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Advances in the knowledge of the double perovskites derived from the conformation and substitution of the material $Sr_2MgMoO_{6-\delta}$ as anode with potential application in SOFC cell

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HIGHLIGHTS

• Review of $Sr_2MgMoO_{6-\delta}$ double perovskite and its derivatives with application as anode in SOFC cells.

- Catalytic, thermal, electrical, power, morphological, structural characteristics and the synthesis methods analysis.
- Carbon deposit resistance and sulfur tolerance analysis.
- Analysis of electrolyte and cathode compatibility with Sr₂MgMoO_{6-δ} double perovskite.
- Study of electrical and power properties in fuels such as hydrogen and hydrocarbons.

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ABSTRACT

Regardless of the manufacturing process such as solid-state reaction, sol-gel, etc., applied in obtaining anodes in solid oxide fuel cells (SOFCs), Sr₂MgMoO₆₋₈ (SMMO) double perovskites are recognized worldwide and widely used as anodic material with potential application in SOFC. This is due to several factors such as high electronic conductivity, high electrocatalytic activity, structural stability under reducing atmosphere, high transition temperature, giant magnetoresistance, reasonable tolerance to carbon formation, and its desired ability to reduce sulfur poisoning. In this review article, the advances of the SMMO double perovskite are analyzed. © 2021 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

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Anode SOFC Electronic conductivity

Introduction

Today, fuel cells represent one of the most efficient solutions to serious environmental problems. It has been faithfully demonstrated that global warming is primarily due to emissions of greenhouse gases such as carbon dioxide [1]. As can be seen in Fig. 1 and Table 1, of the fuel cells available in the energy market, those in the classification of solid oxides (SOFC), are capable of producing electrical energy through the use of combustible gases such as hydrogen and/or methane, which can be obtained from the thermal transformation of biomass with a special interest in agro-forestry waste. These gases promote the generation of electricity in a fuel cell by coming into contact with its components, in the case of a SOFC, it is at the anode where the fuel is oxidized to generate the electrons. This type of cell has been developed very in Mexico and in some Latin American countries. In fact, they are in an experimental stage; however, they constitute an excellent opportunity to take advantage of agro-forestry and wood waste in order to support diverse areas with high energy needs in this country, providing services such as air conditioning in hot or cold seasons, in addition to producing electricity. Additionally, and as can be appreciated in Table 1, the solid oxide fuel cell has three main advantages that guarantee the application of energy on a large scale in the near future, complying with current environmental standards [2]. Firstly, it has demonstrated high efficiency in converting chemical energy into electrical energy and is not limited by the Carnot cycle. For example, according to the literature, if it were possible to combine a solid oxide fuel cell with a gas turbine, it would be possible to obtain up to 70% efficiency [3]. Secondly, there is a very low impact in relation to emissions into the environment. Finally, it has excellent fuel flexibility to use hydrogen, hydrocarbons, solid carbon, and

ammonia. In general, a SOFC requires an oxygen ionconducting electrolyte, as well as an anode where water vapor is formed to allow dilution of the fuel gas. In this sense, and taking into account the increase in energy demand, it is quite feasible to apply new energy technologies, in this case, the SOFC type cells, for sustainable development, contributing to full compliance with environmental codes and policies [2].

The primary structural elements of a SOFC are an anode (porous), an electrolyte (dense), and a cathode (porous). All these elements can be composed of an infinite number of compositions of various oxide-type materials. It is important to mention that the internal morphology of the electrodes for SOFC must have an acceptable particle size (micrometric and nanometric), excellent interconnected porosity disseminated in sponge-like structures [8], optimal pore distribution to ensure the transport of oxygen (cathode) and hydrogen as fuel (anode). By ensuring an optimal morphology in the materials, it can be considered that there will be an acceptable electronic conductivity, and therefore a good performance in the generation of electrical energy [9]. In this sense, perovskites have been used for certain components of the SOFC cell. This is due to important characteristics of this structure such as resistance to coke formation, resistance to sulfur poisoning when using hydrocarbon fuels, as well as stability in oxidation and reduction cycles [10]. Important research activities have been carried out to explore new materials with the double perovskite-type structure in order to understand the source of their properties, improve them and adapt the methods of synthesis of their materials from the laboratory and scale them to the production technology for each application [11,12]. According to the state of the art, the crystal structure of perovskite has been classified as ABO₃ (single perovskite-Fig. 2a), A₂BB'O₆ (double perovskite-Fig. 2b), formed by



Fig. 1 - Fuel cells according to their operating temperature. Own elaboration.

