Development of Coating to Mitigate Chromium Contamination from Bipolar Plates in a Metal-Supported Solide Oxide Fuel (MS-SOFC)

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Metal-Supported Solid Oxide Fuel Cells (MS-SOFCs) are electrochemical devices applicable to sustainable power generation. The main reason for efficiency loss in these cells is chromium contamination, leading to degradation and reduced lifetime. In order to improve cell durability and minimize the need for frequent replacement of its components, an extensive literature review was carried out to select the most suitable materials for the fabrication of bipolar plates and their coatings. Selection criteria included cost, ease of manufacturing, thermal expansion coefficient (TEC), and electrical conductivity, ensuring compatibility with the cell stack materials. Ferritic stainless steels were selected for the plates, and oxides and spinels of specific metals for coatings. These choices will directly impact the commercial and environmental viability of this technology.
Keywords: MS-SOFC. Coating. Chromium Contamination. Chromium Evaporation.

The growing global demand for energy, together with the urgency to reduce greenhouse gas emissions harmful to the environment, has driven the search for alternative sources of clean energy to replace fossil fuels. Hydrogen and biofuels such as ethanol are positioned to play a key role in the energy transition, particularly in electricity generation as well as in mobility, using devices that employ them; in this case, fuel cells such as PEM and MS-SOFC. These technologies are alternatives to enable electrification and possibly overcome dependence on fossil fuels.

However, these devices present limitations regarding efficiency and durability, strongly depending on the materials of the bipolar plates, electrodes, electrolytes, and coatings, among other components. Therefore, the objective of this research is to develop suitable coatings for MS-SOFC bipolar plates at operating temperatures of 600 to 800 °C, improving cell performance by mitigating chromium contamination and plate oxidation. The coatings will be formed using the Physical Vapour Deposition (PVD) process on test coupons simulating bipolar plates. Structural and chemical composition analyses of the coatings will be carried out, aiming to minimize the volatilization and deposition of chromium on the internal components, under MS-SOFC operating conditions, thus improving the efficiency, durability, and sustainability of this electrochemical system.

Materials and Methods

Searches were conducted through websites such as the CAPES journals platform, ScienceDirect, Web of Science, Google Scholar, articles, reviews, and online books, using the keywords SOFC, MS-SOFC, coatings, chromium poisoning, bipolar plates, fuel cell.

Representative references of the existing problems in the fuel cell involving the bipolar plates and the internal components of the stack (cell pile), such as cathode, anode, and solid electrolyte, were found and selected. Various materials were verified and selected for each of the components mentioned, always considering the correspondence between the required properties for the proper functioning of the set, such as oxidation resistance, thermal expansion coefficient (TEC), and electrical conductivity. In addition, the electrochemical process that occurs inside the cell was studied to understand the complete functioning of the MS-SOFC fuel cell for electricity generation.

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Results and Discussion

Among the existing fuel cells, the MS-SOFC (Metal Supported Solid Oxide Fuel Cell) stands out, operating at temperatures between 600 and 800 °C, with continuous high efficiency. The differential of this cell is the possibility of using several fuels such as hydrogen (H_2), whose byproduct is water (H_2O), with zero carbon emission, or when using other fuels such as hydrocarbons (HC), generating very low levels of greenhouse gas (GHG) emissions, releasing carbon dioxide (CO_2), carbon monoxide (CO), and water (H_2O) [3].

However, there are challenges to be overcome, such as the most appropriate choice of metallic support material, the coating to be used, the deposition process, and the thermal and chemical behavior with each component, to ensure the best SOFC efficiency. The metallic support or interconnectors shown in Figure 1 provide electrical connection between the cells, act as a physical barrier separating the fuel (anode) from the oxidizing gases (cathode), and allow more innovative designs with the formation of coatings with thin layers of electrochemically active material (electrodes and electrolyte). The cell can be used in several applications, from power generation to mobility, such as in the automotive sector.

