Evaluation of Cox Fe3-x O 4 cobaltites as ethanol sensing material

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***Abstract* — $Co_xFe_{3-x}O_4$ oxide powders were synthesised by an oxalate decomposition process. Microstructural analysis like X-ray fluorescence spectroscopy confirmed the composition of the prepared powders. These powders were then deposited onto alumina substrates in order to study their response under ethanol gas pulses. The gas sensing experiment was carried by a defined test protocol and several characteristics were tracked. Results showed a direct link between the proportion of cobalt and gas sensing performances.**

Keywords— gas sensor, ethanol, cobalt ferrite, cobaltite, spinel, MOS

I. INTRODUCTION

Metal oxide semiconductors (MOS) are being widely explored in the gas-sensing field [1]. Their capacity as oxidizer and/or reducer is the main key point for their use in this field. These materials are classified into two different types, n-type semiconductors where the majority charge carriers are electrons and the p-type semiconductors with electron deficiency (holes) as majority charge carriers. For gas detection, both have advantages and drawbacks. Thus p-type semiconductors exhibit not only limitations but also encouraging potential for practical uses.

According to the work of Hübner et al. [2], the DC resistive response of the p-type oxide semiconductors is equal to the square root of an n-type semiconductor's response for a same morphology and a same gas. This indicates that p-type semiconductor could be improved in order to detect more accurately various gases. Nevertheless, most p-type materials such as CuO or Co_3O_4 are intensively studied as catalyst materials to improve the oxidation of different gas, as for example volatile organic compound (VOCs).

Spinel oxides are basically described by $(A)[B_2]O_4$ formula where A and B represent tetrahedral and octahedral sites respectively. In a normal spinel like Co_3O_4, divalent cations used to occupy tetrahedral sites: $(Co^{2+})[Co_2^{3+}]O_4$ although in an inverse spinel like Fe_3O_4 they used to occupy octahedral sites : $(Fe^{3+})[Fe^{3+}Fe^{2+}]O_4$. Thanks to this particularity, varying the proportion x in $Co_{3-x}Fe_xO_3$ leads to bring considerable disorder and related properties modifications.

In this scope, this paper presents the elaboration and characterisation of a wide range of cobalt ferrite oxide powder ($Co_xFe_{3-x}O4$, with $1 \leq x \leq 3$) intended to detect ethanol in presence of humidity.

II. EXPERIMENTAL

A. Material systhesis

The powder was synthesised by a co-precipitation method followed by annealing.

The co-precipitation was done by dissolving oxalic acid $H_2C_2O_4.H_2O$ in 95% ethanol. In parallel, in a water-60/40 ethylene glycol mixture, iron chloride $FeCl_2.4H_2O$ and cobalt chloride $CoCl_2.6H_2O$ were added in desired proportions. A small proportion of HCl was added to avoid fast oxidation of iron.

The saline solution was then added to the oxalic solution in a speed of 20 ml per minute in order to get precipitations.

The obtained precipitates were been washed in de-ionised water to eliminate chlorine ions and centrifuged to separate precipitates from mother liquor and finally dried at 80 °C. The oxalate was decomposed in air at 350 °C at a heating rate of 50 °C/h, then was annealed at 900 °C for 1 h and quenched to get pure oxide phase and avoid the spinodal decomposition [3]. Table 1 shows the list of the samples prepared and their respective names as used in this work.

Name	Composition
Co1.16	$Co_{1.16}Fe_{1.84}O_4$
Co1.5	$Co_{1.5}Fe_{1.5}O_4$
Co1.7	$Co_{1.7}Fe_{1.3}O_4$
Co2	Co_2FeO_4
Co2.7	$Co_{2.7}Fe_{0.3}O_4$
Co3	Co_3O_4

Table 1: Prepared samples

B. *Sample fabrication*

The device for testing the gas sensing ability was fabricated with a 15x15 mm alumina substrate. Silver coatings were added on that substrate as electrodes, in order to enhance electrical contact [4]. This was done by decomposing silver oxalate into metallic silver following a soldering procedure [5]. The sensing metal oxide was grind with a mortar and mixed with ethylene glycol. The obtained paste was coated on the substrate between the two electrodes. The full process was already published here [3]. The Figure 1 gives the schematic representation of the device.