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Table 1 – Characteristics of the most important types of fuel cells on the market today.					
Fuel Cell/ efficiency	Operating temperature (°C)	Electrolyte conduction	Advantages	Disadvantages	Reference
^a SOFC/70%	1000–1200	Oxide ions (O ^{2–})	 High efficiency. Generate high-grade waste heat. Fast reaction kinetics. Catalyst not needed. Wide variety of modular configurations. 	 Moderate intolerance to sulfur, at 50 ppm. Lack of practical fabrica- tion process. Technology not mature yet. 	[3,4]
^b MCFC/50%	600—800	Carbonate ions (CO ₃ ⁻²)	 High efficiency. Generate high-grade waste heat. Fast reaction kinetics. Catalyst not needed. 	 High temperature corrosion and intolerance to Sulfur (1–5 ppm). Electrolyte in liquid form, which introduces liquid handling problems. Long start-up time. 	[4]
°PAFC/40%	100–200	Hydrogen ions (H+)	 Highest temperatures among the low-temperature fuel cells. Generate high-grade waste heat. Tolerant to CO₂ and minor air impurities. Stable electrolyte characteristics 	 Partially intolerant to CO and sulphurs. Corrosive liquid electro- lyte introducing complex corrosion and liquid handling problems. Large and heavy. Long start up time. 	[5]
^d PEMFC/60%	60–100	Hydrogen ions (H+)	 Low temperature, pressure and start up time. Solid, dry, non-corrosive electrolyte. High voltage, current and power density. Tolerant to CO2 content in air. Compact and solid build with simple mechanical design. 	 Mid-tolerance to CO (50 ppm) and sulphurs. Reactant gas needs pre- humidification. Requires platinum catalyst. Fragile and expensive PEM. 	[6]
°AFC/60%	<100 °C	Hydroxyl ions (OH⁻)	 Fast start up times. Easy to operate. Lower component cost. Platinum catalyst not Needed. Minimal corrosion. Low weight and volume. 	 Extremely intolerant to CO₂ (350 ppm max) and CO. Requires pure oxygen and pure hydrogen. Liquid electrolyte, intro- ducing complex liquid handling problems. 	[7]

^b Molten carbonate fuel cell.

^c Phosphoric acid fuel cell.

^d Polymer electrolyte membrane fuel cell.

^e Alkaline fuel cell.

octahedrons $B'O_6$ and $B''O_6$, $AA'B_2O_5$ (layered perovskite) and A_2BO_4 (Ruddlesden-Popper type perovskite). Depending on their microstructure, electrical conductivity, crystalline phase stability, electrochemical and catalytic ability, each of the above conformations represents different properties in the electrode materials of a SOFC [13].

Concerning the crystal structure of perovskites, many researchers have had the desire to obtain compounds with ideal cubic structures and advanced properties. In the case, of the double perovskite Sr_2FeMoO_6 , part of the $A_2BB'O_6$ group, studies have been carried out using the Bridgman method to obtain single crystals of this perovskite. It is important to mention that for this method to work correctly, it is necessary to analyze the thermal behavior of the materials to be processed, i.e., a study of the kinetics of the thermal process is required where important parameters such as the energy of the recrystallization process and the recrystallization mechanism are calculated, through well-established mathematical models such as Friedman and Ozawa-Flynn-Wall (free kinetic models) It is concluded that the recrystallization process of



Fig. 2 — Perovskite-type structures: (a) single perovskite (SrTiO₃); (b) double perovskite (Sr₂FeMoO₆). Own elaboration with VESTA software.

the double perovskite Sr₂FeMoO₆ occurs in two stages: nucleation and diffusion [14]. Recently, a kinetics study has been performed on the double perovskite Sr₂FeMoO₆ where, in contrast to the Ozawa-Flynn-Wall and Friedman methods, the Horowitz and Metzger method was used to predict the value of the activation energy (130.47 kJ/mol) and reaction order close to 1 [15]. It is important to mention that the number of publications on thermal process kinetics studies of A2BB'O6 type double perovskites using the mathematical models mentioned above is low. The previously mentioned kinetic models have also been used for the calculation of the activation energy and the oxygen reaction order of perovskites as diesel catalysts. In this case, the study was carried out according to the conformation of perovskite-type ABO₃: LaCrO₃, La_{0.9}CrO₃, La_{0.8}CrO₃, La_{0.9}Rb_{0.1}CrO₃, La_{0.9}Na_{0.1}CrO₃, La_{0.9}K_{0.1}. CrO_3 , and $La_{0.8}Cr_{0.9}Li_{0.1}O_3$. In this case, in addition to the Ozawa-Flynn-Wall method, the Vyazovkin, Flynn-Starink, and Kissinger models were also used, for this research. It is considered that the Vyazovkin model was the best. Except for perovskite with rubidium, the results showed that depending on the substitution made in perovskite, the activation energy changes. Also, the reaction order of oxygen decreases proportionally to the catalytic conversion of soot produced by diesel [16].

It is important to mention that depending on their method of synthesis or manufacture, all these perovskites, have demonstrated to a greater or lesser degree ionic and electronic conductivity. In this sense, the following is a brief description of some of the most important methods for the synthesis of double perovskites.

General methods in the synthesis of materials for double perovskites

The materials that make up the electrodes-electrolytes (doubles perovskites) and seals of a solid oxide fuel cell are critical when it comes to optimizing the operating temperature and thus the overall cost of the cell. In this regard, the synthesis method represents significant importance. According to the literature consulted, the following three methods of synthesis of double perovskites for SOFCs appear in the majority of publications. The characteristics of these methods are briefly discussed below.