The material used for metallic supports must be low-cost, have excellent oxidation resistance, high electrical conductivity, good thermal conductivity, and a TEC close to that of other functional components, in order to prevent mechanical damage to the cell during thermal cycling inherent to MS-SOFC operation. It must also be resistant to oxidizing atmospheres and chemically stable at the operating temperature [1]. Stainless steels (Table 1), based on chromium, nickel, and iron, are widely used as interconnection materials due to their adequate TECs as well as their ability to form protective films and their relatively low cost.

Some metallic alloys are applied, such as Crofer 22 APU, Sandvik Sanergy HT, AISI 441, and AISI 430, which are ferritic stainless steels [4]. The major challenge for these chromium-containing steels, which will be exposed for prolonged periods to typical MS-SOFC operating temperatures (up to 1000 °C), is the potential for chromium migration to the cathode-electrolyte-air triple phase boundary, resulting in the formation of compounds such as Cr_2O_3. This fills pores with chromium, restricts O_2^- diffusion, and reduces the number of active sites in the electrode. The degradation is shown in the second graph of

Figure 1. Conceptual diagram of MS-SOFC based on oxygen ions [6].

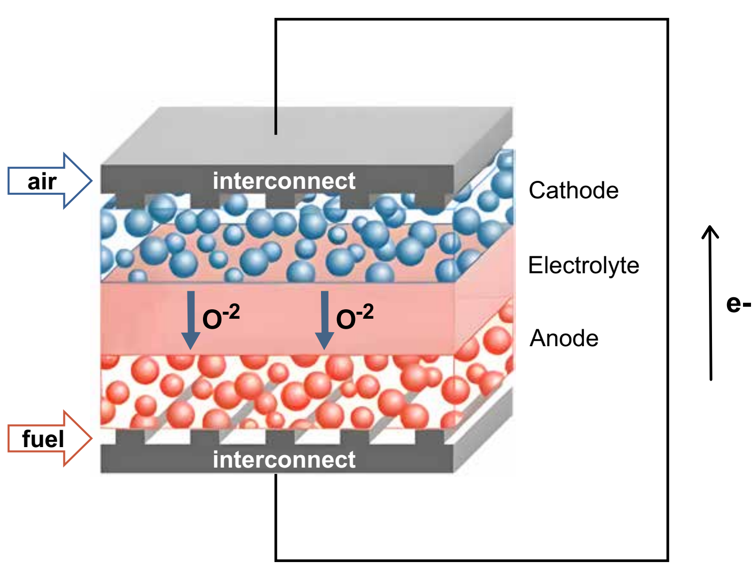
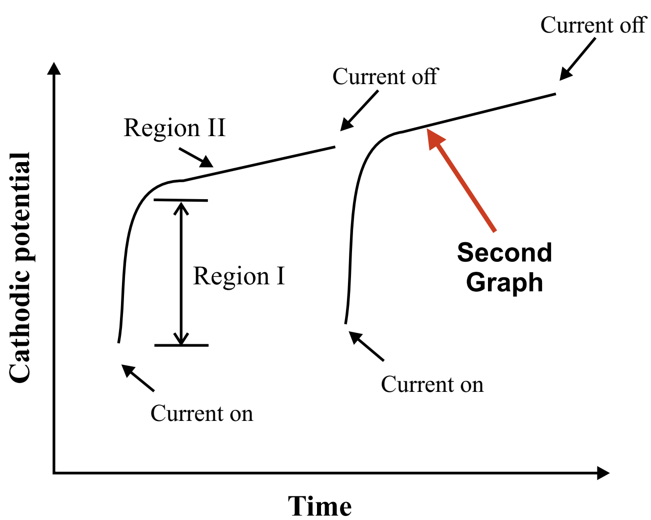


Table 1. Comparison of potential candidates for metallic interconnections [1].