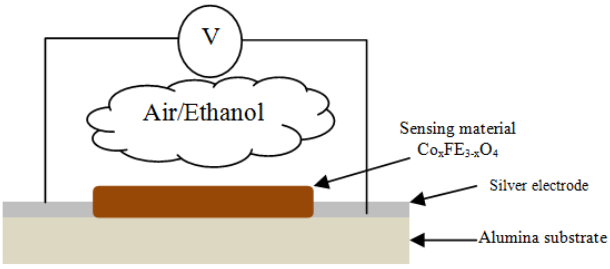

Figure 1: Schematic representation of the fabricated device for performing electrical measurements

C. *Experimental setup and sensing protocole*

The ethanol sensing properties were studied in a homemade gas sensing set up. The device is put onto a thermally controlled hotplate in a Linkam cell. The Linkam cell is linked with 3 gas containers: dry air, 50 ppm of ethanol in dry air, and dry air bubbling in a water-containing flask. The entire gas network is controlled by Brooks 5800S mass flow controllers and the resistance of the device in the Linkam cell is measured using a Keithley 2400 source meter. The entire system is controlled by LabVIEW software.

The gas sensing is measured by passing alternately from air to ethanol-containing air while the resistance of the sensing material is measured and saved. The total flow is 100 sccm and the bubbling line constantly set to 50 sccm so that the RH level obtained is estimated to be almost 50 % with ethanol concentration of 25 ppm at the maximum.

A same measurement protocol was established for all sample devices with the purpose of having comparable sensing results. It is well known that high temperature leads to the desorption of most species at the surface of the sensing materials [6] so the devices were heated to 450 °C at a speed of 2 °C.min^{-1} and decreased by step of 25 °C until 200 °C. At each temperature step, 3 injections of ethanol of 30 min separated by 30 min of recovery under air were done. The whole experiment was carried out at 50 % RH. The resistance of the device was measured every 10 seconds. The detailed protocol is shown is Figure 2.

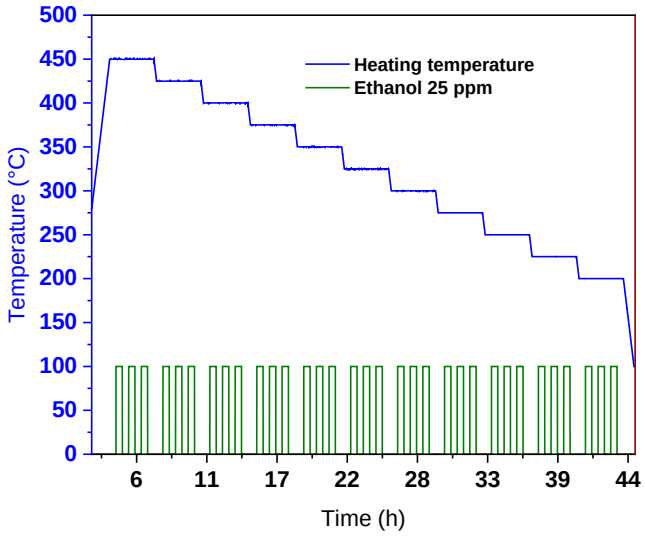

Figure 2: Gas sensing test protocol.

The response of the device was calculated as S(%) defined by $(R_{gas}-R_{air})/R_{air}$ where R_{gas} is the last measured resistance in presence of ethanol and R_{air} is the last measured resistance in air. The mean value was calculated from the three gas injections, at each temperature.

III. Results and Discussions

A. *Microstructural characterisation*

Elemental analysis was performed using X-ray fluorescence (XRF) on all the fabricated devices. From the data obtained, real composition of the powder coated on the device was calculated and presented in table 2.

