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Synthesis and preliminary study of the double perovskite $NdBaMn_2O_{5+\delta}$ as symmetric SOFC electrode material

Oscar L. Pineda [a,b], Zulma L. Moreno [a], Pascal Roussel [c], Konrad Świerczek [b], Gilles H. Gauthier [a,*,1]

[a] Universidad Industrial de Santander, INTERFASE, Bucaramanga, Colombia
[b] AGH University of Science and Technology, Cracow, Lesser Poland District, Poland
[c] Université de Lille, CNRS UMR 8181, Unité de Catalyse et Chimie du Solide (UCCS), ENSCL, F-59000 Lille, France

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ABSTRACT

$NdBaMn_2O_{5+\delta}$ compound has been studied as a possible symmetric SOFC electrode. The A-site and charge ordered $NdBaMn_2O_5$ material has been synthesized by solid-state reaction in a reducing atmosphere at 1100 °C for 12 h; the resulting material crystallizes in a $\sqrt{2}a_p \times a_p \times 2a_p$ tetragonal cell of *P4/nmm* space group. Thermogravimetric analysis coupled to HT-XRD experiment shows that the material is completely stable to redox cycling between air and 5% H_2/Ar up to at least 850 °C. In air, the phase is completely oxidized to A-site ordered $NdBaMn_2O_6$ (*P4/mmm*) and in anode conditions is reduced back to its initial form, with intermediate formation of orthorhombic $NdBaMn_2O_{5.5}$ ordered phase. Considering possible conditions of cell preparation in air (T = 1300 °C for 6 h), a loss of A-site ordering is evidenced but the material is reduced back to ordered $NdBaMn_2O_5$ at 850 °C in diluted hydrogen. Whereas the material reacts strongly with 8YSZ at 1300 °C, no particular chemical affinity with 20GDC is observed neither at high temperature in air nor at 850 °C in anodic atmosphere; TEC coefficients for $NdBaMn_2O_{5+\delta}$, measured in both anode and cathode conditions, are also in good agreement with reported TEC values for a ceria electrolyte. Relatively low values of electrical conductivity are found in diluted hydrogen whereas a sufficient level for the application is obtained in air.

1. Introduction

Solid Oxide Fuel Cell (SOFC) technology is considered as one of the most viable solutions for the future environmental and energetic problems, especially because such devices can operate either with hydrogen or with any organic fuel (fossil or synthetic), and with a relatively higher efficiency of conversion than other traditional technologies [1–3]. Currently, the state-of-the-art materials employed in SOFCs are Yttria Stabilized Zirconia (YSZ) as electrolyte, Ni/YSZ cermet as anode, and Lanthanum Strontium Manganite (LSM) as cathode. Unfortunately, these compounds have several restrictions in terms of efficiency and durability, especially due to their chemical reactivity at the interfaces (electrode–electrolyte or electrode–interconnect) during cell preparation or *in operando* [4–5]. Particularly, the Ni/YSZ cermet presents many difficulties in real operation including redox cycling, Ni coarsening at high temperatures, coking organic fuel utilization and sulfur poisoning [6–8]. On the other hand, LSM cathode requires high temperatures to obtain acceptable efficiency, inducing an early electrode and electrode–electrolyte interface degradation as well [5,9–11]. Many alternative have been proposed in the last 20 years but there is still a lack of highly efficient electrode (and in particular anode) materials able to solve all the above-mentioned issues [6–13]. The symmetric SOFC is an interesting evolution of classical (dissymmetric) SOFC, in which the same electrode material would operate simultaneously as an anode and a cathode. Such device would be a practical way to diminish compatibility issues and would additionally make easier the fabrication, maintenance and operation of SOFCs [14–16].

Recently, double perovskite-type compounds $REBa(Co,Mn)_2O_{5+\delta}$ (RE = Rare Earth) have been considered as SOFC cathodes, wherein the main feature, from the structural point of view, is the RE/Ba ordering stabilizing oxygen vacancies in the lanthanide plane [17–23]. Whereas high Co-containing compositions are not sufficiently stable in highly reducing conditions, $REBaMn_2O_{5+\delta}$ manganites could be very promising materials not only as oxygen storage material but also as SOFC anode [23–27]. The present work deals with a preliminary study concerning the use of $NdBaMn_2O_{5+\delta}$ compound as possible symmetric SOFC electrode.

