



## Detailed impedance and electrical studies of $Zr^{4+}$ doped $La_{0.7}Ca_{0.3}(Mn_{0.5}Fe_{0.5})O_3$ for cathode materials in solid oxide fuel cells

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### ABSTRACT

The solid state reaction approach was used to prepare the  $(La_{0.7}Ca_{0.3})(Mn_{0.5}Fe_{0.5})_{1-x}Zr_xO_3$  (where  $x = 0.1$  and  $0.5$ ) system for use as a cathode in solid oxide fuel cells. The impedance and electrical properties have been investigated. The ac impedance spectra of the samples show a grain boundary contribution to total conductivity and diffusion controlled impedance. A wide range impedance spectroscopy research from 50 to 200 °C revealed both bulk and grain boundary effects. At higher temperatures, oxygen vacancies could be used as ionic charge carriers, indicating an Arrhenius-type thermally activated process. The hopping mechanism for electrical processes in the system was shown by the fluctuation in ac conductivity as a function of frequency.

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### 1. Introduction

Solid oxide fuel cells (SOFCs) transform chemical energy from fuel directly into electric energy, making them a sustainable, clean alternative non-conventional energy source with a wide range of applications. In comparison to conventional fuel cells, SOFCs operate at higher temperatures [1–3]. Hydrogen can be considered the next generation energy carrier because of its clean, portable, and renewable nature [4–5]. SOFCs are one of the most common ways to generate hydrogen. Furthermore, its effectiveness reaches sixty percent on heat recovery and eighty percent on cooling [6,7]. One of its components is the cathode, which is a conducting electrode that helps increase the efficiency of SOFCs. The attributes of the cathode are limited by the high temperature working conditions of SOFCs, which impacts the overall efficiency of the cell [8–9]. In recent years, a number of mixed ionic and electronic cathodes have been created, all of which have demonstrated their potential when used in SOFCs operating at intermediate temperatures [10]. Perovskite oxides with metal doping, such as  $LaCoO_3$ ,

$LaMnO_3$ , and  $LaFeO_3$ , are often utilized as cathodes in SOFCs. However, their electrochemical performance is harmed at low temperatures [11]. Calcium is another suitable element for doping, which results in increased electrical conductivity and thermal expansion compatibility in the YSZ electrolyte [12,13]. As a result, calcium is substituted in the  $LaMnO_3$  system in this work in order to investigate the structural, thermal, dielectric, and conductive properties in order to employ  $LaMnO_3$  as a cathode.  $LaMnO_3$  (LMO) has a wide range of applications in electric and magnetic technological devices [14–19]. They have the perovskite  $ABO_3$  type structure, in which the crystal structure and electrical characteristics are determined by the radii of the A (tetrahedral) and B (octahedral) site ions [19]. Below the Neel temperature ( $T_N = 140$  K),  $LaMnO_3$  has an orthorhombic crystal structure with an antiferromagnetic character. If LMO is synthesized in the air atmosphere, it usually becomes non-stoichiometric and has cation vacancies due to a shift in the La/Mn ratio. Self-doping is the term for this non-stoichiometry, which alters the crystal structure and other physical properties. Self-doping or exogenous dopants can transform the orthorhombic structure to rhombohedral or hexagonal. The typical formula for the family of doped lanthanum manganites is  $La_{1-x}X_xMnO_3$  ( $X =$  dopant metal ions) [10–22], where the dopants can

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