Sensors and Actuators B 223 (2016) 723–729

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

NO sensitivity of perovskite-type electrode materials $La_{0.6}Ca_{0.4}B'_{1-x}B''_xO_{3\pm\delta}$ (B′ = Mn, Cr; B″ = Ni, Fe, Co; x = 0, 0.1, . . ., 0.6) in mixed potential sensors

Daniela Franke[a,*], Jens Zosel[b], Ulrich Guth[a,b]

[a] Institute of Physical Chemistry and Electrochemistry, Technische Universität Dresden, 01062 Dresden, Germany
[b] Kurt Schwabe Institute for Measurement and Sensor Technology Meinsberg, Kurt-Schwabe-Str. 4, 04736 Waldheim, Germany

ARTICLE INFO

Article history:
Received 13 March 2015
Received in revised form
10 September 2015
Accepted 25 September 2015
Available online 19 October 2015

Keywords:
Perovskites
Potentiometric/impedance sensor
Solid-state NO sensor
Catalytic activity

ABSTRACT

Perovskite-type electrode materials of the compositions $La_{0.6}Ca_{0.4}B'_{1-x}B''_xO_{3\pm\delta}$ (B = Mn, Cr; B″ = Ni, Co, Fe; x = 0, . . ., 0.6) were investigated with regard to their NO sensitivity and the cross-sensitivity to NO_2 and propylene in a potentiometric solid electrolyte measuring setup. The highest NO sensitivity was found for nickel and iron manganites with x = 0.2 and 0.3. Dependencies on the NO gas concentration were found using impedance spectroscopy. For some materials, the catalytic conversion of NO, NO_2, methane and propene was determined by thermal investigation in the temperature range of 25–800 °C.

1. Introduction

During the last decades, a growing demand for in situ NO_x gas sensors based on solid electrolytes has been developed in the field of monitoring and control of automotive and industrial exhausts. In addition to the ability of being highly sensitive to NO at temperatures above 500 °C, the sensors should be resistant in harsh atmosphere, compact, inexpensive in production and of minor complexity. The development of these sensors is tied to the production of non-polluting automotive engines and industrial combustion processes in line with tightening emission standards.

Many metal oxides have been tested, regarding their sensing qualities in NO sensing devices. Miura et al. screened binary metal oxides such as Me_xO_y with Me = W, Cd, Ti, Cr, Mn, Ni, Co, La and Ln. Mn_2O_3 and CeO_2 were found to be the most sensitive electrode materials [1]. Miura also described experiments with spinel-type AB_2O_4 (A = Zn, Ni, Cd and B = Mn, Fe, Cr) [1–5] and perovskite-type ABO_3 (A = Ln, Ni, Y; B = Cr, Mn, Fe, Co, Ni) [2]. The potentiometric measurements showed that most of the spinel-type electrode materials are sensitive to NO whereas the perovskites are not. Dutta as well showed that the partial substitution of the A and B ions in a perovskite does not increase the NO sensitivity of the electrode [6]. Nevertheless, the substitution of A and B ions with earth alkali and transition metal ions does vary the electronic structure, and thus, the electronic and catalytic character of the perovskite type oxide is changed as described elsewhere [e.g. 7–13] and may also have an influence on the NO sensitivity of the electrode material. The oxidic materials mentioned above mostly show NO sensitivity up to 500 °C or 600 °C as well as poor selectivity.

In this work, the dependency of the NO sensitivity on the composition of the perovskites $La_{0.6}Ca_{0.4}B'_{1-x}B''_xO_{3\pm\delta}$ (B′ = Mn, Cr; B″ = Ni, Fe, Co; x = 0, 0.1, . . ., 0.6) was investigated by means of potentiometric measurements and impedance spectroscopy at temperatures 500 °C, 550 °C and 650 °C. The cross-sensitivity to other possible gas components of exhaust gases (NO_2, C_3H_6) was ascertained at the same conditions.

2. Materials and methods

The electrode materials $La_{0.6}Ca_{0.4}B'_{1-x}B''_xO_{3\pm\delta}$ (with B′ = Mn, Cr; B″ = Ni, Fe, Co) were prepared via solid-state reaction. La_2O_3, $CaCO_3$ and Me_yO_z (Me = Mn, Cr, Ni, Fe, Co) powders were mixed and ground in a planetary ball mill for 24 h and tempered in alumina crucibles for 17 h. After the reaction, the products were milled again for 8 h and used without further treatment.

* Corresponding author at: Technische Universität Dresden, Electrical and Computer Engineering Department, Solid-State Electronics Laboratory, 01062 Dresden, Germany. Tel.: +49 15739115925.
E-mail address: daniela.franke@tu-dresden.de (D. Franke).

http://dx.doi.org/10.1016/j.snb.2015.09.134
0925-4005/

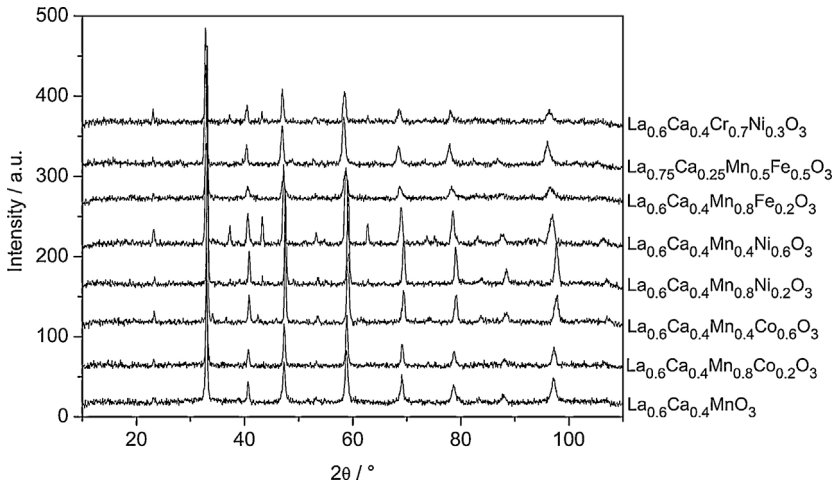

Fig. 1. Diffractograms of selected mixed oxide powder materials.

