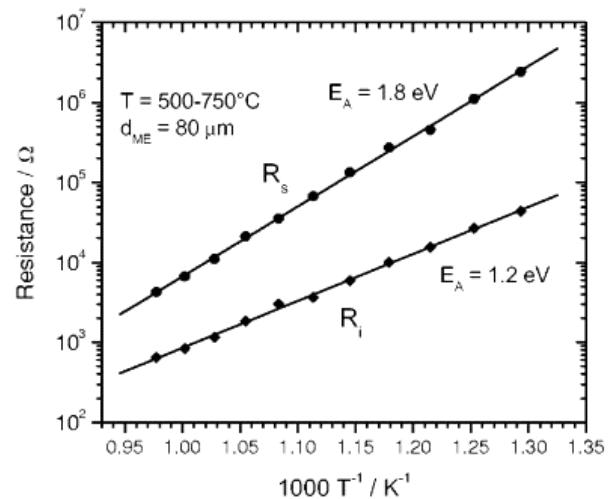


Figure 11. Resistance of BSCF perovskite at different temperatures [37]

The MICE perovskite materials like $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) were studied by Baumann et al [37] and the data exhibited that the surface exchange kinetics improved by the substitution of the A-site cation La in $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ by Sm and Ba. In fact, the electrochemical resistance was $0.09 \text{ }\Omega\text{cm}^2$ for the BSCF at 750°C . Resistance- Temperature diagram of BSCF is depicted in Figure 11. Gędziorowski et al. [38] observed the features of Ba-doped $\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and stated that by increasing the amount of Ba the level of oxygen non-stoichiometry increased, as the result of reduction of the distortion of perovskite structure, which resulted in increasing conductivity; however, the conductivities were lower than the suitable amount for the cathode materials of SOFCs. Li et al [39] investigated the performance of $\text{GdBaCo}_2\text{O}_{5+\delta}$ perovskite material prepared by conventional ceramic method and they stated that the CTE values are close to the standard electrolyte material SDC and the electrical conductivity was $512-290 \text{ S Cm}^{-1}$ in

the temperature range of 500-800 °C. The properties of Sr doped on $\text{PrBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{5+\delta}$ ($x=0, 0.25, 0.5, 0.75, 1.0$) double perovskites synthesized by the Pechini process were studied by Park et al [40] and it was stated that the electrical conductivity of $\text{PrBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{5+\delta}$ enhances with increasing Sr content because of higher oxygen content as a result of smaller size differences between Sr^{2+} and Pr^{3+} and special order of these ions layers in the structure of the double perovskites for all temperature regions. PrMnO perovskites' efficacy as SOFC cathode electrodes are investigated by Ishihara et al and they stated that Sr-doped material is better than the LSM oxides in terms of thermal expansion compatibility with YSZ electrolytes and low They also demonstrated low reactivity with YSZ and cathodic overpotential (Figure 12) as a result of high activity for the dissociation of oxygen [41].

4. Perovskites Utilized in The Anode

To choose appropriate anode materials for SOFCs, several characteristics should be considered. The materials should have a large surface area at TBP, sufficient porosity, high electronic conductivity, good electrocatalytic activity, stability, and thermal durability [42].

Different perovskite-based anode materials used in SOFCs have been studied. For instance, strontium doped lanthanum chromite (LSCr) perovskites exhibit improved properties (electrical conductivity, thermal durability, redox stability) when other cations with lower coordination numbers (such as Fe, Mn, Ni, and Co) are introduced to these materials [43].

Also, LaSrTiO_3 materials due to their excellent electronic conductivity, great dimensional durability and outstanding chemical stability and, high sulfur and coking resistance can make great anode materials [44].

Moreover, there are ferrite-based perovskites that are suitable for SOFC anode applications such as SrFeO_3 , LaFeO_3 , and SmFeO_3 . Nevertheless, these single perovskites require some modifications (like doping with other metal cations with higher oxidation states) to enhance their electrical conductivity and chemical durability [45].

Chen et al developed a cathode-supported SOFC with GDC-impregnated $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) anode electrode working with weakly humidified hydrogen and/or methane as fuel and investigated the performance of the fuel cell at different temperatures. They stated that the performance of the cell is comparable to the cell made of Ni cermet while stable in weakly humidified methane fuel with 0.352 W/cm² maximum power density at 900°C [46].

