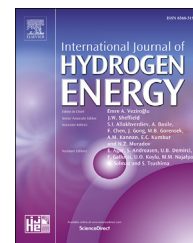




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In-depth study of the Ruddlesden-Popper $\text{La}_x\text{Sr}_{2-x}\text{MnO}_{4\pm\delta}$ family as possible electrode materials for symmetrical SOFC

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ABSTRACT

The Ruddlesden Popper (RP) manganites $\text{La}_x\text{Sr}_{2-x}\text{MnO}_{4\pm\delta}$ with compositions $0.25 \leq x \leq 0.6$ have been successfully synthesized as single phases by solid-state reaction in air. All those materials are not only stable in reducing atmosphere but they also maintain the K_2NiF_4 -type structure with $I4/mmm$ symmetry under redox cycling conditions with limited volume changes. The $x = 0.5$ phase was analyzed by *in situ* high temperature neutron powder diffraction (HTNPD), under flowing hydrogen, showing the formation of oxide-ion vacancies on the equatorial sites of the perovskite planes, during reduction process. The total electrical conductivity was optimized and found maximum for $x = 0.5$ with values of 35.6 S cm^{-1} and 1.9 S cm^{-1} at 800 °C in air and 3% H_2/Ar , respectively, what is judged to be sufficient for an active layer of symmetrical SOFC electrode. First Electrochemical Impedance Spectroscopy (EIS) measurements in both oxidizing and reducing conditions, using an YSZ electrolyte and a GDC buffer layer, are presented giving rise to promising values.

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Introduction

In recent years, many research works have been focused on the development of novel high-performance electrode materials for Solid Oxide Fuel Cells (SOFC), that meet the basic requirements of stability, compatibility with electrolyte, electrical conductivity, (electro-) catalytic activity, and, also, if possible, the lowering of operating temperature. This last

point would have a positive impact on the complexity and cost of such devices [1–3]. To improve the electrode performances, one of the most promising way is the search for Mixed Ionic and Electronic Conducting (MIEC) materials [4]. A basic definition of a SOFC electrode's MIEC would be an electronic conductor in which the formation of oxygen defects (vacancies or interstitial) enables the conduction of O^{2-} anions. Examples of efficient MIEC materials developed for SOFC are doped LaCoO_3 [5], $(\text{Ba,Sr})(\text{Co,Fe})\text{O}_3$ [6], $\text{RE}_2\text{NiO}_{4\pm\delta}$

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(RE = La, Nd, Pr) [7–9] or REBaCo₂O_{5+δ} (RE = Nd, Gd, ...) [10] for cathodes and pure or doped La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3–δ} (LSCM) [11–16] for anodes. About ten years ago, the innovative concept of symmetrical SOFC has been proposed, in which the same material, preferably MIEC, is simultaneously used on both the anodic and cathodic side of the cell [17,18]. Such configuration reduces the manufacturing costs as well as the thermomechanical issues associated to the classical cell's asymmetry. However, such an electrode material for symmetrical cell must fulfill the requirements of both the anode and the cathode, i.e. must presents stability in oxidizing and reducing atmosphere, minimal change of thermal expansion coefficient (due to oxidation-reduction process), sufficient electrical conductivity in both atmospheres and finally electrocatalytic activity towards oxygen reduction and fuel oxidation half reactions [19]. In the last decade, several works have shown that LSCM perovskite is a promising material for use as both anode and cathode, since it is stable in redox cycles and exhibits sufficient electrochemical properties for oxidation and reduction reactions, leading to power densities of 0.5 and 0.3 W cm⁻² at 950 °C using H₂ and CH₄ as fuel, respectively [20]. However, in such perovskite-type manganite, the stability in reducing atmosphere stems from the substitution of the Mn-site with chromium, what dilutes the electroactive element [21,22]. Moreover, some authors report the progressive decomposition of LSCM in dry diluted hydrogen, what could be an issue for long term operation [23].