Sample Name	Estimated Composition	Calculated composition
Co1.16	$Co_{1.16}Fe_{1.84}O_4$	$Co_{1.17}Fe_{1.83}O_4$
Co1.5	$Co_{1.5}Fe_{1.5}O_4$	$Co_{1.48}Fe_{1.52}O_4$
Co1.7	$Co_{1.7}Fe_{1.3}O_4$	$Co_{1.74}Fe_{1.26}O_4$
Co2	Co_2FeO_4	Co_2FeO_4
Co2.7	$Co_{2.7}Fe_{0.3}O_4$	$Co_{2.66}Fe_{0.34}O_4$
Co3	Co_3O_4	Co_3O_4

Table 2: Estimated and calculated composition from XRF spectra

As expected, the spectra obtained by XRF are in good agreement with the desired composition.

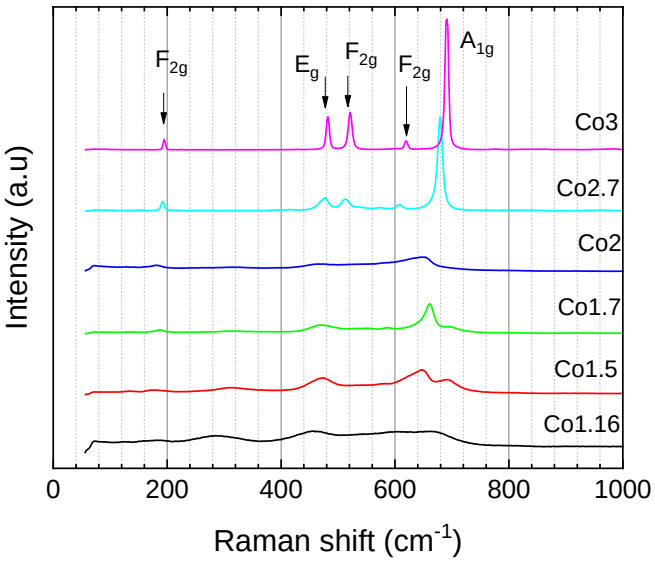

Figure 3: Vibrational spectroscopy of the entire synthesised sample

The Figure 3 shows the vibrational spectra of the samples, it is not easy to compare these results with the literature because of those particular compositions, however works undergone on Co_3O_4 [7] confirm the found vibrational mode and results on Co_2FeO_4 [8] and $Co_{2.7}Fe_{0.3}O_4$ [9] enable to situate the obtained spectrum in the correct zone.

B. Ethanol sensing performance

Ethanol sensing tests were carried out on all the prepared samples using the test protocol presented before.

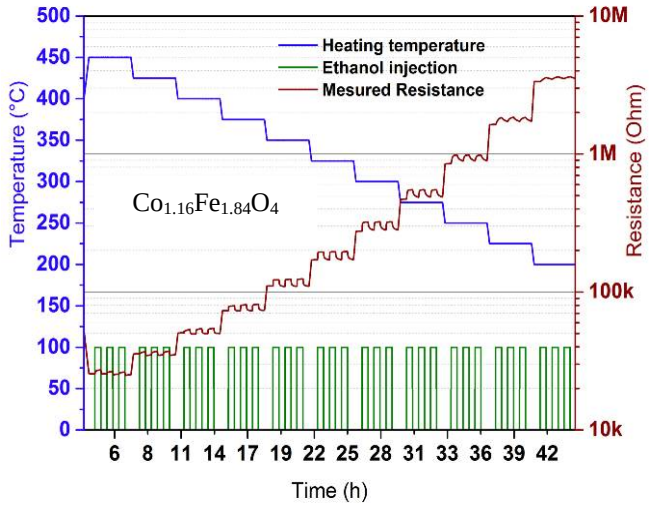

Figure 4: Response of a device Co1.16 (coated with $Co_{1.16}Fe_{1.84}O_4$) to 25 ppm of ethanol under 50% relative humidity

The Figure 4 presents the typical response of the device (herein the Co16 sample as an example) when 25 ppm of ethanol are injected. The first visible fact is that the resistance increases when the temperature decreases which confirms the metal oxide semiconductor behaviour. Thereafter, at each ethanol injection, the resistance moves toward higher values which prove the p-type semiconductor behaviour. