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# Protective coatings for AISI 430 stainless steel at high temperatures using perovskite oxides $La_{0.6}Sr_{0.4}CoO_3$ on spinel type oxide $NiFe_2O_4$

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**Abstract**

Although oxide coatings of perovskite type deposited on ferritic stainless steel AISI 430 provide an efficient barrier to oxygen diffusion, they have shown degradation at high temperatures by formation of intermediate phases with chrome. Other coatings, such as oxide of spinel type, form an effective barrier to the diffusion of chromium; however, they do not prevent oxygen diffusion into the substrate. In this context, in order to protect against oxidation at high temperatures ferritic stainless steel AISI 430 for application as interconnects in ITSOFC, the present work aimed to develop dual layer coatings obtained by deposition of a perovskite oxide, $La_{0.6}Sr_{0.4}CoO_3$, on the coating of a spinel oxide $NiFe_2O_4$. The results showed that the combination of oxide coatings increases oxidation resistance of the ferritic stainless steel and it tends to prevent degradation of the perovskite, which is caused by the diffusion of chromium from substrate to coating creating undesired phases.


*Keywords:* D. Spinel; D. Perovskites; E. Fuel Cells

## 1. Introduction

Fuel cells are electrochemical systems that convert chemical energy into electrical energy without combustion, with greater efficiency and fewer pollutants than the currently available equipment [1]. However, for practical applications, it is necessary to increase the power of such technology, so multiple cells are connected in series to form a stack. This connection from one cell to another is made by means of an interconnecting layer that connects the anode of one cell with the cathode of the adjacent cell [2–5].

The interconnectors are conventionally manufactured from ceramic materials [6], for example, lanthanum chromite ($LaCrO_3$) [7]. However, the replacement of ceramic materials for metallic alloys provides a reduction of manufacturing cost [8], improved mechanical strength and coefficient of thermal expansion compatible with other parts of the cell, higher electrical and thermal conductivity, and ease of manufacturing to complex geometries [9,10]. In this context, Intermediate Temperature Solid Oxide Fuel Cells (ITSOFC), which operate at temperatures ranging from 600 °C to 800 °C allow the use of ferritic stainless steels such as AISI 430 interconnectors [4,11]. However, some issues have to be solved concerning those materials, such as the formation of a layer of chromium ($Cr_2O_3$), the increase in electrical resistance and volatilization of chromium oxide, and irreversible damage of the system [12,13].

In order to make the use of such material possible in the manufacturing of interconnectors, it is necessary to change the composition of the alloy or the application of surface coatings [14] for protection against oxidation. In this context, perovskite type ceramic coatings have been used for protection against oxidation of ferritic stainless steels at high temperatures. However, as reported in the literature, such coatings at high temperatures undergo degradation due to the diffusion of the

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element chromium stainless steel substrate into the coating [15] which can form other oxides, for example, $SrCrO_4$, with low electrical conductivity [16–18].

The perovskite type oxides are effective barriers against the diffusion of oxygen into the substrate [19]. Other authors [1,20–22], proposed jackets spinel type oxides, such as $NiFe_2O_4$, which improved electrical performance and form a barrier to volatilization of chromium, but otherwise do not prevent the diffusion of oxygen within the substrate [3,23]. Among the techniques used to obtain the coated $NiFe_2O_4$ spinel type oxides, are chemical vapor deposition, pulsed laser deposition, plasma spraying, screen printing and slurry coating [20], sputtering [21], spray pyrolysis [10,24] and electrodeposited [1,3]. The used techniques to obtain oxide coatings of $La_{0.6}Sr_{0.4}CoO_3$ perovskite are chemical vapor deposition [25] pulsed laser deposition [26] plasma spraying [27,28] screen printing and slurry coating [29] sputtering [30] dip coating [31] electrodeposition [1,32] and spray pyrolysis [16,33–36].

Among the deposition techniques presented, the spray pyrolysis presents some advantages such as the possibility of obtaining coatings with different thicknesses, low cost and versatility [33]. The electrodeposition offers advantages such as obtaining uniform films deposited on substrates with high reproducibility and the precise control of coating thickness by simply changing the applied charge [37]. In this context, the objective of our work was to get a double layer coating comprising a first layer of NiFe-based coating obtained by a electrodeposition technique, and a second layer made of La, Sr and Co oxide, obtained by spray pyrolysis. The desired phases of spinel type oxide $NiFe_2O_4$ and the perovskite type oxide $La_{0.6}Sr_{0.4}CoO_3$ were obtained after an intercalated thermal treatment or at the end of the two depositions. The obtained coatings were characterized for morphology by scanning electron microscopy (SEM), and chemical composition (EDS) and by diffraction (XRD) X-rays for the crystallographic structure of the formed materials.

