



Structure, thermal stability and electrical properties of $\text{Ca}(\text{V}_{0.5}\text{Mo}_{0.5})\text{O}_3$ as solid oxide fuel cell anode

A. Aguadero^{a,*}, C. de la Calle^b, J.A. Alonso^b, D. Pérez-Coll^a, M.J. Escudero^a, L. Daza^{a,c}

^a CIEMAT, Av. Complutense 22, 28040 Madrid, Spain

^b Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain

^c Instituto de Catálisis y Petroleoquímica (CSIC), C/Marie Curie 2, Campus Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

The $\text{Ca}(\text{V}_{0.5}\text{Mo}_{0.5})\text{O}_3$ perovskite has been prepared in order to study its potential use as anode in SOFC. The crystal structure has been refined, by neutron powder diffraction, in the orthorhombic *Pbnm* space group (no. 62). The electrical conductivity values were over 525 S cm^{-1} in the studied temperature range (25–800 °C). The sample is stable under reducing working conditions (H_2/N_2 10:90, 25–900 °C). This orthorhombic phase transforms at 500 °C in air to the tetragonal $I4_1/a$ scheelite phase. This transition is reversible and, due to the fact that the thermal expansion coefficients of both, the reduced and oxidized phases, are very similar and match well with those of the other cell components ($(10\text{--}13) \times 10^{-6} \text{ K}^{-1}$) this materials are presented as excellent candidates as anodes in SOFCs.

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1. Introduction

Materials with perovskite-like structure are receiving great attention due to their vast range of possible applications. This is mainly due to their capability to present both, electronic and ionic conductivity. Among the huge variety of compounds with the perovskite-like structure, CaVO_3 and CaMoO_3 have been observed to present Pauli paramagnetic and metallic behaviour with one of the highest conductivity values reported at room temperature ($\sim 10^4 \text{ S cm}^{-1}$) [1]. Moreover, oxides with transition metals from the V or VI groups have been observed to present high catalytic activity for some oxidation reactions. For instance, vanadium containing oxides are being studied for selective oxidation of hydrocarbon molecules [2–4] and Mo–V–O oxides are being investigated for some oxidation reactions due to their lower reducibility and oxidative dehydrogenation rates [5–7]. On the other hand, oxides consisting on combination of two transition metals have been used to enhance the structural stability in different atmospheres [8].

Nowadays, the development of an adequate anode material for solid oxide fuel cells (SOFCs) is of great interest. One of the targets is to obtain a mixed electronic-ionic conductor stable in the anodic atmosphere and with high catalytic activity for fuel oxidation. In

this way, $\text{Ca}(\text{V}_{0.5}\text{Mo}_{0.5})\text{O}_3$ is presented as a promising candidate as anode material.

The crystal structure of $\text{Ca}(\text{V}_{0.5}\text{Mo}_{0.5})\text{O}_3$ has been previously defined from synchrotron X-ray powder diffraction (SXPD) data in the orthorhombic *Pnma* space group (no. 62) with no signs of long-range ordering of V and Mo atoms into a supercell; it has been described to be highly conductive and Pauli paramagnetic at low temperatures (10–300 K) [9].

The aim of this work is to study the stability region of the $\text{Ca}(\text{V}_{0.5}\text{Mo}_{0.5})\text{O}_3$ phase, to give accurate structural details from neutron powder diffraction (NPD) data and to investigate its thermal expansion and electrical behaviour under reducing atmosphere, in order to evaluate its potential use as anode material in SOFCs.

2. Experimental

The synthesis of $\text{Ca}(\text{V}_{0.5}\text{Mo}_{0.5})\text{O}_3$ was performed by the citrate route. Stoichiometric amounts of analytical grade of the following reactants: CaCO_3 , NH_4VO_3 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ were dissolved in citric acid (10%). The formed solution was dehydrated leading to an organic resin which was dried at 120 °C and slowly decomposed at 600 °C for 12 h. The reactive precursor powder was calcined first at 900 °C, in 5% forming gas, and after at 1200 °C in 1% of H_2/Ar .

The initial structural characterization of the obtained products was performed by X-ray diffraction in a Bruker-ax D8 equipment (40 kV, 30 mA) in Bragg–Brentano reflection geometry with $\text{Cu K}\alpha$

* Corresponding author. Tel.: +34 91 3349000; fax: +34 91 3720623.

E-mail address: ainara.aguadero@gmail.com (A. Aguadero).