The solid-state reaction method

It is one of the most important techniques for the manufacture of polycrystalline materials as powders or densified solids. This method receives its name because the materials are obtained from a mixture of materials, generally, solids, which react directly. Over several years, this synthesis method has been used and approved by several researchers due to its great advantages such as simplicity, speed, as well as the relatively low cost to synthesize the materials [17,18]. However, it is worth mentioning some disadvantages of this method, for example, some authors mention that it is not easy to have adequate control over the particle size distribution, limited surface area, as well as the high calcination temperature needed for the fabrication of the materials [19]. In recent research, this method has been used to improve stability in redox environments, such as the case of Sr₂Fe_{1.4-} $_{x}Ti_{x}Mo_{0.6}O_{6-\delta}$ perovskite [20]. It is a fact that the internal morphology of materials is important, in this sense, it is feasible to affirm that the solid-state reaction technique makes it possible to obtain a crystalline perovskite structure of sub-micrometric size with acceptable random distribution required for optimum performance of the electrodes in gas diffusion [21].

Sol-gel method

The sol-gel process is used to synthesize nanometric ceramic oxide powders with a high degree of purity at low temperatures. This process involves the preparation of a sol, the gelation of the sol, and the removal of the solvent [22]. This process occurs in the synthesis of perovskite-like oxides and even in spinels. The sol-gel method presents great advantages in the synthesis of glasses, ceramics, and catalysts. Some of

the most important are, for example, the materials obtained have great homogeneity, there is high purity in the final product and the densification of inorganic solids is carried out at relatively low temperatures [23].

Microwave method

This method is one of the synthesis processes that has grown a lot in recent years due to its advantages such as being fast, efficient, simple, and quiet. Based on this method, several attempts have been made to manufacture elements for SOFCs [24,25]. An interesting aspect of this method is that it can be used to induce a combustion process, such is the case of the material Ce_{0.84}Sm_{0.16}O_{1.92} for SOFCs, where the conductivity of up to 0.0287 S cm⁻¹ at 850 °C in air atmosphere was reported [26]. Another variant is microwave-induced solution-polymerization synthesis, which has been another option in obtaining materials for SOFC, for example in obtaining La_{0.8-} Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815} and La_{0.8}Sr_{0.2}(Ga_{0.9}Co_{0.1})_{0.83}Mg_{0.17}O_{2.815} compounds [27].

Properties and characteristics of perovskite derivations type $Sr_2MgMoO_{6-\delta}$ as an anode in SOFC cell

Of the four types of perovskite mentioned in the introductory part, the double perovskite-type $A_2BB'O_6$ (see Fig. 2), have shown excellent properties as ionic and electronic conductor in methane, hydrogen, argon-hydrogen, and air atmospheres, at a temperature of up to 800 °C. Site A (A = A^{2+} , A^{3+}), of the double perovskite, represents alkaline earth, alkaline or rareearth atoms, and the sites B and B'. (B²⁺, B³⁺, B⁴⁺, B⁵⁺, B⁶⁺, B⁷⁺), can be metal ions [28]. It is worth mentioning that this type of perovskites has also been studied considering both their colossal magnetoresistance and the multiferroic character of some compositions [29]. An important aspect of the double perovskites is their magnetic properties, equally, they stand out for the great quantity of oxygen that they can transfer. In this sense the following perovskites stand out: Ba_2FeWO_6 [30], Sr_2MnWO_6 [31], A_2MnMoO_6 (A = Ba, Sr) [32], Sr_2MnWO_6 [33], Ca₂MnWO₆ [34], AA'MnWO₆ (AA' = Ba₂, SrBa, Sr₂, SrCa and Ca₂) [35], $Sr_2Mg_{1-x}Mn_xMoO_{6-\delta}$ [36], $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [37] and $Pr_{0.5}Ba_{0.5}MnO_{3-\delta}$ [3].

