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Synthesis and preliminary study of $Nd_xAE_{2-x}MnO_{4\pm\delta}$ (AE: Ca, Sr) for symmetrical SOFC electrodes

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ABSTRACT

$Nd_xAE_{2-x}MnO_{4\pm\delta}$ (AE: Ca, Sr) manganites with x = 0.25, 0.4, 0.5 and 0.60 are part of the Ruddlesden-Popper family of generic formula $A_{n+1}B_nO_{3n+1}$ with n = 1. The compositions range that can be successfully synthesized by the sol-gel method in air has been identified. While Sr compounds are stable in reducing atmosphere (3% H_2/Ar - 850 °C/16 h), Ca ones decompose when submitted to such atmosphere. $Nd_{0.5}Sr_{1.5}MnO_{4\pm\delta}$ was analyzed by High-Temperature X-ray diffraction (HT-XRD) showing TEC values of $12.7 \times 10^{-6}\ K^{-1}$ and $14.4 \times 10^{-6}\ K^{-1}$ in air and 3% H_2/N_2 (25–800 °C), respectively. Using standard conditions for electrode elaboration, the material reacts with YSZ electrolyte, but is chemically compatible with GDC electrolyte. A small polaron-type behavior is observed for the electrical conductivity of $Nd_{0.5}Sr_{1.5}MnO_{4\pm\delta}$ in air and 3% H_2/Ar, with respective values of $33.4\ S\ cm^{-1}$ and $0.9\ S\ cm^{-1}$ at 800 °C, meeting the preliminary requirements for use as symmetrical SOFC electrode.

1. Introduction

In recent years, the interest in the development of symmetrical Solid Oxide Fuel Cells (S-SOFCs) has motivated the exploration of new electrode materials, with preferably Mixed Ionic and Electronic Conducting (MIEC) behavior that could be used in both oxidizing and reducing conditions [1]. The family of K_2NiF_4-type Ruddlesden-Popper (RP) manganites present structural and transport properties that make them promising electrode materials for S-SOFCs, namely due to their stability with respect to reducing conditions and possible oxygen non-stoichiometry in both atmospheres [2–5]. Nevertheless, all the corresponding RP manganites for SOFC applications have been dedicated to La/Sr at the A-site and for example, to the best of our knowledge, no report concerning the electrochemical properties of Ca-based RP manganites, neither as SOFC cathode nor anode, has been described yet. Aiming to explore the influence of the alkaline earth element on the electrical (and, in future, the electrochemical) properties at high temperature of the RP manganites for both SOFC anode and cathode application, we embarked on the comparative study of $Nd_xAE_{2-x}MnO_{4\pm\delta}$ (AE: Ca, Sr) manganites with a special focus on the $0 < x \leq 0.6$ composition range [6–9]. A second interest of this work, is the comparison of the effect of Nd instead of La as substituting element in Sr_2MnO_4.

Previous studies concerning Nd/Sr K_2NiF_4-type such as $Nd_{2-x}Sr_xNiO_{4+\delta}$ (x = 0, 0.2, 0.4) [8] and $Nd_{2-x}Sr_xCoO_{4+\delta}$ (x = 0.8, 1.0, 1.2) [7] showed that it is possible to obtain such compounds using either a citric acid method or a solid state method (with sintering at 1200 °C in air). Moreover, a study performed on $RE_{0.5}Sr_{1.5}MnO_{4\pm\delta}$ (RE: La, Pr, and Nd) series shows the possible preparation of $Nd_{0.5}Sr_{1.5}MnO_{4\pm\delta}$ in oxidizing atmosphere by solid state method (at 1300 °C for 48 h), presenting the same *I4/mmm* structure as for the La analogue [6].

On the other hand, most of the studies concerning $Ln_xCa_{2-x}MnO_4$ materials (Ln = Pr, Nd, Sm, Gd, Ho) have been focused on the evaluation of their magnetic, electrical, magnetoresistance and charge ordering properties, *i.e.* low temperature behavior [10–12]. According to Nagai et al., after synthesis in air at 1300 °C for 48 h, the Nd-doped calcium manganites $Nd_{1-x}Ca_{1+x}MnO_4$ present an orthorhombic RP structure with space groups *Acam* for $0.73 \leq x < 0.85$, *Bmab* for $0.55 \leq x < 0.73$ and a tetragonal structure with space group $I4_1/acd$ for $0.85 \leq x \leq 1$ [13]. Some other authors report that, after synthesis at 1100 °C for 24 h, the material $Ca_{2-x}Nd_xMnO_4$ presents a tetragonal structure with space group $I4_1/acd$ for $0 \leq x \leq 0.2$ and an orthorhombic structure with space group *Fmmm* for $0.3 \leq x \leq 0.4$. A maximum electrical conductivity of $\sigma = 120\ S\ cm^{-1}$ was obtained when x = 0.1 at 600 °C [14] *vs.* $26.7\ S\ cm^{-1}$ for $Sr_{2-x}La_xMnO_{4\pm\delta}$ at the same temperature [15]. Except the study of Poeppelmeier et al. describing

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that $CaMnO_4$ can be reduced at 300–325 °C using a flow of 10% H_2/He [16], no study concerning the stability of the substituted materials in SOFC anode conditions has been reported to date.