The performances of various $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{X}_{0.5}\text{O}_{3-\delta}$ samples prepared with combustion gel approach with $\text{X}=\text{Co}, \text{Fe}, \text{Ti}, \text{Mn}$ were tested by Danilovic et al [47] as SOFCs anode. The results depicted that the sample with Co had the highest catalytic activity, while the one with Ti had the lowest catalytic activity when the fuel was CH_4 . They, also, reported that the power density of the cell is the highest when

the Fe was utilized as the dopant when the feed was CH_4 or H_2 , but when the feed contained H_2S and CH_4 the sample with Ti showed the best performance.

Figure 13 depicts the power densities and conductivities of LSC perovskites. Fowler et al [48] investigated the application of $\text{La}_{1-x}\text{Sr}_x\text{Cr}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ material synthesized by solid-state reaction method as SOFC anode. It was reported that the $\text{La}_{0.33}\text{Sr}_{0.67}\text{Cr}_{0.33}\text{Fe}_{0.67}\text{O}_{3-\delta}$ exhibited the lowest anodic polarization resistance (0.275 Ωcm^2) at 800 °C due to the higher amount of oxygen loss when the content of Fe was high. Furthermore, these perovskites exhibited excellent ionic conductivity. The resistance of the perovskite versus temperature is demonstrated in Figure 14.

Chemical compatibility with different electrolytes and phase stability of $\text{Sr}_2\text{BMoO}_{6-\delta}$ ($\text{B} = \text{Mg}, \text{Ni}$ and Co) and $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ double perovskites have been evaluated by Gomez et al. The findings show that the mentioned perovskites are highly reactive with $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{2-\delta}$ at 800 °C. Nevertheless, their reactivity with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ was low.

Both perovskites demonstrated low durability against carbonation in the intermediate temperature range 600–800 °C, but $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ showed stability in pure CO_2 and H_2 atmospheres [49].

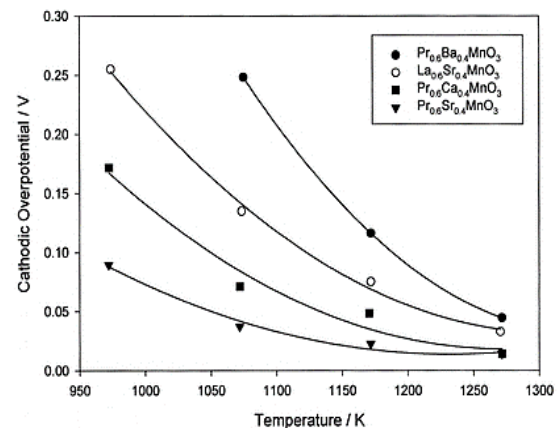


Figure 12. Cathodic overpotential of PrMnO and LSM perovskites [41]

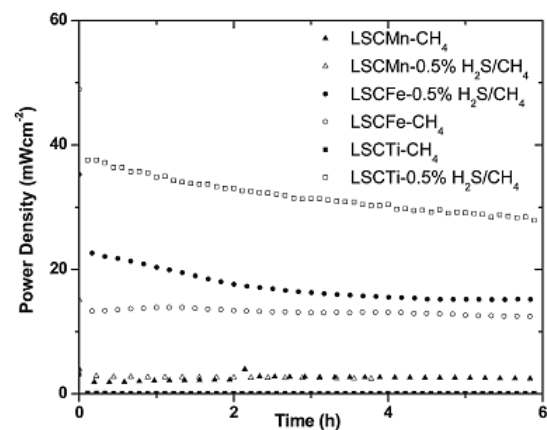


Figure 13. Power Densities of LSC perovskites with various dopants [47]

Li et al [50] tested the properties of different $(La_{0.3}Sr_{0.7})_{1-x}TiO_{3-\delta}$ ($x = 0, 0.03, 0.05, 0.07, 0.10$) perovskites, prepared by solid-state reaction approach, using an electron-blocking method and they stated that when the A-site deficiency increased the electronic conductivity decreased but the ionic conductivity increased. Moreover, it can improve the thermal durability of the samples and the samples showed stable electrical performance in different situations. The electrical conductivities of the samples are available in Figure 15.