One of the most important aspects of a SOFC is the power density and, electrical conductivity at different temperatures, which leads to a high or low anodic or cathodic polarization of a double perovskite. Sr_2BMoO_6 with B = Mg, Mn, Fe, Co, or Ni double perovskites, has recently attracted considerable interest both in basic research and in applications [38]. For example, the materials $Sr_2MgMoO_{6-\delta}$ and $Sr_2MnMoO_{6-\delta}$, due to their ionic-electronic conductivity properties, have shown good results when studied in H_2 , H_2/H_2S (5 ppm), and CH_4 [39]. In a hydrogen atmosphere, and the case of double perovskite $Sr_2MgMoO_{6-\delta}$, its power densities at temperatures of 850, 800, and 750 °C are from 968, 838, and 642 mW/cm² respectively. Compared to double perovskite Sr₂MnMoO_{6-δ}, at 800 and 750 °C, lower values have been obtained for 658 and 467 mW/ $\rm cm^2$ respectively. The two previous perovskites, $\rm Sr_2MgMoO_{6-}$ $_{\delta}$ and Sr_2MnMoO_{6-\delta}, have also been studied with dehydrated methane at 800 °C, obtaining power density values of 438 and 118 mW/cm² respectively. Regarding the use of H₂/H₂S and for the perovskite Sr₂MgMoO₆₋₈ values have been obtained up to 829 mW/cm² at a temperature of 800 °C [15]. In such an investigation, the two perovskites (Sr2MgMoO6-8 and Sr2-MnMoO_{6-δ}) demonstrated an electrical conductivity of approximately 10 S/cm an 800 °C with H₂ and methane. However, in other research, when analyzed in an atmosphere with air, perovskite Sr₂MgMoO_{6-δ}, maintains an electrical conductivity of up to 3×10^{-3} S/cm and increases to 0.8 S/cm in argon-5% H_2 to 800 °C [40]. It is possible that, due to the low concentration of oxygen vacancies, this perovskite may also have low catalytic activity, as well as electrical conductivity, however, because no impurities such as molybdenum oxides have been found (MoO) or magnesium (MgO), such perovskite has demonstrated stability at temperatures above 900 °C in oxide-reductive environments [41]. It is worth mentioning that this double perovskite that compared with LSCM, displayed more active and stable cell performance [42]. In this double perovskite ($Sr_2MgMoO_{6-\delta}$), the effect of some current collectors such as silver has also been studied (Ag), gold (Au), and platinum (Pt), together with the electrolyte La_{0.8}Sr_{0.2-} Ga_{0.83}Mg_{0.17}O_{3-δ} at a temperature of 800 °C. The authors conclude that such perovskite presents a low catalytic activity for the oxidation of both H_2 as CH_4 [43]. The use of the electrolyte mentioned above is due to the chemical compatibility of the double perovskite $Sr_2MgMoO_{6-\delta}$, which has also been studied concerning electrolytes La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2} O3-8 (600 µm of thickness), La0.6Sr0.4Co0.8Fe0.2O3-8, Ce0.8Gd0.2 $O_{2-\delta}$ and $Zr_{0.84}Y_{0.16}O_{2-\delta}$. In this case, a power density of 330 mW/cm² to 800 °C for the cell formed by the material $Sr_2MgMoO_{6-\delta}/Ce_{0.8}Gd_{0.2}O_{2-\delta}/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}/La_{0.6}Sr_{0.4}$ $Co_{0.8}Fe_{0.2}O_{3-\delta}$ in hydrated H₂; and up top 270 mW/cm² to 800 °C for the cell $Sr_2MgMoO_{6-\delta}/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}/La_{0.6}Sr_{0.4}$ Co_{0.8}Fe_{0.2}O_{3-δ}. According to the authors, the double perovskite $Sr_2MgMoO_{6-\delta}$ is highly stable in reducing atmosphere and non-stoichiometric oxygen (>0.06–1000 °C and 10^{-16} atm). Also, its conductivity remains in the range of 0.002 (oxidative atmosphere) to 0.8 S/cm (5%H₂/Ar) to 800 °C [44].

Some researchers have opted for double perovskite substitution Sr₂MgMoO_{6-δ}, Such is the case with the incorporation of the lanthanum element (La) on site A, to obtain the anode $Sr_{2-x}La_xMgMoO_{6-\delta}$ (0.6 \leq x \leq 0.8), which is part of a SOFC with the cathode (SrCo_{0.8}Fe_{0.2}O_{3- δ}), electrolyte (La_{0.8}Sr_{0.2}Ga_{0.83-} $Mg_{0.17}O_{2.815}$) and a protective layer ($La_{0.4}Ce_{0.6}O_{2-\delta}$) located between the cathode and the electrolytic material. In this case, several power density values were determined in methane, ethane, and propane as fuels [45]. The authors mention that, for example, in hydrated methane at 850, 800 and 750 °C, maximum values of 646, 492 and 215 mW/cm² respectively, not much different from those obtained in dehydrated methane, where, at the same operating temperatures, values of 614, 472 and 206 mW/cm² respectively. In the case of ethane and propane, the power densities that have been obtained in hydrated and dehydrated ethane are 178 and 185 mW/cm² respectively to 800 °C, as well as 173 and 123 mW/cm² in hydrated and dehydrated propane respectively at the same temperature. Another example of partial substitution is observed in the double perovskite anode Sr_{2-x}Sm_xMgMoO₆₋ $_{\delta}$ (0 \leq x \leq 0.8), which has been investigated in an atmosphere

