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Characterization of $YCoO_3$ film used for CO gas detection

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In this work the preparation and the subsequent characterization of yttrium cobalt perovskite ($YCoO_3$) based CO sensors are presented. In particular $YCoO_3$ powder preparation and characterization by XRD and by preliminary Temperature Programmed Desorption (TPD) and Temperature Programmed Reduction (TPR) experiments is described, as well as the development of thick film sensors and of a test system. Moreover, experimental results showing the good characteristics of the obtained sensors are presented.

1. Introduction

Attention has been paid in the last years to the development of solid state devices for the detection of toxic gasses in the air. SnO_2-based sensors are the most popular choice for environmental monitoring due to their sensitivity to different air pollutants when they are operated at temperatures higher than 350 °C, otherwise, if used at lower temperatures, they heavily suffer from the interaction with water vapor which behaves as an interfering gas. Alternatives to SnO_2 can be proposed for specific applications: as an example perovskite materials, which act as excellent catalysts for CO oxidation (Arakawa et al.,1988; Salker et al., 2005; Brosha et al., 2000) and are therefore, the natural candidates for the development of CO sensors.
Perovskite-related materials are described by the general formula ABO_3, in which the A ions can be rare earth, alkaline earth, alkali and other large ions; the B ions can be 3d, 4d, 5d transitional metal ions which occupy the octahedral site. Perovskite materials can tolerate significant partial substitution and non-stoichiometry characteristics still keeping the perovskite structure. Different perovskite materials have already been proposed as solid state CO sensors (Fergus, 2007). They exhibit excellent ability in oxidation of CO. For example Chai et al (2000) reported the sensing properties of $La_{0.8}Sr_{0.2}Co_{1-x}O_{3-\delta}$ as function of temperature and Cu content, in a range of 50-200 ppm of CO. Salker et al. (2005) proposed thick films of $LaCoO_3$ and metal oxides for sensing temperature and carbon monoxide, and showed that $LaCoO_3$ presents a good behavior between 200-250 °C as a CO sensor. Brosha et al. (2000) measured mixed potential response to CO in air at 600 and 700 °C on zirconia based perovskite sensors. Martinelli et al. (1999) fabricated a thick films of $LaFeO_3$ and $SmFeO_3$ by screen-printing

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technology on alumina substrates with comb-type Au electrodes. The gas-sensitive electrical response of the thick films was tested in laboratory, in environments with different gases (CO and NO_2) in dry and wet air. Malavasi et al.(2005) proposed a thin film of $NdCoO_3$ made by rf-magnetron sputtering and its sensing properties toward the CO were analyzed in a temperature range between 250 and 400 °C for CO concentration up to 1000 ppm. In this work the authors investigate the possibility of using $YCoO_3$ perovskite as a sensing material. With respect to $LaCoO_3$ indeed, this perovskite shows some structural differences because Y^{+3} ions have a smaller radius with respect to $La^{3+,}$ and therefore the goal lies in the understanding about the implications of such difference once used across sensing applications. To this aim the preparation and subsequent characterization of yttrium cobalt perovskite ($YCoO_3$) based CO sensors are presented. In particular $YCoO_3$ powder preparation is described and the characterization by XRD and preliminary TPD, TPR and Gas Chromatography (GC) analysis of the obtained powder are presented. These preliminary tests showed that the material reacts with CO in the temperature range (150°-250 °C), in this range there is also the evidence of a very small amount of adsorbed oxygen, this suggests that a direct adsorption of CO takes place on the yttrium cobalt perovskite surface. This behavior makes this material a good candidate for the development of CO conductivity sensors. In fact the use of this material allows to operate at a lower temperature with respect to other materials, and to develop low-power sensors. Given the encouraging results obtained in the preliminary study, thick film sensors were prepared and a test system was developed in order to further asses the performance of yttrium cobalt perovskite as CO sensors. Finally experimental results showing the good characteristics of the obtained sensor are presented.

2. Material and methods

2.1 Powder preparation and characterization

The $YCoO_3$ powder was prepared by means of the sol-gel technique. An aqueous solution of $Y(NO_3)_3{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and citric acid was prepared and heated with continuous stirring. The as-obtained gel was thermally decomposed at 150 °C and the final sintering was performed from 300°C to 900°C for more then 24 hours. An analysis with X-ray diffraction was used to confirm the expected perovskite structure.

2.2 X-Ray Diffraction characterization

X-ray diffraction (XRD) data were collected with a Panalytical X'Pert PRO diffractometer with Cu Kα radiation operated at 40 kV and 40 mA. The diffractometer data were recorded for 2θ values between 20° and 80°. PDF2 powder diffraction database was used for phase analysis.

Figure 1 shows the XRD patterns of the sample. The presence of orthorhombic perovskite structure (PDF# 01-088-0423 Yttrium Cobalt Oxide) was confirmed by the presence of diffraction peaks at 34,2425°,34,9416,°, 62,1037° 2 θ. The phase was pure and homogeneous.