The present work deals with i) the definition of the compositions range that can be easily prepared in air by sol-gel technique in both $Sr_{2-x}Nd_xMnO_4$ and $Ca_{2-x}Nd_xMnO_4$ series, ii) the chemical reactivity of the materials with common electrolytes and iii) the structural behavior in reducing conditions as well as the electrical conductivity measurements at high temperature in SOFC cathode and anode atmospheres.

2. Experimental

The manganites $Nd_xAE_{2-x}MnO_{4\pm\delta}$ (x = 0.25, 0.4, 0.5 and 0.6) were synthesized by sol-gel method. Stoichiometric amounts of Nd_2O_3 (≥99,9% Alfa Aesar), $CaCO_3$ (≥99,5% Alfa Aesar), $MnCO_3$ (≥99,9% Aldrich) and $SrCO_3$ (≥99,9% Aldrich) were initially dissolved in a solution made of concentrated HNO_3 (65% Merck) and citric acid (CA, ≥99,5% Merck) added in a molar ratio of CA:(metal ion)$_{total}$ = 3:1. The resulting solution was heated at 80 °C under constant stirring using a hot plate; the temperature was slowly raised to 120 °C in order to reduce the volume of the liquid and ethylene glycol (≥99% Panreac) was added in a proportion of 1.5 mL per gram of final product. Such conditions were kept over several hours until the gel started to form. The resulting mixture was heated at 200 °C until a completely solidified and dry dark gel was obtained, that was subsequently calcined at T~300 °C then ~500 °C for 3 h in air in order to ensure total organic matter decomposition and to obtain ashes. Finally, the ashes were grinded in an agate mortar and then pressed into pellets that were heat treated in air at 1000 °C and 1100 °C for 6 h each, with intermediate grinding. The resulting powders were characterized by XRD using a D8-AVANCE Bruker diffractometer operated in Bragg-Brentano geometry, equipped with a beam of $CuK\alpha_{1,2}$ radiation (λ = 1.5418 Å). Data collection was performed in a measurement range of 5–70° (2θ) for qualitative analysis and 5–140° (2θ) for Rietveld analysis, with a measurement step of 0.01526° (2θ) and a time integration of 0.2 or 1 s per step for qualitative or Rietveld analysis, respectively.

The materials stability in reducing atmosphere was studied in a tubular furnace. 1 g of each manganite was submitted to a gas flow of dry 3% H_2/Ar with a constant flow rate of 50 $cm^3\,min^{-1}$ at 850 °C for 16 h. The chemical compatibility of the potential electrode materials with both 8YSZ ($(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$) and 10GDC ($Ce_{0.9}Gd_{0.1}O_{1.95}$) electrolytes was studied by mixing powders in a manganite:electrolyte weight ratio of 50:50, which were grinded in an agate mortar and pressed into pellets at 1500 psi before being treated at 1100 °C for 10 h in air, using a temperature typical of electrode elaboration process with longer treatment duration to clearly identify by XRD any reactivity phenomenon [3]. In each case, the materials were analyzed by XRD, before and after heat treatment, to observe the possible formation of new phases or eventual structure changes due to the reduction or the reactivity with electrolyte, respectively.

For $Nd_{0.5}Sr_{1.5}MnO_{4\pm\delta}$ compound arbitrary chosen as representative of the series, the thermal behavior during redox cycling was studied using High Temperature X-ray Diffraction (HT-XRD) technique. A sequence of three continuous cycles of heating and cooling was carried out in air then in dry diluted hydrogen (3% H_2/N_2) and, finally, in air again to simulate the material re-oxidation, each from Room Temperature (RT) to 800 °C. Data were collected every 50 °C with heating and cooling rates of 5 °C min^{-1} on a Bruker D8 diffractometer operated in Bragg-Brentano geometry, equipped with a beam of $CuK\alpha_{1,2}$ wavelength with an Anton Paar XRK900 reaction chamber, and a LynxEye detector. The evolution of the cell parameters as a function of the temperature was determined using the "cyclic refinement" option of FullProf software [17]. Thermogravimetric (TG) measurements were carried out from RT to 1000 °C with a first cycle in N_2 (at 5 °C min^{-1}) followed by a slower cycle in 3% H_2/N_2 (at 2 °C min^{-1}), using a Hiden-Isochema gravimetric analyzer (model IGA-003).