of H₂ and commercial gas with a certain amount of H₂S (5 ppm), together with the materials La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃₋ $_{\delta}$ and SmBaCo₂O_{5+x} as electrolyte and cathode respectively. The results indicate acceptable electrochemical performance and tolerance to both carbon and H₂S. The electrical conductivity in such conformation reached a value of 16 S/cm in hydrogen at 800 °C, and a power density of 907 mW/cm^2 to 850 °C. However, such power density is reduced when using the gas containing H_2S , obtaining 726, 435, and 163 mW/cm² to 850, 800, and 750 °C respectively. An interesting aspect of this research is the calculation of the thermal expansion coefficient (TEC) which is indispensable to be compatible with the other elements of the SOFC cell, in this case, a value of 13.5 \times 10⁻⁶ K⁻¹ at N₂ [46]. Some research, which has also focused on the substitution of site A, is mainly directed to the study of sulfur tolerance. In this sense, the double perovskite Ba₂MgMoO₆ has demonstrated acceptable stability in contact with up to 140 ppm of H₂S to 800 °C. This result is far superior to the material Ni/YSZ, which exhibits permanent degradation when exposed to 2 ppm at H_2S [47]. In the study of the replacement of double perovskites, aluminum has also been included, which has been introduced in the site of magnesium according to $Sr_2MgMoO_{6-\delta}$ to increase electrical performance. In this sense, the material has been considered Sr₂Mg_{0.95-} Al_{0.05}MoO_{6-δ} obtaining an electrical conductivity value of up to 5.4 S/cm to 800 °C, which, according to the authors, is 312% higher than perovskite Sr₂MgMoO_{6-δ} without doping, which is mainly due to the experimental conditions [31]. Here too, chemical compatibility with the electrolytes was observed $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}, \quad Ce_{0.8}Gd_{0.2}O_{2-\delta}, \quad and \quad Zr_{0.92}Y_{0.08}O_{1.96},$ although if impurities were present (SrMoO₄, SrZrO₃, and MgO) when treated with the electrolyte $Zr_{0.92}Y_{0.08}O_{1.96}$ [48].

In the research of double perovskites, the structure, interconnectivity, and size of the crystal are of utmost importance. For example, in perovskite $Sr_2MgMoO_{6-\delta}$ obtained by the combustion method, a crystal size of approximately 150 nm has been achieved, determined by the Rietveld method, with a specific area of 5.6 m²/g and with dissemination in the form of a sponge, which contributes to the proper release of a significant amount of gases in the combustion process [49]. Just as the above mentioned is important for the correct functioning in a SOFC so is the electrical conductivity of a perovskite, which depends to a great extent on its structural distortion [50]. It is worth mentioning that the double perovskite Sr_{2-} MgMoO_{6- δ} has been reported as tetragonal (I4/m) [51,52], monoclinic (P21/n) [53], cubic (Fm3m) [54], and triclinic (I1) [19], also, such perovskite has demonstrated reversible behavior between triclinic to cubic structures as temperature and the location of the oxide increases MoO₆ in the perovskite octahedron [55]. In the case of double perovskite with replacement in site A by manganese ($Sr_2MnMoO_{6-\delta}$), monoclinic structures have been reported [56], cubic [57], and tetragonal [11], with space groups P21/n, Fm3m, and P42/n respectively. Another example is perovskite $Sr_2Mg_{1-x}Fe_xMoO_{6-\delta}$ (x = 0, 0.2, 0.5) showing a transition from triclinic to tetragonal from iron (Fe) doped [6].

Other double perovskites like $Sr_2CrMoO_{6-\delta}$, $Ca_2CrMoO_{6-\delta}$, and $Ba_2CrMoO_{6-\delta}$, are represented by cubic structures (Fm-3m), orthorhombic (Pbnm), and hexagonal (P6₃-mmc) respectively, obtaining up to 92 S/cm of electrical conductivity in the cubic perovskite, in a temperature interval between 300 and 850 °C and with an argon atmosphere with H_2 (5%). In this case, the authors mention that the cell formed by the anode, electrolyte, and cathode types Sr₂CrMoO_{6-δ}, La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-δ}, and La_{0.7}Ca_{0.3}CrO_{3-δ} respectively, reached a maximum power density in the range of 428, 306 and 208 mW/cm² at temperatures of 850, 800, and 700 °C respectively. It was also considered good stability of the anode in question under H₂ atmosphere with H₂S (100 ppm) [58]. Some researchers have opted for the study of the perovskites, but in substitution of the site B, such is the case of the material $Sr_2Mg_{1-x}Mn_xMoO_{6-}$ $_{\delta}$ (x = 0, 0.2, 0.5, 0.8, and 1), where it was found that the greatest catalytic activity (>Sr₂MnMoO_{6- δ}), occurs when x = 0.5, i.e. the compound $Sr_2Mg_{0.5}Mn_{0.5}MoO_{6-\delta}$, which is mainly due to the concentration of oxygen vacancies, as well as the presence of Mn^{2+} , Mo^{6+} , Mn^{3+} , and Mo^{5+} cations [59]. To improve such catalytic activity against combustible gases such as methane, other double perovskites have been studied, such as the anode $Sr_2Mg_{0.5}Fe_{0.5}MoO_{6\mbox{-}\delta}$, that from the partial substitution with iron, the valence pairs (Fe^{2+} , Mo^{6+}) and (Fe^{3+} , Mo^{5+}) and a high concentration of oxygen valences, has demonstrated electrical conductivity of up to 28 S/cm at 800 °C, which is a relatively low [60]. However, other substitutions have achieved much higher electrical conductivities, such as double perovskite Sr_2MMoO_6 , (M = Mg, Mn, Fe, Co, Ni) where an approximate value of 1000 S m/cm was obtained in an atmosphere of 5%H₂/Ar [61]. It should be clarified that this high electrical conductivity was obtained with M = Fe and also maintains a semiconductor behavior in the range between 150 and 550 °C.