2.3 TPD, TPR and GC analysis

Oxygen TPD experiments show no oxygen desorption from temperatures above 100 °C up to temperatures higher than 700 °C: the oxygen evolution at so high temperatures

induces to suppose that it is probably due to lattice oxygen or to some form of strongly adsorbed surface species.

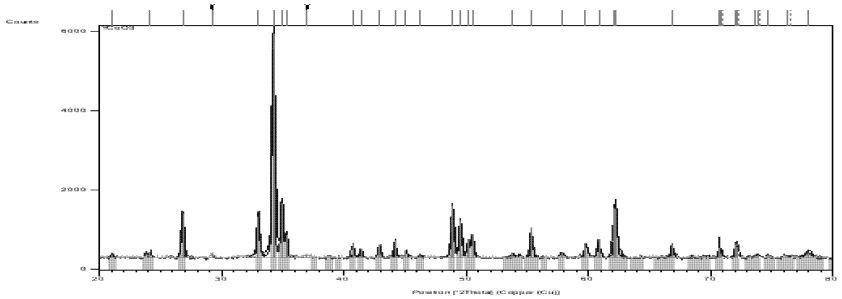

Figure 1. XRD pattern of YCoO3

The presence of small amounts of some surface species strongly chemisorbed but sufficiently mobile at lower temperatures can be revealed by TPR experiments, which show reduction peaks at lower temperatures. This could mean that the presence of a gaseous reducing substance like H_2 or CO on the catalyst surface could activate the mobility of oxygen surface species.
A relevant CO oxidation catalytic activity of the powder was shown by GC analysis (Autosystem Perkin Elmer), in the range 150-250 °C.
As a consequence of these studies a direct bond between CO and the sensor surface, influencing the material conductance due to adsorption and ionization reactions is expected, in particular we can assume these two reactions:

$$CO + S \underset{k_i}{\overset{k_f}{\rightleftarrows}} (CO - S)$$

$$(CO - S) \underset{k'_i}{\overset{k'_f}{\rightleftarrows}} (CO^+ - S) + e$$

where *S* indicates an adsorption site, whereas *e* indicates a free electron.
As already discussed, oxygen TPD experiment results allow us to expect an influence of oxygen ions on the resistance of yttrium based perovskite in the considered temperature range (150 °C – 260 °C). In presence of both oxygen and CO some reactions between adsorbed CO and oxygen can be expected, e.g.:

$$2(CO^+ - S) + O_2 \longrightarrow 2(CO_2)_{gas}$$

A reaction of this type can make the material response to CO and oxygen mixtures different from the response to mixtures of inert gas and CO, in particular a reduced response is expected.

2.4 Sensor preparation

In order to obtain a sensor, an organic vehicle (containing mainly ethyl-cellulose and α-terpineol) binder was used and mixed with the perovskite powder, then the obtained compound was deposited on an alumina substrate by drop coating and heated in a oven at 150 °C for 1 hour.

2.5 Sensor operations

The porous film obtained as described consists of large grains of p-type $YCoO_3$ semiconductor. On the surface of these grains a certain charge can be localized due the chemisorption of different chemical species. In particular in the experiment described hereafter we expect that on the surface, ionized intrinsic defects, CO^+ and, in air mixtures, a small amount of O_2^-, O^{2-}, O^- are the charged surface states. The sensor resistance is related to the surface voltage barrier, V_s, due to this localized charge by the following relationship:

$$R = R_0 \exp(-qV_s / kT) \tag{1}$$

Where R_0 depends on carrier mobility (that weakly depends on temperature), on the sensor geometry and on the density of bulk carriers. This density is given by the amount of ionized acceptor. In presence of CO the potential V_s decreases and the film resistance increases; the same occurs in presence of water vapour. Moreover the free electrons produced by the oxidation of CO can occupy some vacancies, reducing the bulk density of carriers. In presence of oxygen, on the other hand, V_s increases; moreover some electrons are trapped on the surface creating some more vacancy in the material, and the resistance decreases.

In this large grained layer, it is expected that the dominant effect determining the sensor response is the variation of the surface charge density, i.e. the potential barrier height.

2.6 Measurement system

The obtained sensor was placed in a stainless steel measurement chamber (see figure 2).

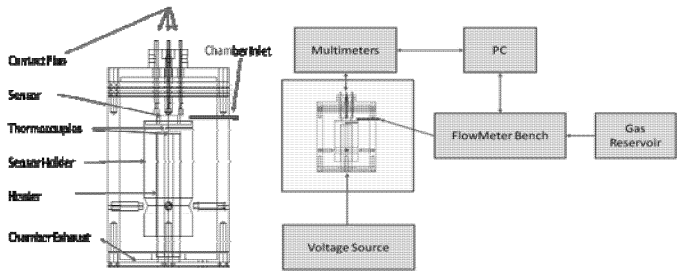

Figure 2.a) Measurement Chamber section . b). Overall measurement set up.

