

In situ high temperature neutron powder diffraction study of $\text{La}_2\text{Ni}_{0.6}\text{Cu}_{0.4}\text{O}_{4+\delta}$ in air: Correlation with the electrical behaviour[☆]

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Abstract

The knowledge of the thermal evolution of the crystal structure of a cathode material across the usual working conditions in solid oxide fuel cells is essential to understand not only its transport properties but also its chemical and mechanical stability in the working environment. In this regard, high-resolution neutron powder diffraction (NPD) measurements have been performed in air from 25 to 900 °C on O₂-treated (350 °C/200 bar) $\text{La}_2\text{Ni}_{0.6}\text{Cu}_{0.4}\text{O}_{4+\delta}$. The crystal structure was Rietveld-refined in the tetragonal $F4/mmm$ space group along all the temperature range. The structural data have been correlated with the transport properties of this layered perovskite. The electrical conductivity of O₂-treated $\text{La}_2\text{Ni}_{0.6}\text{Cu}_{0.4}\text{O}_{4+\delta}$ exhibits a metal (high T)-to-semiconductor (low T) transition as a function of temperature, displaying a maximum value of 110 S cm⁻¹ at around 450 °C. The largest conductivity corresponds, microscopically, to the shortest axial Ni–O₂ distance (2.29(1) Å), revealing a major anisotropic component for the electronic transport. We have also performed a durability test at 750 °C for 560 h obtaining a very stable value for the electrical conductivity of 87 S cm⁻¹. The thermal expansion coefficient was $12.8 \times 10^{-6} \text{ K}^{-1}$ very close to that of the usual SOFC electrolytes. These results exhibit $\text{La}_2\text{Ni}_{0.6}\text{Cu}_{0.4}\text{O}_{4+\delta}$ as a possible alternative cathode for IT-SOFC.

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1. Introduction

One of the most important handicaps for the commercialization of solid oxide fuel cells (SOFC) is their high operating temperatures (900–1000 °C). Nowadays, the efforts in this area are focused on reducing the operating temperature without decreasing the cell efficiency. For these purpose, ‘mixed ionic electronic conductors’ (MIEC) appear to be some of the most promising cathode materials [1,2] due to the improvement of the kinetic of the cathode reaction by replacing the triple phase boundary zone (cathode-electrolyte-air) to a double inter-phase (cathode-air) at low temperatures (650–850 °C). In this case, MIEC materials provide not only the electrons for the reduction of oxygen but also the ionic conduction required to ensure

the transport of the formed oxygen ions between the double inter-phase and the electrolyte.

Materials with K₂NiF₄ structure, have received considerable attention as novel cathodes for intermediate temperature SOFC’s due to its interesting transport properties [3–5]. The crystal structure of these phases can be described as a staking of perovskite layers alternating with rock salt layers along the *c* direction [6]. The oxygen transport occurs via a complex mechanism combining interstitial migrations in the rock salt layers and vacancy migration in the perovskite planes [7,8]. The contribution of the interstitial mechanism appears to be more important than the vacancy migration mechanism, since higher oxygen contents can be achieved in these compounds, usually with a positive effect on their ionic conductivity [9,10]. In this way, treatments under high oxygen pressure on K₂NiF₄ materials appears to be a promising method to improve the transport properties of this compounds by means of incorporating interstitial oxygen into the crystal lattice and by increasing the ionic mobility of the oxygen atoms [11].

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