The product powders were mixed with an organic binding agent and screen printed on YSZ disks (ø 12 mm, height 1 mm) followed by sintering at 1000 °C for 1 h. A screen printed YSZ disk is clamped to a YSZ tube and contacted with a gold wire. Inside the tube, a Pt/air reference electrode (Pt mesh) is inserted. The EMF is measured between the Au and the Pt wire. The measurements were performed between 500 °C and 650 °C. The gas mixtures contained concentrations of NO, NO_2 or C_3H_6 between 0 and 1000 ppm and 1.5 vol.% O_2. N_2 was used as the carrier gas. The gas flow (at room temperature) was set to 25 ml/min or 50 ml/min.

XRD studies were recorded in a Bruker D 8 Advance with CuKα radiation in the range of $2\theta = 10°–110°$ at room temperature. Sorption measurements were carried out in a COULTER SA 3100 and interpreted using the BET method.

Catalytic measurements were evaluated by means of IR spectroscopy using an Excalibur FTS 3000 (Varian, Germany) and the Merlin program package. Therefore, powder samples were placed in a tube furnace and heated stepwise between room temperature and 800 °C under the treatment with test gas mixtures of several hydrocarbons and 1.5 vol.% oxygen (hydrocarbons being methane and propene). In addition, the catalytic activity of the materials to NO (with and without adding 1.5 vol.% oxygen to the gas mixture) and NO_2 (gas mixture containing 1.5% oxygen) was investigated.

The impedance measurements were carried out with the Im6e system (Zahner elektrik) and interpreted using the Thales program package. The impedance plots were recorded in the range of 10 mHz to 1 MHz at 550 °C and 650 °C using an AC voltage amplitude of 10 mV. The electrode materials were screen printed on both sides of the YSZ disks and contacted with gold wires. Both electrodes were placed in the same test gas. The measurements were carried out in NO, NO_2 and C_3H_6 containing atmosphere under the same conditions as used for the potentiometric measurements.

3. Results

3.1. Crystal structure and specific surface area

XRD studies of the manganite and chromite powders given in Fig. 1 for selected materials show the typical reflections of the orthorhombic $GdFeO_3$ crystal structure. Materials with low B″ content ($x \leq 0.2$) are pure while a higher B″ content induces impurities of reactants and related perovskites up to 7 mass%. Detailed evaluation of the XRD data of the manganites is described elsewhere [14–16]. The XRD analysis of the chromites can be understood similarly.

Sorption measurements using the BET evaluation method show specific surface areas of 1 m^2/g to 4 m^2/g explaining grain sizes in the low μm range.

3.2. Potentiometric measurements in nitrogen oxide

A detailed evaluation of the results using $La_{0.6}Ca_{0.4}Mn_{1-x}Ni_xO_{3\pm\delta}$ and $La_{0.6}Ca_{0.4}Mn_{1-x}Co_xO_{3\pm\delta}$ ($x = 0, \ldots, 0.6$) in the potentiometric setup is shown elsewhere [17]. In this article, the measurements are extended to Fe manganites and Ni/Fe chromites and compared to the previous results. As in [17], we calculated the sensitivity from the potential-φ(NO)-plot by evaluating the slope at 50 ppm NO. φ(NO) is the concentration of NO in the measuring gas mixture in ppm. The potential-φ(NO)-plots of all measurements are logarithmic and follow the general equation $E = A + B^* \ln \varphi(\mathrm{NO})$ (with E being the potential, A and B being constants) as described in [21] for non-Nernstian behavior of a mixed potential electrode. The mixed potential is derived from the Butler–Volmer equation relating the potential to the current density for e.g. the reduction of oxygen and the simultaneous oxidation of CO at the triple phase boundary (TPB) as described in [26]. In [26], Miura et al. describe the establishment of the mixed potential at the TPB for the case that the rate of the charge transfer through the electrochemical double layer is the limiting step. Garzon et al. add the theory for other rate-limiting processes like excess voltage, mass transport through the test gas and catalytic activity [27]. Fergus compares the two borderline cases of the Butler–Volmer equation, low excess voltage on one side, high excess voltage on the other side, and their influence on the value of the mixed potential [28]. The above-mentioned theories describe the establishment of the mixed potential at the TBP in the non-Nernstian case. Recent studies by Traversa and Wachsman show that the establishment of the potential at the TPB cannot always be explained by the mixed potential theory. They demonstrated the additional dependency of the electrode potential on area and grain size/porosity of the electrode material as well as geometry of the electrode [29,30].

Fig. 2 shows a comparison of the electrode materials with regard to their NO sensitivity at 550 °C and at low nitrogen oxide contents (up to 100 ppm). As a result, the Fe ($x = 0.1$ and 0.2) and Ni ($x = 0.2$ and 0.3) containing manganites are the electrode materials with the highest NO sensitivities. The La rich $La_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{3\pm\delta}$ (in Fig. 2 at x-axis position 0.5 as labeled) also shows high NO sensitivity whereas $La_{0.6}Ca_{0.4}Mn_{0.5}Fe_{0.5}O_3$ is not NO sensitive (not pictured). The Co manganites and the Fe and Ni chromites are not