Candidate Material	Matrix Structure	TEC x 10^{-6} K^{-1} (RT–800 °C)	Oxidation Resistance	Electrical Conductivity	Mechanical Strength	Manufactur-ability	Cost
Cr-based alloy	CCO	11.0 – 12.5	Good	Good	High	Hard	Very Expensive
Fe-stainless steel	CCO	11.5 – 14.0	Good	Good	Low	Easy	Cheap
Ni-superalloy	FCC	14.0 – 19.0	Good	Good	High	Easy	Expensive

Figure 2, due to the rapid increase in polarization potential in region I, followed by a much slower increase in polarization potential in region II, when a current is applied to the cell [5], decreasing its electrochemical oxygen reduction properties, affecting cell efficiency and lifetime [5].

Figure 2. Cathodic potential for O_2 reduction reaction [5].



To improve the durability of MS-SOFCs, protective coatings with low electrical resistance are used, capable of acting as effective barriers against chromium migration to the interconnection surface. Among the materials, spinels and perovskites stand out, compounds based on elements such as Mn, Co, Cu, Ni, defined below [1].

Perovskites, with the general formula ABO_3, contain trivalent rare-earth cations (La, Y, or Sr) at the A site and transition metal cations (Cr, Ni, Fe, Co, Cu, or Mn) at the B site. This material has high electronic conductivity in oxidizing atmospheres and good stability under low oxygen partial pressure conditions. However, despite advances, perovskites have limitations as barriers against volatile Cr species and oxygen diffusion [1].

Spinel oxides, with the general formula AB_2O_4, have a crystalline structure characterized by the distribution of divalent, trivalent, or quadrivalent cations in octahedral and tetrahedral sites, while oxygen anions are arranged in a face-centered cubic lattice. These materials have been widely used due to their effectiveness in mitigating the migration of volatile Cr species and the formation of Cr_2O_3 layers on the interface surface. In addition, they have high electrical conductivity and a TEC compatible with the other components of the cell. The properties of spinels can be optimized by adjusting the selection and proportion of cations A and B, allowing improvements in the structural stability and functionality of the material [1].

According to Mah and colleagues [1] (Table 2), spinel oxide is the best option among the coatings cited.

Several techniques are employed in the deposition of spinel-based coatings, including the sol-gel method, Physical Vapor Deposition (PVD – specifically Magnetron Sputtering), electroplating, and electrophoretic deposition (EPD) [1]. The PVD process was selected for its efficiency in producing dense and uniform coatings and reducing residual stresses on the substrate, since deposition occurs at low or moderate temperatures [7]. This thermo-physical method consists of vaporizing the target material into atomic particles, which are directed as a gaseous plasma toward the substrates, promoting the controlled deposition of atoms on the surface.

Table 2. Comparison of various coating materials [1].

Coating Material	Electronic Conductivity,	Inhibition of Cr Migration	Reduction of Oxidation Rate	Deposition Simplicity
Reactive Element Oxide	Fair	Poor	Good	Good
Rare-Earth Perovskites	Good	Fair	Poor	Fair
Spinel Oxide	Good	Good	Fair	Good

This process involves the use of two electrodes connected to a high-voltage source inside a vacuum chamber, allowing the deposition of one or multiple materials. In addition, the deposited materials replicate the stoichiometry of the target, ensuring homogeneous and reproducible coating adhesion [7].

Conclusion

Based on the study carried out so far, it is verified that the metal-supported solid oxide fuel cell (MS-SOFC) stands out as one of the most promising within fuel cell technology, due to its high energy efficiency and greater flexibility in the use of different fuels. Chromium deposition contamination on cell components, however, remains a problem resulting from operating conditions characterized by high temperatures and oxidizing environment.

In this context, spinels emerge as a highly promising alternative as coatings, as they present high chemical stability, excellent ability to suppress volatile Cr compounds, good electrical conductivity, and a thermal expansion coefficient (TEC) compatible with the other components of the cell. Thus, spinel-based coatings will be applied to ferritic stainless steel coupons, which will be subjected to the operating conditions of an MS-SOFC. Analytical and performance tests will then be carried out, with the objective of identifying the characteristics and improvements that may contribute to increasing the efficiency and lifetime of the fuel cells in question.

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