2. Experimental

$NdBaMn_2O_5$ (NBM) powder was prepared by solid-state reaction. Amounts of Nd_2O_3 (Aldrich, 99.9%, previously treated at 200 °C in a vacuum furnace), $MnCO_3$ (Chempur, Pure p.a.) and $BaCO_3$ were

* Corresponding author. Tel.: +57 7634 4000 (Ext. 2528).
E-mail address: gilgau@uis.edu.co (G.H. Gauthier).
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thoroughly weighed in the cationic ratio Nd: Ba: Mn = 1:1:2. Then, corresponding proportions were mixed, pressed into pellets and placed on palladium foils, using sacrificial powder bed. Later, the mixture was heat treated in cycles of 12 h at 1100 °C in 1%H_2/Ar atmosphere with intermediate grindings.

A phase analysis after the synthesis was performed by X-ray diffraction at room temperature, using a PANalytical X'Pert Pro powder diffractometer working in Bragg Brentano geometry with Cu-K$\alpha_{1,2}$ wavelengths. The diffractometer was operated over the angular range 2θ = 10°–110° for LeBail analysis, using a step size of 0.013° (2θ) and an acquisition time of 1 s per step.

In order to examine the redox behavior of the material in oxidizing then reducing conditions, thermogravimetric analyses were carried out on ~500 mg of NBM material using a Rheometric Scientific STA 1500 apparatus. A two step experiment was performed: first, an oxidizing step in air atmosphere between room temperature (RT) and 500 °C, followed by a reduction in 5%H_2/N_2 atmosphere in the same range of temperatures. In both steps, heating and cooling rates of 2 °C min^{-1} were used (20 mL min^{-1} flow). Redox stability of the material in both cathode and anode conditions was also studied by High-Temperature XRD (HT-XRD) in air on a Rigaku Smartlab diffractometer equipped with an Anton Paar DHS1100 heating device. The sample was placed in an alumina sample holder. In agreement with TG measurements on air (see below), the data were collected in the range 2θ = 20–80° (total counting time = 10 min per scan), with a 0.010° step, in three segments: (i) from RT to 250 °C every 50 °C, (ii) from 250 to 350 °C every 20 °C and (iii) from 350 to 850 °C every 50 °C, before cooling (one scan every 50 °C). High-Temperature XRD (HT-XRD) was then carried on the same sample in 3%H_2/N_2 using a Bruker D8 diffractometer equipped with an Anton Paar XRK900 Reactive Chamber. The sample was placed in a Macor© glass-ceramic sample holder. Following the TG curve of the sample re-reduction (see below) the data were collected in the range 2θ = 20–80° (total counting time = 15 min per scan), with a 0.015° step in three segments: (i) from RT to 250 °C every 50 °C, (ii) from 250 to 550 °C every 20 °C and (iii) from 550 to 850 °C every 50 °C, before cooling (one scan every 50 °C). The same heating and cooling rate of 0.1 °C s^{-1} was used in all those measurements. In each case, the cell parameters were cyclically refined (LeBail technique), using the FullProf Suite program [28]. The background was fitted with a 6-coefficient polynomial function and a pseudo-Voigt function was used to model profile shapes, including the Cagliotti function variables U, V, W, the Gaussian–Lorentzian mixing parameter η and two asymmetry parameters. The values of standard deviations were corrected according Berar and Lelann's description [29].

Considering the elaboration of a NBM-based symmetric cell, a pure $NdBaMn_2O_5$ powder was preliminary treated at 1300 °C in air for 6 h followed by reducing conditions (1%H_2/Ar) at 850 °C for 6 h in a tubular furnace, to study the redox behavior of the material after a high temperature sintering treatment in air. For the electrolyte chemical compatibility tests, $NdBaMn_2O_{5+\delta}$ powder was mixed in equal amounts by weight with powders of the most commonly used SOFC electrolytes: 8YSZ (8 mol%Y_2O_3 doped zirconia, ESL ElectroScience) and 20GDC (20 mol%Gd doped Ceria, Fuel Cell Materials). The mixtures were pressed into pellets and heat treated at 1300 °C during 6 h in air and at 850 °C for 6 h in 5%H_2/Ar (for YSZ, both treatments were made successively and separately for 20GDC). In all cases, the resulting powders were examined by XRD, as described before. Some of the XRPD data were recorded using a Bruker D8 diffractometer operated in Bragg-Brentano geometry, equipped with a Ni filter, a beam of Cu-K$\alpha_{1,2}$ radiation (λ = 1.540598 and 1.54439 Å) and a one-dimensional LynxEye detector. In this case, the patterns were collected at room temperature in the 2θ range of 10–140° using a 2θ step size of 0.0153°.

Electrical conductivity (σ) of $NdBaMn_2O_{5+\delta}$ sinter was measured using four-probe DC method on a sample with cuboid shape. Since the pellet showed *ca.* 20% porosity, Bruggeman's effective medium theory correction was applied, in order to obtain specific resistivity [30]. For studies, the sample was placed between outer (current) electrodes made of gold, with inner (voltage) electrodes prepared by wrapping several times around the sinter a thin Pt wire. Initially, the material was reduced to near $NdBaMn_2O_5$ composition, and then, the measurements were conducted in 5 vol.%H_2/Ar atmosphere from room temperature (RT) up to about 550 °C, with heating and cooling rates equal about 1.5 K min^{-1}. It was followed by a similar run in air up to 550 °C, during which a dynamic oxidation of the material took place. Finally, one more heating and cooling cycle was measured in air, based on which the electrical properties of the oxidized $NdBaMn_2O_6$ were studied. For Seebeck coefficient (α) measurements, a dynamic method was applied, with temperature gradients of *ca.* 2–5 °C induced by an additional heater placed near one of the sides of the sinter. To calculate the values of α, a linear fit of the thermoelectric voltage dependence on temperature was applied.

3. Results and discussion

3.1. Synthesis and structural characterization

The XRD pattern of the $NdBaMn_2O_5$ sample is represented in Fig. 1 and confirms the formation of a single phase of the desired composition corresponding to the oxygen vacancy ordered double perovskite-type structure. Although the refinement could have been performed using XRD data in the *P4/mmm* space group with $a_p \times a_p \times 2a_p$ ordering (a_p being the parameter of the pristine perovskite cell), the compound

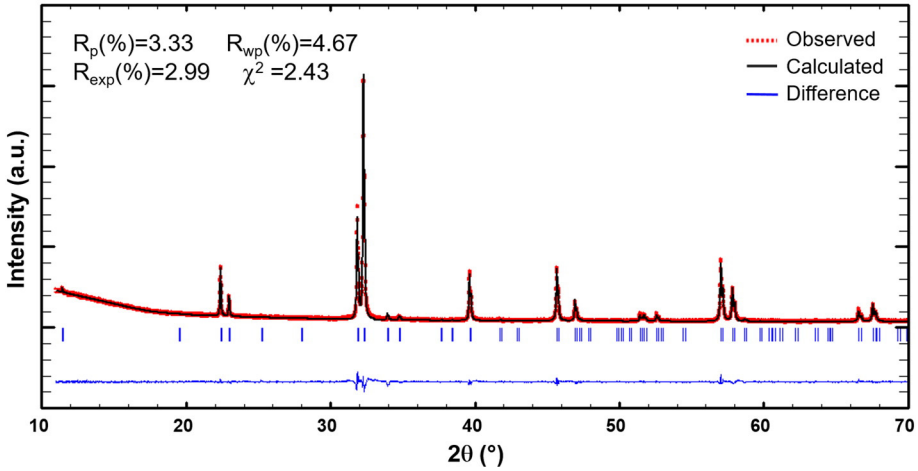

Fig. 1. Graphical result of LeBail analysis in *P4/nmm* symmetry of synthesized $NdBaMn_2O_5$ using RT-XRD data.

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