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SCIENCE DIRECT
Journal of Power Sources 151 (2005) 52–56
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Neutron powder diffraction study of the influence of high oxygen pressure treatments on $La_2NiO_{4+\delta}$ and structural analysis of $La_2Ni_{1-x}Cu_xO_{4+\delta}$ $(0 \leq x \leq 1)$

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Accepted 7 February 2005
Available online 13 June 2005

Abstract

Materials formulated $La_2Ni_{1-x}Cu_xO_{4+\delta}$ $(0 \leq x \leq 1)$ have been prepared by the nitrate-citrate route, having an orthorhombic K_2NiF_4 structure with *Fmmm* ($x = 0$) and *Bmab* ($0.1 \leq x \leq 1$) space groups. $La_2NiO_{4+\delta}$, which resulted to be the compound with the highest capability to accommodate excess oxygen ($\delta = 0.16$), underwent heat treatments (873–1098 K) under high oxygen pressure (200–250 bar). This led to an increase of excess oxygen in the structure. Rietveld refinements on neutron powder diffraction data probe the excess of oxygen to be accommodated as interstitial defect at the atomic position (1/4, 1/4, z; $z \approx 1/4$), which requires the displacement of four neighbouring oxygen atoms from their normal positions. This result is in agreement with a non-stoichiometry model which induces the stabilization of oxygen vacancies in the perovskite layer of these materials. The defect concentration determined from Rietveld refinement agrees well with the data obtained from thermogravimetric analysis. Results obtained herein reveal heat treatment under high oxygen pressure (873 K, 200 bar) as a promising method to enhance transport properties in K_2NiF_4-type structures.

Keywords: Neutron powder diffraction; Interstitial oxygen defect; K_2NiF_4 structures; Mixed conductors

1. Introduction

One of the main requirements to achieve the rapid commercialisation of the solid oxide fuel cell (SOFC) systems is the necessity to operate them at intermediate temperatures (550–850 °C) [1]. In this area mixed ionic electronic conductors (MIEC) are presented as a promising alternative to prepare cathodes as they decrease the overpotential of the oxygen reduction at the triple phase boundary (TPB), leading to a meaningful decrease of the operating temperature [2,3]. Other possible applications of MIEC concern membranes for oxygen purification or for partial oxidation of hydrocarbons as well as oxygen pumps and sensors [4,5].

Perovskite-like oxides have been the most widely studied as cathodes for SOFC applications, however these materials do not fulfil all the technological requirements for the adequate performance of SOFC systems [6,7]. This has led to an increasing interest in the search for new mixed conductors, where K_2NiF_4 structures have called considerable attention [8].

The crystal lattice of K_2NiF_4 structures can be described as a stacking of perovskite layers alternating with LaO rock salt layers. These compounds have shown to exhibit a wide range of oxygen hyperstoichiometry, which involves a considerable improvement of the transport properties [9–11].

The aim of this work is to study the mechanism of oxygen introduction in $La_2NiO_{4+\delta}$ by heat treatments under high oxygen pressure and to correlate it with the changes in its structure and transport properties. To fulfil this purpose neu-

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doi:10.1016/j.jpowsour.2005.02.085