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Short communication

Synthesis and electrical properties of new rare-earth titanium perovskites for SOFC anode applications

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Abstract

New oxides of general formula $Ln_{2/3-x}TiO_{3-3x/2}$ (Ln = La, Pr and Nd; $0.07 \leq x \leq 0.13$) have been prepared by a new synthetic route, starting with precursors $Ln_{2/3-x}Li_{3x}TiO_3$ with perovskite structure. Precursors were prepared by the ceramic method and a modified Pechini sol–gel process, and both were treated with nitric acid 2 M to exchange lithium ions by protons, leading to new phases $Ln_{2/3-x}TiO_{3-3x}(OH)_{3x}$. These phases were calcined in order to dehydrate them and obtain the anion defect oxides $Ln_{2/3-x}TiO_{3-3x/2}$. All the phases showed perovskite-type X-ray powder diffraction patterns during the successive steps of the synthesis. Anionic vacancy content was calculated by an indirect method, taking into consideration the metallic relation, determined by induced coupled plasma (ICP), and the absence of Ti(III), checked by electron paramagnetic resonance (EPR). AC electric measurements carried out under different atmospheres (N_2, Ar, H_2/Ar, air and O_2) showed a conductivity increase under reducing atmosphere, due to the reduction of Ti(IV) to Ti(III). Considering their electrical behavior, these new phases become candidates for solid oxide fuel cell (SOFC) anode materials.

Keywords: SOFC; Sol–gel process; Perovskites; Electrical properties; Impedance spectroscopy

1. Introduction

Perovskite oxides have some quite interesting properties, such as ionic conductivity [1], superconductivity [2], magnetoresistance [3] and ferroelectricity [4]. In solid oxide fuel cells (SOFCs), perovskites such as strontium and magnesium doped $LaGaO_3$ exhibit high oxygen ionic conductivity and have been well studied as electrolytes [5,6]. Other perovskites with mixed conductivity like $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xCo_{1-x}O_3$ have been used as SOFC cathodes [7,8]. Another perovskite compound with only electronic conductivity, $La_{1-x}M_xCrO_3$ (M = Ca and Sr), has been investigated as an interconnector for SOFCs [7]. Perovskites have also been studied as potential SOFC anodes. The principle requirements for this use are electronic conductivity and chemical stability under reducing conditions. Chromium and titanium based perovskites are the most promising SOFC anode materials, especially lanthanum strontium titanates [9–11].

The synthesis of new perovskites with oxygen vacancies under non-drastic conditions is a challenge for solid-state chemistry. The use of ionic exchange reactions followed by thermal treatments to obtain metastable phases is well known [12,13], and more recently this method has been used to synthesize other perovskites [14,15]. The principle requirement for this kind of reactions is high ionic mobility in the starting compounds. There is no change in the structure due to the different ions in the lattice after the reaction. This is the case in lanthanum lithium titanates, which have high lithium conductivity [16,17] and no structure variation after the ionic exchange, as reported in tetragonal $La_{2/3-x}Li_{3x}TiO_3$ [18]. In the present study, the conditions of the synthesis for other rare-earth lithium titanates, with perovskite cubic structure, have been established, and the electrical behavior of these compounds for their use as SOFC anodes has been examined.

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