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Preparation and Characterization of CO Sensors based on Pd modified $YCoO_3$ Perovskite

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Abstract:
In this paper the authors present the characterization of *CO* resistive sensors based on *Pd* modified $YCoO_3$ perovskite, mainly addressed to its cross-sensitivities to different gases. In particular, sensors based on $YCo_{0.95}Pd_{0.05}O_3$ and on $YCo_{0.90}Pd_{0.10}O_3$ in addition to those based on 1% *Pd* supported on $YCoO_3$ were tested; this materials showed a good performance at relatively low temperatures in terms of both *CO* sensitivity and response speed. The proposed sensors were tested with mixtures of CH_4, NO_2, and *NO* as interfering gases. Promising results were obtained in the temperature range 150°C – 200 °C, where the sensitivity towards CH_4 results very low, whereas the response to NO_2 and to *NO* is not negligible, but it is of the opposite sign with respect to the one towards *CO*. These results indicate that the proposed perovskitic materials are suitable candidates for low power *CO* sensor development.

Key words: Perovskite, *CO* resistive sensors, metal oxide sensors, sensor characterization.

Introduction

A perovskite structure is any material with the same type of crystal structure as calcium titanium oxide ($CaTiO_3$), shown in Figure 1.

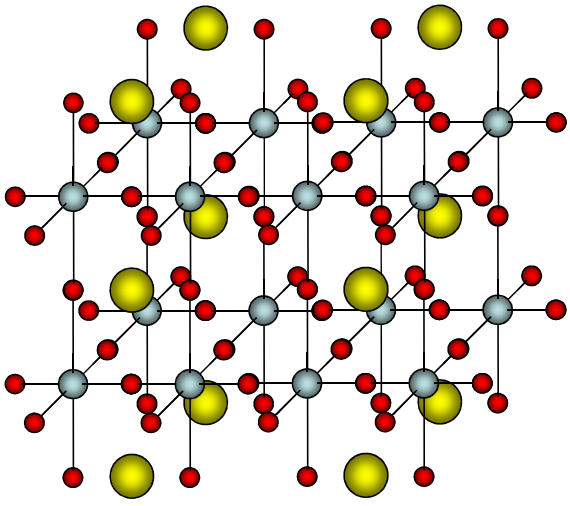


Fig. 1. Structure of Perovskite

The general chemical formula for perovskite compounds is ABX_3, where 'A' and 'B' are two cations (that can be $^{+2-+4}$ and $^{+4-+2}$ ions respectively) of very different sizes, and X is an anion that bonds to both. The 'A' atoms (yellow) are larger than the 'B' atoms (blu-cyan). The ideal cubic-symmetry structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold cuboctahedral coordination. The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion can produce several lower-symmetry distorted versions. This means that perovskite materials can tolerate significant isomorphic substitutions and non-stoichiometry while still maintaining the Perovskite structure. The possibility of introducing different dopants or lattice defects in order to adapt and tune the sensing characteristics of the film to the target applications is very attractive, giving to these materials an outstanding versatility.

Perovskites have been known for long times as oxidation catalysts and have been employed by one of the authors in order to study the oxidation of methane and other organic volatile compounds ($LaCoO_3$, $LaMnO_3$, $LaFeO_3$, either in their stoichiometric composition or non-stoichiometric composition [1]).

Moreover, inexpensive sol-gel method can be used for these compounds, since it allows to carry out reproducible preparations and high purity structures.

On the other hand the metal oxide conductometric sensors, employed for example

in *CO* detection, base their response on their oxidation capabilities, and this clearly indicates the suitability of perovskites for the development of *CO* sensors.
Some perovskite materials have already been employed as solid state *CO* sensors, $LaCoO_3$ being the most intensively studied example among them [2].
On the basis of the knowledge reached in the use of $LaCoO_3$ perovskite as *CO* sensing material, the authors have prepared $YCoO_3$ perovskite, with the aim of exploiting the effect of distortions introduced in the perovskite structure by a cation like Y^{3+}, smaller than La^{3+}, which could make cobalt ions and lattice oxygen more reactive.
The proposed material structure and elemental composition were characterized by XRD and SEM, then the proposed material was studied as catalyst in *CO* oxidation and finally employed in sensors for *CO* detection.

As determined by catalytic activity studies, the catalytic properties in *CO* oxidation of $YCoO_3$ are of the same order as those of $LaCoO_3$ (used as reference material) and, at low temperature, higher than those of commercial SnO_2, indicating the promising properties of the $YCoO_3$ as sensor material [3].

