$SrCo_{1-x-y}Fe_yM_xO_{3-\delta}$ and $Sr_{0.9}Ba_{0.1}Co_{1-x}M_xO_{3-\delta}$ (M = Ti, Ir) perovskites: promising cathode materials for Solid-Oxide Fuel Cells

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INTRODUCTION

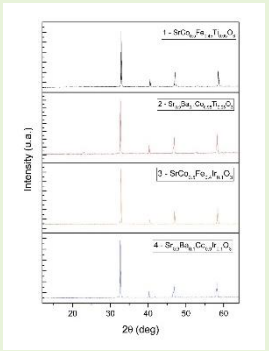
The Hydrogen economy is based on replacing fossil fuels with this gas. The combustion of hydrogen is clean, gives off more energy than any other and it is a clear example of circular economy. Solid oxide fuel cells (SOFCs) are electrochemical devices that convert the chemical energy of H_2 directly into electrical energy at temperatures between 600 and 850°C. The high efficiency, its stability, and its clean conversion make these devices highly attractive [1,2]. Presently, scientific community is developing new cathode materials, which can operate at these temperatures. One of the most promising cathode materials for SOFCs is the high-temperature cubic phase $SrCoO_{3-\delta}$, with a perovskite structure, due to its high electrical conductivity and its large number of oxygen vacancies. However, this is not the case for its hexagonal phase, which is easily stabilized below 900°C by cooling down the cubic perovskite.

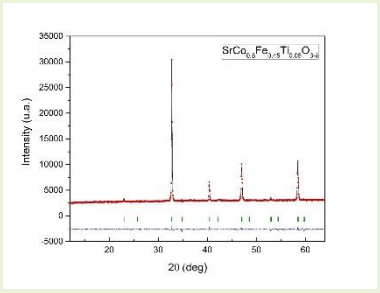
Recent studies have demonstrated the stabilization of a cubic or tetragonal perovskite in the $SrCoO_{3-\delta}$ system, at room temperature, by partially replacing Co by Ti and Ir atoms ($SrCo_{1-x}M_xO_{3-\delta}$ M= Ti, Ir) [3,4]. In this work, Fe has been introduced to minimize the amount of Co, due to its high cost and toxicity, and in order to decrease the high thermal expansion coefficient (TEC) of $SrCoO_{3-\delta}$. On the other hand, part of the Sr has been replaced by Ba to increase the unit cell size and to improve the oxygen diffusion. Both $SrCo_{1-x-y}Fe_yM_xO_{3-\delta}$ and $Sr_{0.9}Ba_{0.1}Co_{1-x}M_xO_{3-\delta}$ (M = Ti, Ir) perovskites have been synthesized by soft chemistry methods.

SYNTHESIS METHOD

Very reactive precursors have been obtained by **wet-chemistry techniques**. A mixture of the corresponding nitrates were dissolved in a citric acid aqueous solution. The solution was slowly evaporated and the resulting gel was decomposed at temperatures up to 600ºC. Later, an additional annealing was carried out at 1100ºC during 12h.

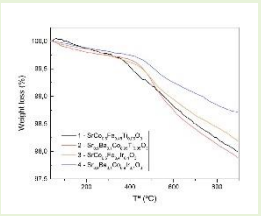
STRUCTURAL CHARACTERIZATION





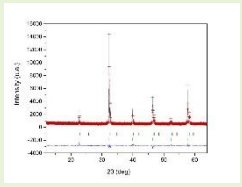
The different cathode materials were obtained as well-crystallized **perovskite phases**. A crystalline tetragonal (P4/*mmm*) perovskite structure was identified by XRD. Secondary phases were not detected.

THERMOGRAVIMETRIC ANALYSIS



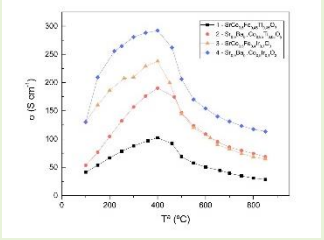
In all cases an overall **weight loss** is observed. The samples have undergone a weight loss between 1,30 and 2,13% corresponding to 0,16 and 0,28 oxygen atoms per formula.

CHEMICAL COMPATIBILITY



No reaction between the synthetized cathodes and the electrolyte (LSGM) is observed.

TRANSPORT PROPERTIES

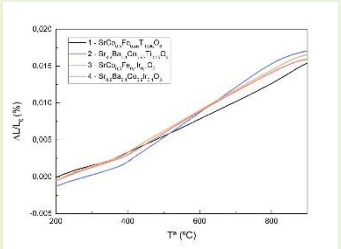


Conductivity was measured in sintered rectangular bars of 10x3x3 mm^3, with Pt leads, by the four points technique, in air atmosphere.

High values of conductivity (29-113 S cm^{-1}) were achieved at 850ºC.

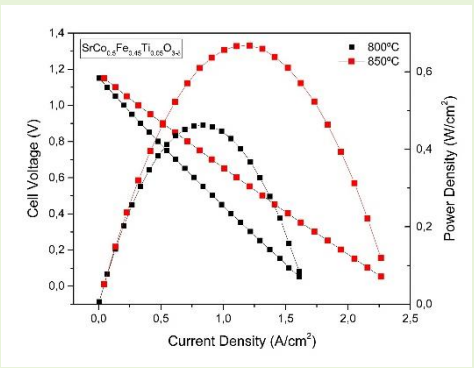
Ba-doped samples give the highest conductivity between the studied samples.

DILATOMETRY

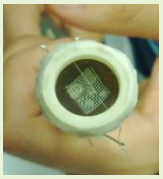


TEC $Fe_{0.45}Ti_{0.05}$ = 23.49·10^{-6} K^{-1}
TEC $Ba_{0.1}Ti_{0.05}$ = 26.49·10^{-6} K^{-1}
TEC $Fe_{0.4}Ir_{0.1}$ = 27.25·10^{-6} K^{-1}
TEC $Ba_{0.1}Ir_{0.1}$ = 32.88·10^{-6} K^{-1}

SINGLE CELL PERFORMANCE



In the fuel cell test, the electrodes were supported on a 300-µm-thick pellet of the electrolyte (LSGM) with $SrMo_{0.8}Fe_{0.2}O_3$ as anode.



The fuel cell test gave **maximum power densities** of 462 and 667 mW/cm^2 at 800 and 850ºC, respectively, using pure H_2 as fuel and air as oxidant.

CONCLUSIONS

- $SrCo_{1-x-y}Fe_yM_xO_{3-\delta}$ and $Sr_{0.9}Ba_{0.1}Co_{1-x}M_xO_{3-\delta}$ (M = Ti, Ir) materials with perovskite structure have been synthesized by the citrates method.
- **Electrical conductivity values** of the samples (29 and 113 S cm^{-1} at 850 °C) are comparable to those reported in the literature for classical SOFCs cathode materials.
- A **maximum power density** of 667 mW/cm^2 at 850 °C was achieved for $SrCo_{0.5}Fe_{0.45}Ti_{0.05}O_{3-\delta}$.
- The **chemical compatibility** with the electrolyte LSGM showed no reaction between the cathode and the electrolyte materials.
- All these properties endorse $SrCo_{1-x-y}Fe_yM_xO_{3-\delta}$ and $Sr_{0.9}Ba_{0.1}Co_{1-x}M_xO_{3-\delta}$ (M = Ti, Ir) as **promising cathode materials for IT-SOFCs**.

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