Sun et al. [51] evaluated Mo doped $Pr_{0.5}Ba_{0.5}MnO_{3-\delta}$ (Mo-PBMO) double perovskite material synthesized by modified sol-gel approach as anode material for solid oxide fuel cell. The results of analyses showed that the perovskite has a large amount of oxygen deficiency. This property can improve the oxygen diffusion and electrochemical properties of the double perovskite by introducing Mo to the perovskite structure.

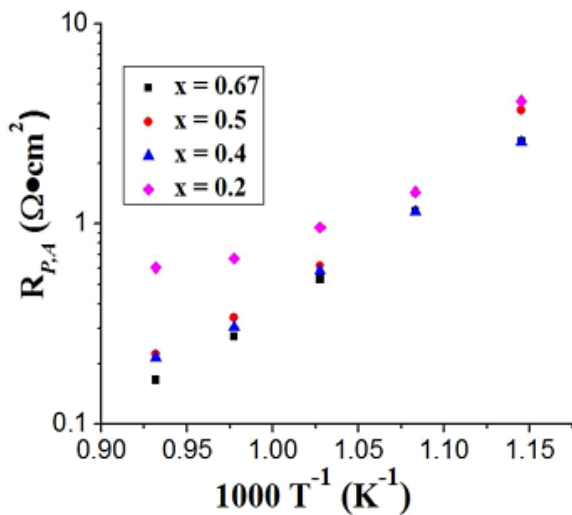


Figure 14. Resistance of LSCrFe samples at different temperatures [48]

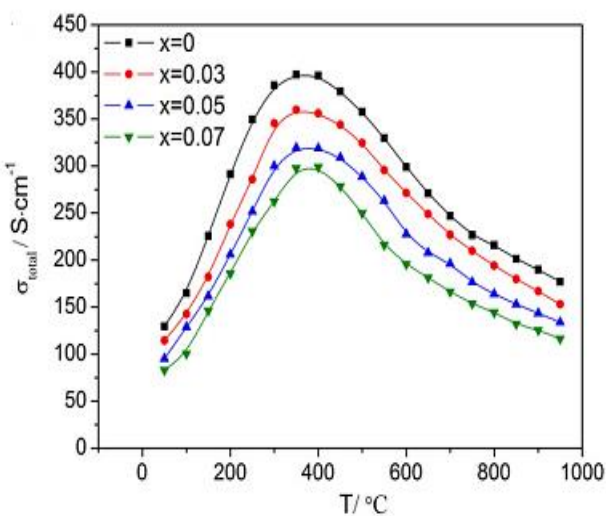


Figure 15. Conductivities of LST samples at different temperatures [50]

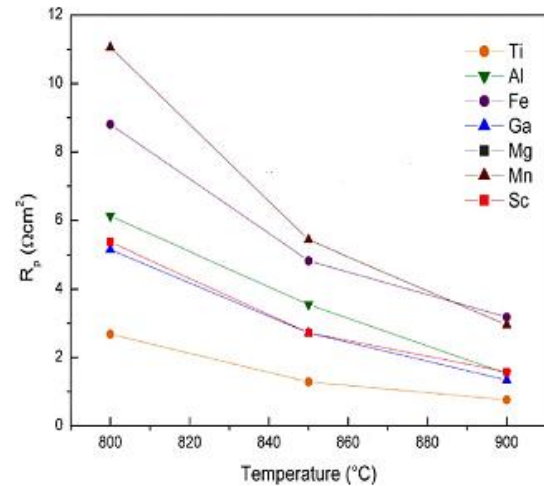


Figure 16. Polarization Resistance of LSTX-YSZ anodes with various dopants at different temperatures [54]