On the other hand, in some previous works [4][5]. the authors already investigated also the possibility of using $YCoO_3$ perovskites modified with different induced defects or dopants, and a number of experiments has been already performed introducing metal vacancies (*Co* or *Y*), by dispersing *Pd* on the surface and by introducing *Pd* in the framework. In this last type of material only a fraction of *Pd* is really active but the lattice undergoes modifications caused by the ascertained presence of *Pd* atoms in the lattice of perovskite structure

Several thick film prototype sensors were developed through a screen printing technique in order to test the different proposed powders.

All the tested materials showed a p-type behavior and a satisfactory performance in terms of sensitivity and of response speed. Experiments proved that the sensing mechanism is due both to a direct and reversible bond of *CO* to the material surface, and to the oxidation of *CO* due to pre-adsorbed oxygen present on the surface when operating in air. The best performance was achieved by using *Pd* supported $YCoO_3$. This active phase, due its catalytic activity with respect to *CO* oxidation, allows for decreasing the sensor optimum operating temperature and the response time, while enhancing the sensor sensitivity [4]. Hereafter the preparation of prototype *CO* sensors based on this material is described and its performance also in terms of cross sensitivity to different gases is presented.

Powder and Sensor Preparation

$YCoO_3$ 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 in molar ratio 1:1:2 was heated under continuous stirring. The solid gel obtained in the final part of this treatment was then dried and decomposed at 150°C, and subsequently calcined at increasing temperature (with a long isothermal step at 350 °C) up to 900°C, and maintaining this temperature constant for more than 48 hours.
The same procedure was employed for preparing $Y(Co\text{-}Pd)O_3$ perovskite introducing the correct amount of $Pd(NO_3)_2 \cdot 2H_2O$ in the starting solution.
In the case of 1% *Pd* on $YCoO_3$, part of the original perovskite was impregnated with a solution of $Pd(NO_3)_2$, heated and calcined in order to add *Pd* active phase on the surface.
The sensors were obtained through a classical screen printing technology (Ami 485 screen printer with 350 mesh frames). On the opposite sides of an alumina substrate the chemical sensor electrodes and the heater were deposited with the geometry shown in Figure 2. A paste prepared with the perovskite powder and an organic vehicle was deposited by drop coating on the substrate, and dried at 250°C for 3 hours in an oven.

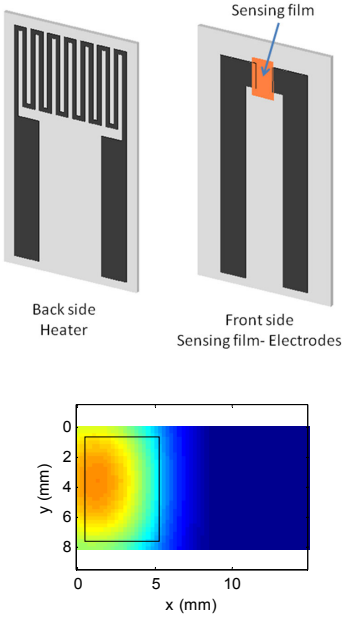


Fig. 2. Upper images - Sensor structure: Alumina substrate (size 8x15x0.26 mm) with heater on one side, and sensor electrodes and sensing layer on the other side (red area, size 1.5 mm^2). Lower image – Simulated temperature distribution.

Sensor Operations

As already pointed out in some previous works [4], the porous film obtained as described consists of large grains (tens of μm) of $YCoO_3$ semiconductor. On the surface of these grains a certain charge can be localized due the chemisorption of different chemical species.
In particular, some previous studies seem to point out that both a direct bond to the semiconductor surface and a reaction of *CO* with pre-adsorbed oxygen are involved in the sensing mechanism, so that the following reactions can be considered:

$$CO + S_{CO} \underset{k_{-CO}}{\overset{k_{CO}}{\rightleftharpoons}} (CO - S_{CO}) \qquad (CO \ \ adsorpion) \tag{1}$$

$$(CO - S_{CO}) \underset{k_{-CO^+}}{\overset{k_{CO^+}}{\rightleftharpoons}} (CO^+ - S_{CO}) + e^- \qquad (CO \ \ ionization) \tag{2}$$

$$O_2 + 2S_O \underset{k_{-O}}{\overset{k_O}{\rightleftharpoons}} 2(O - S_O) \qquad (O \ \ adsorption) \tag{3}$$

$$(O - S_O) + e^- \underset{k_{-O^-}}{\overset{k_{O^-}}{\rightleftharpoons}} (O^- - S_O) \qquad (O \ \ ionization) \tag{4}$$

$$(O^- - S_O) + CO \xrightarrow{k_{CO_2}} CO_2 + S_O + e^- \qquad (CO \ \ oxidation) \tag{5}$$

where S_X indicates the surface adsorbing sites for the species X (e.g. oxygen or metal atoms), whereas (X-S_X) indicates the adsorbed species X (X = O, O^-, CO, CO^+), and k_X are the rate reaction constants.

For the stoichiometric material the first mechanism seems more relevant, and, moreover, the maximum sensitivity to *CO* in a dry environment is reached at a relative high temperature (above 250°C). On the other hand, the presence of *Pd* promotes oxygen adsorption and favors *CO* oxidation allowing to reach the maximum response at a lower temperature (around 200°C), as it can be seen in Figure 3. Both introduction of *Pd* in the framework and dispersion of *Pd* on the surface of the material are effective in enhancing the sensor performance. But, for perovskite with *Pd* in the framework, only the fraction of *Pd* on the surface is really active and contributes to the sensor response improvement.

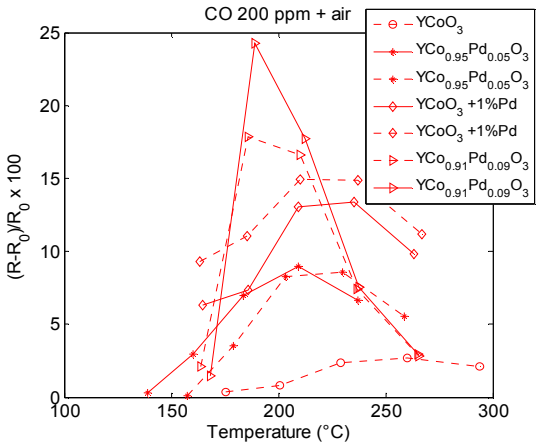


Fig. 3. Responses of different materials to a mixture of CO (200 ppm) and air as a function of the temperature. Sensor exposure time to CO is 2 minutes. Total flow is 100 mL/min.

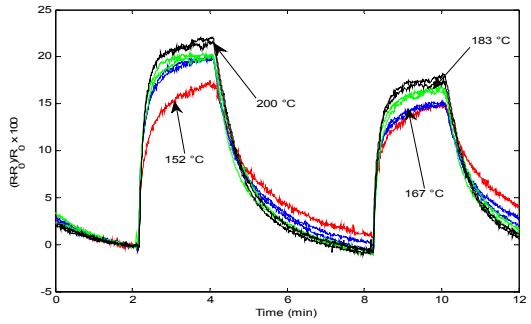
In this figure and in the following, the sensor response is evaluated by the following expression:

$$r = \frac{R - R_o}{R_0} \times 100 \tag{6}$$

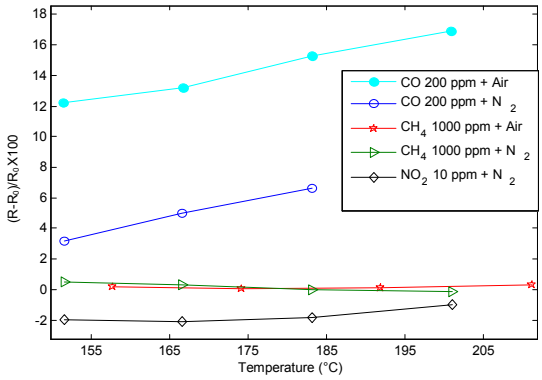
Where R indicates the value of the film resistance reached at the end of gas injections, whereas R_0 is the baseline resistance in air.

Experimental Results

In this section some results obtained with sensors based on *Pd* doped $YCoO_3$ are presented.
The sensors were tested to investigate their sensitivity to *CO*, CH_4, *NO* and NO_2 at different concentrations. The experiments were carried out by exploiting a Teflon chamber and a Bronkhorst mass flow controller bench.
The total flow during measurement is 100 mL/min.
Some results are reported in Figure 4*a)* and 4*b)*. The experiments point out, as shown in Figure 4*a),* the possibility to obtain repeatable measurements even over long time periods, with short response times also at relatively low temperatures. In Figure 4*b)* the sensor normalized responses to mixtures of different gases in N_2 and synthetic air are reported. Promising results were obtained in the temperature range 150 °C – 200 °C, where the sensitivity towards CH_4 results very low, whereas the response to NO_2 is not negligible, but it is of the opposite sign with respect to the one toward *CO*.



a)



b)

Fig. 4. a) Sensor responses to CO in Air (400 and 200ppm, 100mL/min flow) vs. time for different temperatures. b) Sensor normalized response vs temperature for different mixtures. Measurement protocol: 2 minutes of gas injection, 4 minutes recovery time in air flow. (100mL/min total flow).