The chamber is equipped with a heater and a temperature control system (based on a TECNOLOGIC TLK39 PLC and on two thermocouples, one in thermal contact with the sensor and the other with the heater) able to set the sensor temperature in the range 80 °C to 280 °C with a 2 °C accuracy.

Two flowmeters (operating in the range 5mL/min 200mL/min) are used to obtain, from gas reservoirs containing certified CO mixtures, a gas flow with a known composition to be fed to the measurement chamber. Nitrogen or synthetic dry air are used as carrier gases. During the measurements the total flow issued to the chamber is kept constant

whereas its composition can be varied. This allows to test the sensor under chemical transients and in different chemical conditions.
Both the temperature and the sensor resistance are measured by AG34410A multimeters. The measurement system is controlled by a dedicated PC that sets the flowmeters, acquires data from the multimeters, and performs data processing.

3. Experimental Results

The experimental results presented hereafter were obtained with a fixed total flow of 100 mL/min. The sensor response to CO was tested at first in an inert gas (nitrogen), in order to verify the assumed direct adsorption on the surface. Data shown hereafter proved that a reversible chemisorption takes place, causing a large resistance change (increase). In Figure 3, the response of the developed sensor is plotted as a function of CO concentration in nitrogen at the temperature of 240 °C and 200 °C. In the same figure the response to CO, measured in CO and air mixtures, is shown. As expected a lower response is found in air and CO experiments, where oxygen could contribute to the reduction of resistance both directly and in a indirect way (that is by oxidizing the adsorbed CO producing gaseous CO_2). Nevertheless at the temperature of 240 °C the resolution of the sensor is estimated to be close to 20 ppm also in dry air mixtures. In this figure the sensor response is evaluated as follows:

$$\text{Sensor Response} = \left(R_{CO} - R_{carrier}\right) / R_{carrier} x100$$

where R_{CO} and $R_{carrier}$ indicate the resistance steady state values at the operation temperature in the CO mixture and in the pure carrier gas (nitrogen or air), respectively.

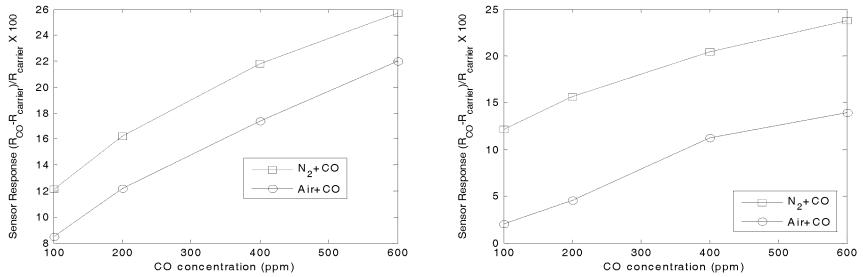

Figure 3. sensor response in air and nitrogen CO mixtures. Left plot –240 °C. Right plot-200 °C.

In Figure 4 the sensor responses in air and nitrogen mixtures at the concentrations of 400 ppm and 600 ppm are plotted as a function of the temperature: it can be seen that good performance can be obtained at temperature higher than 200 °C also in air mixtures. Finally to show the repeatability of the obtained results Figure 5 shows some repeated measurement cycles.

4. Conclusions

Yttrium cobalt perovskite was proposed as a sensing material for CO sensors. Some prototypes, prepared by drop coating deposition, demonstrate the suitability of this material in terms of sensitivity to CO also at relatively low temperatures. Further work

will concern the study of the influence of water vapour and interfering gasses, as well as the development of micro-sensors for low power operation.

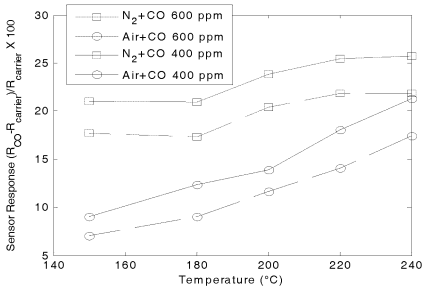

Figure 4. Sensor response as a function of temperature

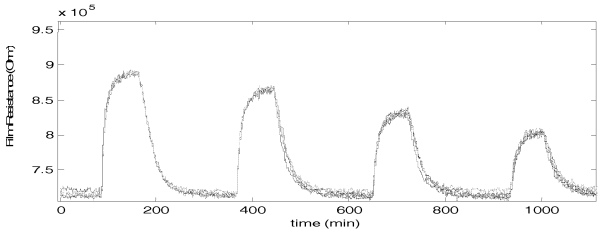

Figure 5. Sensor response to different CO and nitrogen dry mixtures (CO concentrations of the four pulses 600 ppm-400 ppm- 200 ppm -100 ppm).

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