A perovskite that has been shown to have a higher power density value than perovskite $Sr_2MgMoO_{6-\delta}$, also in H₂, is the material $Sr_2CoMoO_{6-\delta}$ with which a value of 1017 mWcm⁻² and 634 mWcm⁻² at H₂ and hydrated methane respectively at a temperature of 800 °C, where an electrolyte type La_{0.8}Sr_{0.2-} $Ga_{0.83}Mg_{0.17}O_{2.815}$ with a thickness of 300 μ m [62]. Another example of the use of cobalt as a dopant can be seen in a cell formed by the double perovskite anode Sr₂Mg_{1-x}Co_xMoO₆₋ $_{\delta}$ (x = 0–0.7), the electrolyte $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{6-\delta},$ and the cathode SmBaCo₂O_{5+ δ}, reporting a power density value of up to 120 mW/cm^2 , a coefficient of thermal expansion of $13.9 \times 10^{-6} \text{ K}^{-1}$, close to the mentioned electrolyte, in a temperature range between 50 and 1300 °C, when x = 0.7, i.e. the composition $Sr_2Mg_{0.3}Co_{0.7}MoO_{6-\delta}$. Regarding electrical conductivity, the authors report an approximate maximum peak at 300 °C of up to 12 S/cm [63]. Two other perovskites where in addition to the substitution of magnesium by cobalt, nickel has been used, and which have shown good results in power density for a SOFC cell, are the anodes Sr_2CoMoO_6 and Sr_2 -NiMoO₆. Such perovskites present a tetragonal-type space group (I4/m) at room temperature. In the case of replacement with cobalt, a power density of up to 735 and 527 mW/cm² in H₂ and hydrated methane with current densities of 1380 and 920 mA/cm² respectively at 800 °C. For perovskite with nickel replacement, a maximum of 273 mW/cm², and according to the authors, the addition of nickel favors oxidation into methane [64]. Although nickel substitution allows high catalytic activity in the double perovskite Sr₂NiMoO₆, the tetragonal structure can deform at temperatures above 800 °C, and its stability in redox environments is drastically reduced, with new phases appearing such as Sr₃MoO₆, SrMoO₃, SrMoO₄, and

nickel metals [65,66]. In other investigations, and depending on the increase of electronic defects, as well as the reduction of energy (band gap) and where nickel has also been considered to replace magnesium, good behavior of the material has been reported $Sr_2Mg_{0.3}Ni_{0.7}MoO_{6-\delta}$ coupled to the electrolyte $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$ to obtain a maximum power density of 160 mW/cm² at 800 °C in an atmosphere of 5% H₂/Ar. It should be clarified that such electrolyte is slightly reactive with the double perovskite when tests were performed at 1300 °C. Although the addition of nickel indeed increases electrical conductivity, only a maximum of approximately 1.3 S/cm was reached for the anodic composition $Sr_2Mg_{0.3}$. $Ni_{0.7}MOO_{6-\delta}$ [67].