The Ruddlesden Popper (RP) phases are compounds whose structure results from the intergrowth of perovskite-type and NaCl-type structures. The general formula of RPs is A_{n-1}A'B_nX_{3n+1}, where A and A' represent alkali, alkaline earth, or rare earth metal (such as La or Sr), B refers to transition metal, and n is the number of octahedra's layers in the perovskite-like stack. Manganese based RPs have been shown to be thermodynamically more stable under reducing conditions than their parent perovskites [16,24] and could be an interesting alternative to the classical way, i.e. the stabilization of perovskite manganites at the anode side, implying the dilution of the B site with more stable elements like Cr or Ti [25]. In addition, their crystal structure are known to be able to accommodate a significant amount of non-stoichiometric oxygen [26], a good argument for ionic conductivity properties. For instance, pure or doped rare earth nickelates RE₂NiO_{4+δ} (RE = La, Nd, Pr) have been reported as promising cathode materials [27], mainly due to their excellent mixed ionic and electronic conduction properties [28–30]. However, recent studies evidenced possible reactivity between RE₂NiO_{4+δ} and gadolinium-doped ceria (GDC) or Ytria-stabilized Zirconia (YSZ) electrolytes [31] preventing its use without additional barrier layer. Additionally, based on neutron diffraction studies, it has been found that La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{4–δ} [32,33] or Pr_{0.5}Sr_{1.5}Cr_{0.5}Mn_{0.5}O_{4–δ} [34], heated in a reducing atmosphere, can create, via manganese reduction, oxygen ion vacancies, without affecting the crystal structure (I4/mmm Space Group).

Munnings et al. recently studied the La_xSr_{2-x}MnO_{4+δ} solid solutions (0 ≤ x ≤ 1.4) as cathode materials, reporting good stability until 800 °C in air, thermal expansion coefficients matching with YSZ and GDC electrolytes ones and a

moderate electrical conductivity (maximum of ~6 S cm⁻¹ for x = 0.2 at 900 °C in air [35]). In addition, different members of the La_xSr_{2-x}MnO_{4+δ} (x = 0.4, 0.5, 0.6) [36] and La_xSr_{1.5}MnO₄ (x = 0.35, 0.4, 0.45) [37] series revealed suitable electrochemical properties for use as cathode materials. Very recently, it was also demonstrated that La_{0.6}Sr_{1.4}MnO_{4+δ} compound is a potential candidate as electrode for intermediate-temperature symmetrical solid oxide fuel cells (IT-SSOFCs), due to sufficient stability in both oxidizing and reducing atmospheres, thermo-mechanically compatibility with Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) electrolyte and acceptable electrochemical properties in hydrogen and methane [38–40]. Nevertheless, no comprehensive study has been published concerning the influence of the La/Sr ratio in the La_xSr_{2-x}MnO_{4+δ} series with respect to the redox and thermomechanical stability, the compatibility with classical electrolytes, and finally the conduction and electrocatalytic properties (in both anodic and cathodic conditions), i.e. all the essential prerequisites that make a material an efficient electrode for SSOFC. In the present work, we report on the synthesis and preliminary study of the La_xSr_{2-x}MnO_{4+δ} compounds to define a range of compositions that could be used for a future optimization of composition vs. performance as electrode material for symmetrical SOFC. In addition to electrical and first electrochemical evaluation of the materials, we report on the specific use of *in situ* neutron powder diffraction that gives insight into the process of oxygen vacancies formation during reduction.

Experimental

Materials synthesis

La_xSr_{2-x}MnO_{4+δ} powders with x = 0, 0.25, 0.4, 0.5, 0.6 and 0.7 were prepared by traditional solid state reaction. The range of composition was chosen in order to obtain materials that can be easily prepared in air, since the compounds with higher lanthanum content require reducing conditions, i.e. diluted hydrogen, to be prepared [41]. Stoichiometric amounts of La₂O₃ (Alfa Aesar 99.99%), SrCO₃ (Sigma Aldrich 99.9%) and MnCO₃ (Sigma Aldrich 99.9%) were mixed and milled in an agate mortar for 2 h. The La₂O₃ and SrCO₃ powders were pre-calcined at 1000 °C and 500 °C for 1 h, respectively. The resulting powders were uniaxially pressed into pellets of approximately 10 mm diameter that were afterward heat-treated using three successive thermal cycles at 1300 °C for 6 h for the compositions x ≥ 0.25, and at 1500 °C for 12 h for x = 0, with intermediate grinding steps in all cases. The samples were then characterized by powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE powder diffractometer working in Bragg Brentano geometry with Cu-K_{α1,2} radiation equipped with 1D Bruker LynxEye detector. Based on those XRD data, structural informations were extracted by Rietveld or LeBail refinements using the FullProf Suite program and its graphical interface WinPLOTR [42].

The oxygen stoichiometry of the as-synthesized powders, related to the oxidation state of Mn, was determined by iodometric titration, performed in triplicate for each composition [43].

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