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Characterization and electrochemical behaviour of nanostructured calcium samarium manganite electrodes fabricated by RF-Magnetron Sputtering

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ABSTRACT

$Ca_{1-x}Sm_xMnO_3$ ($0 \leq x \leq 0.4$) films were successfully fabricated on Indium Tin Oxide (ITO) coated quartz glass substrates by radio frequency magnetron sputtering technique (RF- magnetron sputtering) from compacted nanosized powder targets, and subsequent annealing at 800 °C in air, for 6 h. X-ray diffraction shows a pure typical perovskite phase for $x \geq 0.1$. Scanning electron microscopy and atomic force microscopy revealed that the films surface is dense, with low roughness, depending on the Sm content, even though a few cracks were observed. Crystallite size was found to decrease with the Sm content. The electrodes were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The oxide electrode's capacitance was estimated using both techniques and the corresponding roughness factors evaluated. The values obtained from the two methods show a good agreement. A comparison between the voltammetric data and those referred in the literature allowed finding out that the redox reaction occurring at the electrode surface involves the pair Mn^{4+}/Mn^{3+}. EIS measurements confirm the voltammetric data and they also give additional information about the film porosity and the charge transfer resistance. This last parameter is associated with the oxidation and reduction of the pair $Mn^{3+}/Mn^{4+}$and after normalized by the roughness factor shows an increase with samarium content.

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1. Introduction

Oxides are promising materials to be used as electrodes for the elimination of different kinds of pollutants and removal of metallic ions from solution, besides being environmental friendly [1]. Different materials are used as electrodes, namely oxides with perovskite-type structure like ABO_3 (A = lanthanide or alkaline earth metal and B = transition metal) because of the wide range of ions and valences that the structure can accommodate and consequently presenting interesting variations on their chemical and physical properties [2–7]. This type of oxides exhibits high electronic conductivity, mobility of the oxide ions in the crystal, and variations on the oxygen content, leading to promising candidates for electrode materials with technological applications. A great variety of electrode materials with perovskite-type structure have been exploited in the past for applications on electrochemical sensors [8,9], fuel cells [10–14] and oxidation or reduction catalysts [15–18].

Until now most studies were carried out for a variety of different hole-doped manganites $Ln_{1-x}A_xMnO_3$ bulk samples and films (Ln = trivalent rare-earth cation; A = divalent alkaline earth cation) [19–23]. In contrast there are only a few reports on electron-doped materials, corresponding to Mn^{4+} rich composition. The present work is inserted in this context; more precisely it regards the effect of the partial replacement of Ca^{2+} ion by a trivalent ion on the $CaMnO_3$ properties. This substitution induces a reduction of Mn^{4+} ions to Mn^{3+} ions due to charge compensation and consequently modifies the oxide properties. Due to their ionic radius and valence

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