In replacing magnesium with nickel, the double perovskite has also been synthesized Sr₂Ni_{0.75}Mg_{0.25}MoO₆ of tetragonal structure (room temperature) as an anode for an intermediate temperature SOFC. The structure undergoes a structural change from tetragonal to cubic in the range of 237-247 °C. It is important to mention that such perovskite is stable above 900 °C in a hydrogen atmosphere (50%) with nitrogen (50%), Also, in an oxidative environment, conductivity is maintained in the range 4 \times 10⁻³–7 \times 10⁻³ S/cm at a partial pressure of oxygen (pO₂) of 0.21 atm (atm) between 400 and 800 $^{\circ}$ C respectively, but by increasing the pO₂ to 1×10^{-19} atm an increase in electronic conductivity of 33.37 S/cm is observed due to the concentration of oxygen holes and electronic defects [68]. However, in other SOFC cells, formed by the double perovskite-type anode where there is a complete substitution of magnesium by nickel (Sr_2NiMoO_6), the electrolyte $La_{0.9}$. $Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (TEC = 12.17 \times 10 $^{-6}$ K $^{-1}$), and the cathode $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (TEC = 19.2 \times 10 $^{-6}$ K $^{-1}$), the better electrical conductivity of 60 S/cm in hydrogen, power densities up to 819 mW/cm² in H₂ atmosphere at 850 °C and average thermal expansion coefficient of 12.14 \times 10⁻⁶ K⁻¹ have been obtained, therefore, the double perovskite is considered a good candidate [69]. Titanium, is another element that has been used as an alternative in the development of double perovskites for anodic purposes in SOFC with high electrical performance, resistance to sulfur poisoning from hydrocarbons, as well as carbon deposition. One example is the double perovskite $Sr_2TiMoO_{6-\delta}$ formed from two ABO₃ forming perovskites (SrTiO₃ and SrMoO₃). Regarding the electrical properties, with this perovskite, we have obtained approximate values of 200 S/cm in a range between 450 and 850 °C. In general, an anode must meet at least 100 S/cm [70]. Such a result in conductivity is higher than some double perovskites of interest, for example, the materials Sr2-MgMoO_{6-δ} (8.6 S/cm in H₂) [15], Sr₂TiNi_{0.5}Mo_{0.5}O_{6-δ} (17.5 S/cm 17.5 S/cm with H₂) [71], and (PrBa)_{0.95}(Fe_{0.9}Mo_{0.1})₂O_{5+ δ} (59.2 S/ cm at 5%H₂/Ar) [72], using a temperature of 800 °C. It should be mentioned, that the double perovskite $Sr_2TiMoO_{6-\delta}$ exhibits an acceptable thermal (TEC = 11.2 \times $10^{-6}~\text{K}^{-1}\text{,}$ between 30 and 1000 °C) and chemical compatibility with the electrolytes $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{1.9}$ en 5% H₂/Ar. Regarding its power density, up to 1009 mW/cm² has been achieved when impregnated with particles of palladium [73]. Another element that has stood out in the manufacture of the double perovskites is vanadium (V). Its importance lies in the size of its cation (V^{5+}) , which is very close to that of molybdenum (Mo^{6+}); In addition, vanadium oxide (V_2O_5) resists to a certain degree sulfur poisoning in various oxidation reactions, for example, the $Sr_2MgMo_{0.95}V_{0.05}O_{6-\delta}$ which has resistance to H_2S with up to 1% in the feed gas (a mixture of 6%CH₄, 6%O₂, 4%CO₂, 1%H₂S and 84% N₂), however, compared to other perovskites mentioned in this research, those synthesized in 5% H₂/Ar, present a low electronic conductivity of 7.71 S/cm at 727 °C, and even lower in air with values up to 0.494 S/cm at the same temperature [74]. As well as vanadium, the aliovalent replacement of niobium cations (Nb⁵⁺) by Mo⁵⁺ cations have also been studied to increase the concentration of oxygen vacancies, for example, the Sr_2Mg ($Mo_{0.8}Nb_{0.2}$) $O_{6-\delta}$, which in air and 5%H₂/N₂ atmosphere, has shown a thermal expansion coefficient of 13.5 \times $10^{-6}~K^{-1}$ and 14.6 \times $10^{-6}~K^{-1}$ respectively, very close to those required in electrolytes for SOFC cells. This double perovskite reacts with electrolytes type YSZ and ScSZ, it also presents a semiconductor behavior, as well as a maximum electrical conductivity of 0.2 S/cm at 800 °C in 10%H₂ dehydrated, such conductivity is low, and it is further reduced by increasing the partial pressure of oxygen [75].

An attempt at manufacturing symmetrical SOFC cells is the $Sr_2Co_{1+x}Mo_{1-x}O_6$ (x = 0.1, 0.15, 0.2) double perovskite, used as an anode-cathode next to the electrolyte La_{0.8}Sr_{0.2}Ga_{0.83-} Mg_{0.17}O₃. Using hydrogen as fuel at 800 °C, and considering as anode (x = 0.1), cathode (x = 0.2) and anode/cathode (x = 0.15), a power density of 660, 540 and 460 mW/cm² respectively was achieved. It is worth mentioning that for the symmetrical fuel cell, i.e. using as anode and cathode the $Sr_2Co_{1,15}Mo_{0.85}O_6$, the authors consider that a relatively high value was obtained. Besides, the variation of the thermal expansion coefficient from 6 \times 10 $^{-6}$ to 15 \times 10 $^{-6}$ K $^{-1}$, is considered compatible with the electrolyte [76]. The substitution of magnesium in the double perovskite Sr₂MgMoO₆₋₈ has led researchers to consider other elements besides cobalt and nickel, as an example the material $Sr_2MMoO_{6-\delta}$ (M = Mg, Mn, Fe, Co, Ni, Zn) [77]. Recently, $Sr_2MgMo_{0.9}TM_{0.1}O_{6-\delta}$ (TM = Co, Mn, Ni), obtained in air and through the combustion method, has been studied. In reducing atmosphere, it has shown a semiconductor type behavior. One of the most interesting aspects of the material is the value of the activation energy, which presents approximate values of 0.3 eV for cobalt addition, and at the same time a value of up to 0.8 S/cm in electrical conductivity with the same element at 800 °C. On the other hand, for manganese and nickel, there is a value close to 1 eV. The authors mention that with only 10% in the partial substitution with cobalt or nickel, in the molybdenum site, the electrical properties are significantly improved [78]. It has also been mentioned that the replacement of molybdenum by cobalt, nickel or manganese, increases the concentration in the number of oxygen vacancies, which is attributed to the compensation of the load due to the oxidation states of manganese concerning molybdenum [79].