## 2. Materials and methods

### 2.1. Coating elaboration

The ferritic stainless steel AISI 430 was used as the metal substrate; its chemical composition is shown in Table 1 (according to supplier´s information). The samples were cut into $20 \times 20 \times 0.5\ mm^3$ dimensions and sanded until 1200, then subsequently cleaned for 10 min in an acetone ultrasound bath.

Table 1
Chemical composition of the ferritic stainless stell substrate (wt%).

| Cr | C | Si | Mn | Mo | Ni | Co | Al | Nb | Fe |
|---|---|---|---|---|---|---|---|---|---|
| 16.03 | 0.05 | 0.32 | 0.4 | 0.01 | 0.26 | 0.018 | 0.001 | 0.02 | Bal. |

In order to obtain a two-layer coating, a NiFe coating was first deposited by the electrodeposition technique. The composition of the used electrolyte for electrodeposition and the used process parameters are shown in Table 2. Nickel sheets were used as the anode. The parameters for electrodeposition process are based on articles [38], with some slight modifications.

The second coating layer was obtained by spray pyrolysis, the precursor solution was prepared from lanthanum nitrate hexahydrate $La(NO_3) \cdot 6H_2O$, strontium nitrate $Sr(NO_3)_2$ and cobalt nitrate hexahydrate $Co(NO_3)_2 \cdot 6H_2O$ in molar proportions of 0.6:0.4:1.0 to obtain the desired stoichiometry $La_{0.6}Sr_{0.4}CoO_3$. In Table 3, the operational parameters for the spray pyrolysis technique are summarized, based on earlier works published by our group [16].

To form the desired phases, $NiFe_2O_4$ spinel in the first layer and $La_{0.6}Sr_{0.4}CoO$ perovskite in the second layer, heat treatment was performed at a temperature of 800 °C for 2 h with a heating rate of 5 °C $min^{-1}$. Three kinds of samples were prepared with different combinations of heat treatment (Fig. 1): Sample 1

Table 3
Parameters used in the spray pyrolysis process to obtain the La, Sr and Co oxide coating.

| Deposition parameters | | | |
|---|---|---|---|
| Temperature (°C) | Substrate distance/cm | Pressure (Kpa) | Deposition time/min |
| 550 | 20 | 294.2 | 30 |

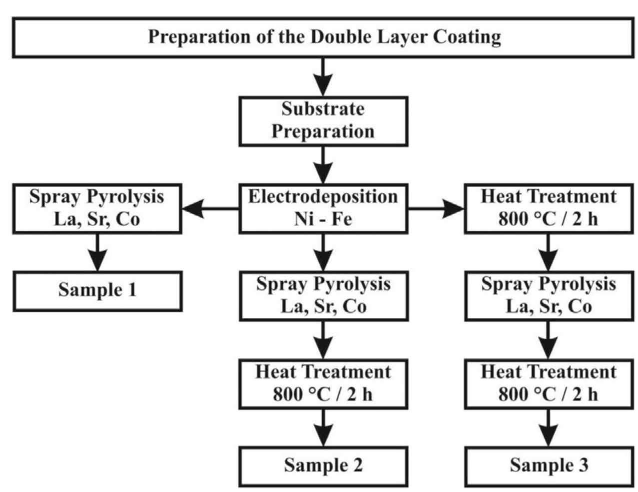

Fig. 1. Flowchart of the coating process.

Table 2
Solution composition and electrodeposition parameters for obtaining the NiFe coating.

| Salt concentrations in water/(g $L^{-1}$) | | | | Deposition parameters for electrodeposition | | | |
|---|---|---|---|---|---|---|---|
| $NiSO_4$ $6H_2O$ | $NiCl_2 \cdot 6H_2O$ | $H_3BO_3$ | $FeSO_4 \cdot 7H_2O$ | pH | Temperature (°C) | Current density mA $cm^{-2}$ | Time (h) |
| 40 | 5 | 10 | 20 | 2.5 | 60 | 5.5 | 1 |