Its catalytic activity enhanced for H_2 and CH_4 oxidation reactions [51]. Steiger et al [52] studied the performance of $La_{0.3}Sr_{0.55}TiO_{3-\delta}$ (LST) and LSTN mixed perovskite-type structure using citrate gel method and they reported that good sulfur tolerance and stability, and $0.58 \Omega cm^2$ polarization resistance at $850^\circ C$. Yoon et al [53] observed the effect of Co, Mn, and Fe doping in $La_{0.08}Sr_{0.92}M_{0.2}Ti_{0.8}O_{3-\delta}$ as SOFC anode with CH_4 as fuel. The results demonstrated that the Co and Fe doped perovskites showed higher catalytic activity, which can be related to high oxygen vacancies and high multivalent redox couples' ratio. However, the sample exhibited high polarization resistance at $800^\circ C$. Miller et al [54] tested the characteristics of $La_{0.33}Sr_{0.67}Ti_{0.92}X_{0.08}O_3$ doped with various dopants X ($X = Al^{3+}, Ga^{3+}, Fe^{n+}, Mg^{2+}, Mn^{n+},$ and Sc^{3+}), and they observed that the type of dopant can influence the redox characteristics, electrochemical performance, and morphology of the samples. It is also mentioned that at $900^\circ C$ $La_{0.33}Sr_{0.67}TiO_{3-\delta}$ sample had the lowest polarization resistance while the sample doped with Mg demonstrated the highest polarization resistance which is depicted in Figure 16.

Fu et al studied the performance of $La_{0.4}Sr_{0.6}Ti_{1-x}Mn_xO_{3-x}$ ($x = 0, 0.2, 0.4, 0.6$) perovskites as SOFCs' anode materials. The results revealed that the $La_{0.4}Sr_{0.6}Ti_{0.4}Mn_{0.6}O_{3-\delta}$ (LSTM4646) perovskite oxide is thermally compatible with the used electrolyte (YSZ) and shows low polarization resistance ($0.32 \Omega cm^2$), high catalytic activity and stability in moderately humidified hydrogen atmosphere. the electronic conductivity is of $1/5 S/cm$ in wet $Ar/4\% H_2$ ($PO_2 = 10-18$ bar) at $810^\circ C$ [55].

Choi et al [56] investigated the effect of doping Ce in $Sr_{1-x}Ce_xCo_{0.2}Fe_{0.8}O_{3-\delta}$ ($x = 0.10, 0.15,$ and 0.20) samples prepared by EDTA-citrate complexing approach and they stated that the higher Ce doping in A-site could lead to more stable perovskites. In addition, the samples showed excellent

conductivity at temperatures <600 °C, but at higher temperatures, the samples break down and did not perform well. It is also mentioned that the sample with Ce demonstrated good sulfur tolerance in the presence of H_2S in the fuel. Cascos et al improved the characteristics of $SrMo_{1-x}M_xO_{3-\delta}$ ($M = Fe$ and Cr , $x = 0.1$ and 0.2) perovskite materials to be used as intermediate temperature solid oxide fuel cells' anode electrode. They doped aliovalent Mg ions at the B-site of the perovskite oxide and test the fuel cell's output power at 850 °C which was about 900 mW/cm². They reported high ion conductivity and good thermal compatibility with the LSGM electrolyte for $SrMoO_3$ perovskite [57].

As Figure 17 demonstrates, the electronic conductivity of the samples decreases by increasing the content of Mg. That would be due to this fact that Mg^{2+} ions can perturb the conduction paths. However, the obtained conductivities for $x=0.1$ and 0.2 (146 and 114 S cm⁻¹ respectively) at 850 °C are adequate for proper performance of the cell with hydrogen as fuel. The effect of doping Co on the electrochemical performance, stability, and sulfur tolerance of $La_{0.3}Sr_{0.7}Co_{0.07}Ti_{0.93}O_3$ perovskite was investigated by Cui et al [58].

The perovskite was synthesized by solid-state reaction method and it was reported that the electrocatalyst performance and electrical conductivity of the sample increased by the introduction of Co to its structure and it achieved the maximum 300 mW cm⁻² power density at 900 °C in the presence of H_2S in the fuel. The Co nanoparticles on the surface can reduce the polarization resistance of the anode and also, the material showed high sulfur tolerance and redox stability. The Power Density-temperature diagram is depicted in Figure 18.