As it has been observed throughout this research, the substitution of the double perovskite $Sr_2MgMoO_{6-\delta}$ has shown positive effects in a wide range of partial pressures (PO₂), however, under oxidation conditions, it can be unstable in the presence of manganese and iron, equally, in reducing atmospheres in the presence of cobalt and nickel [80]. Therefore, important contributions have been made to improve the chemical stability as well as the electrocatalytic activity of the

double perovskite, such is the case of the cubic structure material Sr1.9VMoO6-8 synthesized by solid-state reaction, where very good electrical conductivity has been obtained in the range of 1364–499 S/cm in a temperature interval between 100 and 850 °C [81]. This conductivity is higher than the traditionally used anode, Ni/YSZ (495 S/cm at 800 °C in H₂) in SOFC, as well as the double perovskites Ba₂FeMoO_{6-δ} (191 S/cm at 850 °C in H₂), Ca₂FeMoO_{6-δ} (306 S/cm at 850 °C in H₂) [82], and (PrBa)_{0.95}(Fe_{0.9}Mo_{0.1})₂O_{5+δ} (59.2 S/cm an 800 °C in 5%H₂/Ar) [72]. However, in other investigations and due to sintering conditions, such as time (20 h) and temperature (1300 $^{\circ}$ C), even higher values of up to 3000 S/cm have been obtained in the perovskite Sr_{1.9}VMoO_{6-y} [83]. Another relevant aspect is the value of the coefficient of thermal expansion (TEC), in this case, 13.3×10^{-6} K⁻¹ in the range of 30–1000 °C in 5%H₂/Ar for the double perovskite Sr_{1.9}VMoO₆₋₈. Such a result at TEC is very similar to the $Sr_2MgMoO_{6-\delta}$ double perovskites $(12.7 \times 10^{-6} \text{ K}^{-1})$ [84], and Sr₂FeMoO_{6- δ} (13.9 $\times 10^{-6} \text{ K}^{-1}$) [85]. It is worth mentioning that the use of particles of palladium, as well as the material Ce_{0.8}Sm_{0.2}O_{1.9}, significantly increased the electrochemical performance of the $Sr_{1.9}VMoO_{6-\delta}$ double perovskite in hydrogen oxidation.

It is evident that each perovskite shown in this article represents important differences in their ionic-electronic conductivity properties, morphology, thermal expansion coefficient, power density, etc., and therefore have the potential for a large number of novel applications. For example, recently it has been reported the application in the study of fingerprints, important in criminal science, by using the double perovskite $Sr_2MgMoO_6:xEu^{3+}$ (x = 0–0.50) studied by photoluminescence spectra techniques [86].

Conclusion

The analysis of the various conformations of the Sr₂MgMoO₆₋ $_{\circ}$ double perovskite has been carried out, focusing mainly on its use as an anode in SOFC-type cells, considering its catalytic, thermal, electrical, power, morphological and structural characteristics and the synthesis methods used to obtain it. In general, the different presentations of the double perovskite, present acceptable electrical conductivity, power density, and thermal expansion coefficient, in redox environments, as well as resistance to sulfur poisoning derived from fossil fuels. Regarding the latter, it is very important to innovate simulation techniques to reduce the problems of coal and sulfur as much as possible. It is important to consider that, experimental conditions such as temperatures, sintering times, grinding, purity of reagents, among others, constitute a key aspect in the final behavior of perovskite as the ion-electronic transport and diffusion processes in the triple-phase boundary. In this sense, it is necessary to choose carefully the method of synthesis used in the manufacture of perovskite, for example, solid-state reaction, sol-gel, impregnation, among others. As has been observed in this research, there is a large number of materials (alkaline earth, metals, rare earth) that can be used in the manufacture of double perovskites, however, it is necessary to optimize how these intervene and are accommodated in the final structure, to improve important properties such as oxygen diffusion, which would help in electrocatalytic activation, this with the aim that the materials are more resistant to carbon formation and consequently reduce resistance to polarization. In this sense, it is concluded that the next generation double perovskites, should be able to work with various doping elements from the sites that make up the A₂BB'O₆ double perovskite and generate higher yields overall, regardless of the fuel used as natural gas, synthetic gas, H₂, CH₄, etc. Finally, we can conclude that the study of SOFCs has increased in recent years, as well as the enormous amount of properties derived from the multiple compositions that can be obtained for anodes and cathodes. Of such properties, the catalytic capacity of the double perovskites stands out. Another important aspect is the position in which the Bsite cations are located, which can define, for example, the power density of the material, as well as the resistance to sulfur and carbon deposits. In this sense current research must be directed towards creating new and better double perovskites that will establish a new podium in the transportation and industrial sector.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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