Finally, total electrical conductivity values were measured as a function of temperature using the four-probe DC technique (BioLogic SP-300 Potentiostat-Galvanostat). For electrical characterization, the synthesized compound was previously isostatically pressed in the form of dense pellet (cylindrical, 5 mm in diameter and 7 mm in thickness) and sintered at 1400 °C for 24 h leading to a relative density of 91%. The measurements were performed from 800 to 100 °C using gold wires and gold paste for contacts in both atmospheres (air and 3% H_2/Ar). It is worth noting that in such conditions of measurements, the material is already in its reduced state when conductivity data in diluted hydrogen are collected. A direct current was injected through the two outside terminals, being between ± 5 and ± 100 mA in air and between ± 0.5 and ± 2 mA in dry 3% H_2/Ar, and the voltage was measured between the two inside terminals. Conductivity values were corrected from porosity according to the empirical equation proposed in [18].

3. Results and discussion

3.1. Structural analysis

The XRD patterns of the as-synthesized powders, after two successive heating cycles at 1000 and 1100 °C for 6 h are shown in Figs. 1 and 2 for $Nd_xSr_{2-x}MnO_{4\pm\delta}$ and $Nd_xCa_{2-x}MnO_{4\pm\delta}$, respectively. For $Nd_xSr_{2-x}MnO_{4\pm\delta}$, single phase materials are formed in those conditions for x = 0.4 and 0.5. Impurities of $SrCO_3$ (~10.8 wt%) and Nd_2O_3 (~0.9 wt %) are detected in $Nd_{0.25}Sr_{1.75}MnO_{4\pm\delta}$ (x = 0.25) and $Nd_{0.6}Sr_{1.4}MnO_{4\pm\delta}$ (x = 0.6) samples, respectively. Thus, the solubility range of Nd^{3+} in $Nd_xSr_{2-x}MnO_{4\pm\delta}$ is found as 0.25 < x < 0.6 using synthesis in air. For $Nd_xCa_{2-x}MnO_4$ series, XRD analysis shows the formation of single phases for x = 0.25, 0.4 and 0.5. On the contrary, for x = 0.6, the secondary phases $Ca_2Nd_2MnO_7$, $Nd_xCa_{1-x}MnO_3$ and Nd_2O_3 are detected (Fig. 2). The solubility of Nd in Ca_2MnO_4 seems favored by the similar ionic radius of Nd^{3+} ($R_{Nd^{3+}}{}^{IX}$ = 1.163 Å [19]) with respect to Ca^{2+} ($R_{Ca^{2+}}{}^{IX}$ = 1.18 Å [19]). A similar trend was reported for Sr_2MnO_4, where the solubility is higher for La^{3+} ($R_{La^{3+}}{}^{IX}$ = 1.216 Å [19]) than for Nd^{3+} [15], because the ionic radius of Sr^{2+} ($R_{Sr^{2+}}{}^{IX}$ = 1.3 Å [19]) is in better agreement with a bigger size of the Rare Earth. These results agree well with the previous reports concerning the fact that $Nd_xCa_{2-x}MnO_{4\pm\delta}$ form a solid solution for 0 ≤ x ≤ 0.5 [13,14,20]. It is worth mentioning that this series exhibits

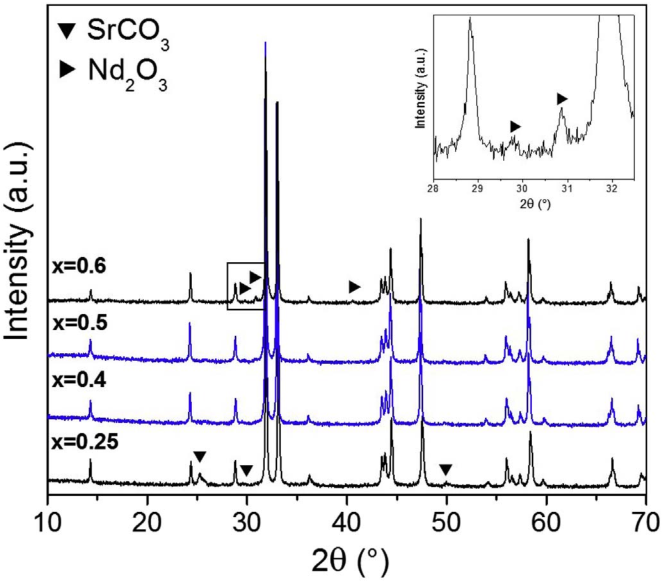

Fig. 1. X-ray powder diffraction patterns of $Nd_xSr_{2-x}MnO_{4\pm\delta}$ (x = 0.25, 0.4, 0.5 and 0.6). In blue, the compositions that could be prepared as pure phases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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