$Sr_2FeNb_{0.2}Mo_{0.8}O_{6-\delta}$ (SFNM20) double perovskite's performance as a solid oxide fuel cell's anode has been investigated by Ding et al and they reported that this anode materials showed significant performance, redox cycling in hydrocarbon fuels, and high resistance against carbon build-up. The SFNM20 perovskite demonstrated 5.3 S cm⁻¹ electronic conductivity and 520 mW cm⁻² maximum power density with hydrogen as fuel.

The perovskite material was durable when using different fuels (Figure 19). This figure confirms that the anode material is stable for different fuels and it has high fuel flexibility [59].

Research shows that the substitution of Sr, Ba, and Ce in the A-site of these perovskites can enhance their electrochemical properties. However, some studies suggest that the mentioned perovskite materials require further modification to have higher porosity, durability, and conductivity, therefore, further investigation is needed to tailor the structure and properties of perovskites in order to make them more attractive, applicable, and efficient

choices for SOFCs. Table 2 contains a summary of the literature.

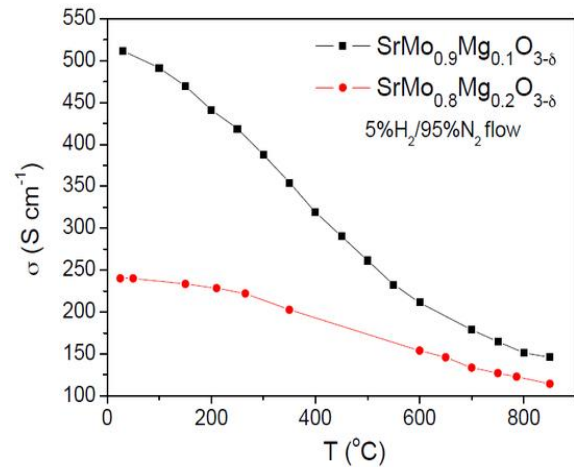


Figure 17. Electronic conductivity of SMMO perovskites [57]

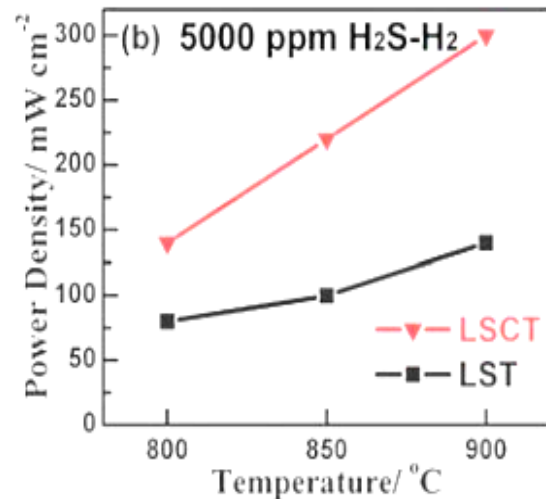


Figure 18. Power Densities of LST and LSCT perovskites with pure H_2/H_2S at different temperatures [58]

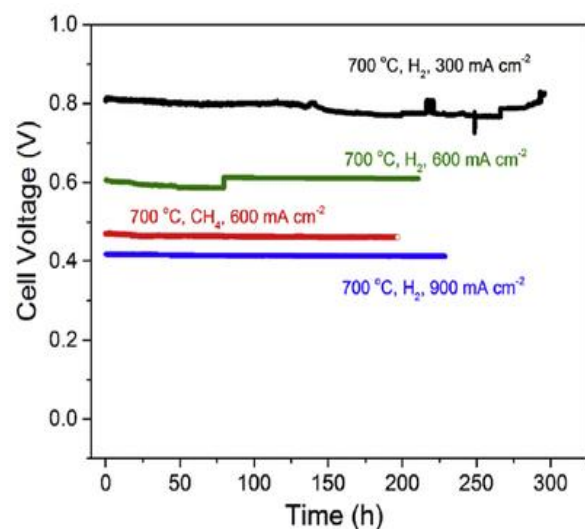


Figure 19. Durability of cell with various fuels [59]