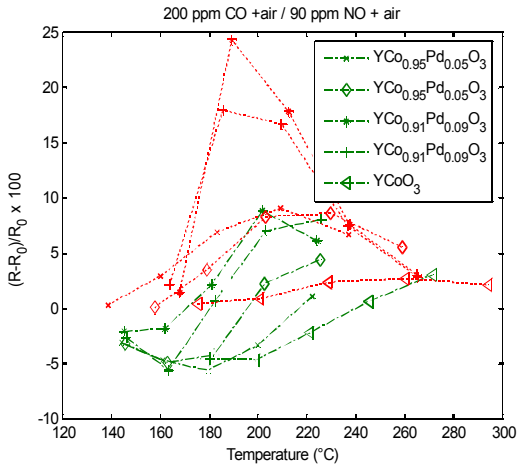


Fig. 5. Dotted lines - Sensor responses to a mixture of air and NO (90 ppm). Dot-dashed lines - Sensor responses to a mixture of air and CO (200 ppm). Measurement protocol: 4 minutes of gas injection, 8 minutes recovery time in air flow. (100mL/min total flow).

NO behaves as an oxidizing gas at low temperatures, whereas at higher temperatures it produces a positive sensor response, behaving as an electron donor. This can be noticed from Figure 5, where the response to a mixture of air and 90 ppm of *NO* is shown and compared to the response to a mixture of air and *CO*.

The following different reaction paths, already suggested for interaction with SnO_2 surface, could explain this behavior [6]

$$(O^- - S_O) + NO \rightarrow NO_2 + e^- \quad (7)$$

$$2NO + e^- \rightarrow O^- + N_2O \quad (8)$$

$$2NO + 2e^- \rightarrow 2O^- + N_2 \quad (9)$$

Moreover, it appears that *Pd* doping results in a reduced sensitivity to *NO* in the low temperature range (below 200°C). The obtained results show that it would be possible to perform a differential detection of *CO* and NO_x, that could be achieved both by tuning the *Pd* density and the measurement temperature.

Conclusions

The presented results indicate that the proposed perovskite is a suitable candidate for low power *CO* sensor development. The possibility of combining *Pd* modification with non-stochiometric material will be explored in the future.

References

[1] R. Spinicci, M. Faticanti, P. Marini, S. De Rossi, P. Porta , Catalytic activity of $LaMnO_3$ and $LaCoO_3$ perovskites towards VOCs combustion, *Journal of Molecular Catalysis A: Chemical* 197, 147–155 (2003); doi: 10.1016/S1381

[2] T. Arakawa K. Takada, Y. Tsunemine and J. Shiokawa, CO gas sensitivities of reduced perovskite oxide $LaCoO_3$, *Sensors and Actuators B: Chemical* 14, 215-221 (1988); doi: 10.1016/0250-6874(88)80068-4

[3] A. Fort, M.Mugnaini, I.Pasquini, S.Rocchi, V.Vignoli, R. Spinicci, Characterization of $YCoO_3$ film used for CO gas detection, *Chemical, Engineering Transactions* 23, 153-158, (2010); doi: 10.3303/CET1023026

[4] A.Fort ,M.Mugnaini,L.Romualdi, S.Rocchi, V.Vignoli, M.Gregorkiewitz, R. Spinicci Development and characterization of low power perovskite CO gas sensors, *Proc. of the 2011 IEEE Instrumentation and Measurement Technology Conference,* 1 – 4 (2011); doi: 10.1109/IMTC.2011.5944239

[5] A.Fort, M. Mugnaini, S. Rocchi, L. Romualdi, R. Spinicci, and V. Vignoli, Development and characterization of $YCoO_3$ based CO gas sensors, *Proceedings of the 14th International Symposium on Olfaction and Electronic Nose.* 1362, 55-57 (2011), doi: 10.1063/1.3626304

[6] A. Szychowska, M. Wróbel-Jędrzejewska, I. Chylak, I. Kocemba, J. Rynkowski, Investigation of CO Oxidation by NO with Application of Semiconductor Gas Sensors, *Polish Journal of Environmental Studies*. 17, 421-425, (2008)