



Short communication

The effect of doping in the electrochemical performance of $(\text{Ln}_{1-x}\text{M}_x)\text{FeO}_{3-\delta}$ SOFC cathodes

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ABSTRACT

A family of iron perovskites with the general formula $\text{AFeO}_{3-\delta}$ ($\text{A} = \text{Ln}_{1-x}\text{M}_x$; $\text{Ln} = \text{La, Nd and/or Pr; M} = \text{Sr or/and Ca}$) has been prepared keeping fixed the A cation radius (r_A) and cation size mismatch to isolate the effect of divalent dopant concentration from the A-cation steric effects. The electrochemical behaviour of these compounds for their application as SOFC cathodes was evaluated by using $I-V$ curve measurements and ac impedance spectroscopy over three electrodes electrolyte supported cells processed under identical conditions. In contrast with the bulk behaviour, trends are more difficult to observe due to microstructural effects, but results seem to indicate that the doping level, x , does not influence in a significant way the electrochemical performance of iron perovskites with identical $\langle r_A \rangle$ and $\sigma^2(r_A)$.

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1. Introduction

Classical LSM ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) compounds have shown good and stable performance as cathode materials in Solid Oxide Fuel Cells (SOFCs) operating at temperatures above 800 °C, however their performance decreases rapidly as the temperature decreases [1]. Cobalt containing perovskite oxides usually exhibit higher ionic conductivities than LSM due to a greater concentration of oxygen vacancies. Nevertheless, their thermal expansion coefficients (TECs) are much larger than those corresponding to the electrolytes [2,3]. Iron perovskites such as LSF ($\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$) are also good candidates as SOFC cathodes [4] showing a better-matched TEC while maintaining the high mixed conductivity and good catalytic activity for oxygen reduction. In addition, LSF perovskites tend to react more slowly with the typical yttrium-stabilized zirconia (YSZ) electrolyte than LSM and LSC compounds at the operating temperature. Then, the LSF cathodes give promising high power outputs and long-term stability.

The present $(\text{Ln}_{1-x}\text{M}_x)\text{FeO}_{3-\delta}$ system has been chosen to study the systematic effect on their properties of different parameters that control the A-site of the perovskite structure ($\text{A} = \text{Ln}_{1-x}\text{M}_x$).

The A-site is generally composed by combinations of trivalent lanthanide ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd}$) and divalent alkaline-earth cations ($\text{M} = \text{Ca, Sr, Ba}$) which produce different average sizes, $\langle r_A \rangle$, and charge of the A-site. This directly affects the oxidation state and average size of the B-site cation (Fe for this case), given by the doping level x . Apart from the average A size and doping, there is a third factor that affects the properties of perovskite materials: the variance of the A-cation radius distribution, $\sigma^2(r_A)$, that arises from the size mismatch of the cations occupying the A-site. The effects of the size mismatch and disorder have been studied in AMnO_3 perovskites [5] and extended to other systems such as A_2CuO_4 superconductors [6], and ATiO_3 , [7] and ACoO_3 [8] perovskites. These studies have shown interesting trends with the A-site parameters in several properties such as the magnetoresistive response, superconducting critical temperatures, and ferromagnetic T_c , for example.

Following these studies it has been considered interesting to carry out similar studies for iron perovskites that have properties of potential use as SOFC cathodes. In this sense, we aim to study separately the effects of doping x , average size $\langle r_A \rangle$, and disorder $\sigma^2(r_A)$ over the structure and properties of a series of $(\text{Ln}_{1-x}\text{M}_x)\text{FeO}_{3-\delta}$ perovskite oxides. In a previous work we observed that when doping level x is isolated from the other two parameters several trends in the structure, microstructure, and conductivity of the samples in bulk could be clearly distinguished [9]. To our knowledge, that has been the first time that the effect of the parameter x has been

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