Table 2. Summary of used perovskites as SOFCs anode, cathode and electrolyte

Application	Electrolyte	Cathode	Anode	Ref.
SOFC	$\text{SrTi}_{1-x}\text{Nb}_x\text{O}_{3-\delta}$ ($x = 0.2$)	$\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ (NCAL)	$\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ (NCAL)	[60]
SOFC	$\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$	$\text{Ni-Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$	[61]
SOFC	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.7}\text{Mg}_{0.3}\text{O}_{3-\delta}$	$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$	[62]
SOFC	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$	[63]
SOFC	LaGaO_3	–	Nickel–Gd-doped CeO	[64]
SOFC	Fe-doped $\text{SrTiO}_{3-\delta}$	–	–	[65]
SOFC	$(\text{La}, \text{Sr})(\text{Ga}, \text{Mg})\text{O}_3$	$(\text{La}, \text{Sr})\text{CoO}_3$	$(\text{La}, \text{Sr})(\text{Ga}, \text{Mn})\text{O}_3$	[66]
SOFC	$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{X}_{0.5}\text{O}_{3-\delta}$ ($\text{X}_- = \text{Mn}, \text{Fe} \& \text{Al}$)	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{X}_{0.5}\text{O}_{3-\delta}$ ($\text{X}_- = \text{Mn}, \text{Fe} \& \text{Al}$)	[67]
SOFC	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3-\delta}$	$(\text{La}_{0.75}\text{Sr}_{0.25})\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$	$\text{Gd}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$	[68]
SOFC	$\text{BaZr}_{0.85}\text{Y}_{0.15}\text{O}_3$	Ni	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$	[69]
SOFC	LaGaO_3	$\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_3$	Ni–Fe bimetal	[70]
SOFC	$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.3}\text{Fe}_{0.7}\text{O}_3$	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.3}\text{Fe}_{0.7}\text{O}_3$	[71]
SOFC	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$	$\text{SrFe}_{0.9-x}\text{Cu}_x\text{W}_{0.1}\text{O}_{3-\delta}$	–	[72]
SOFC	$\text{La-BaZrYO}_{3-\delta}$	$\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ (NCAL)	$\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ (NCAL)	[73]
SOFC	$\text{BaCe}_{0.7-x}\text{Sm}_x\text{Zr}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$	$\text{Ni-BaCe}_{0.7-x}\text{Sm}_x\text{Zr}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$	–	[74]
SOFC	$\text{La}_x\text{Sr}_{1-x}\text{Ga}_y\text{Mg}_{1-y}\text{O}_{3-\delta}$	$\text{Pr}_{0.8}\text{Sr}_{0.2}\text{Co}_x\text{Z}_{1-x}\text{O}_{3-\delta}$ ($\text{Z}=\text{Mn}, \text{Fe}$)	–	[75]
SOFC	Al-doped $\text{La}_{1-x}\text{Sr}_x\text{ScO}_3$	–	–	[76]

5. Conclusions

Fuel cells are among the significant electricity producers. One of the major drawbacks of the SOFCs that can lead to several problems like thermal degradation and long start-up time is the high operating temperature of the cell (800-1000 °C). To reduce the operating temperature to intermediate (600-800 °C) or lower temperature usage of some specific materials for both electrodes is necessary. Perovskite-based materials are proven to be appropriate materials to have efficient SOFCs at low or intermediate temperatures. In this review, we focused on the studies that investigated the characteristics and performance of various perovskite-based materials to give a comprehensive view of the approaches that can be utilized to improve the efficiency of the solid oxide fuel cells at lower temperatures. It is understood from the literature that is reviewed that the introduction of various dopants is a promising approach to modify the characteristics of the perovskites and make them suitable electrodes for SOFCs. La and Sm- based perovskites with Co, Cr, or Ti in B-site of the mixed oxides showed good electrocatalytic activity, conductivity, expansion compatibility with standard electrolytes (YSZ- SDC), stability, and in some cases excellent sulfur tolerance as SOFC's anode and cathode material.

Declaration

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The authors also declared that this article is original, was prepared in accordance with international publication and research ethics, and ethical committee permission or any special permission is not required.

Author Contributions

All authors conceived the study together. N. Caylak Delibaş and A. Niaei contributed to the formation of the idea, and in scientific support, S.B. Gharamaleki and M. Mansouri were in charge of the preparation of the literature review, and writing the article.

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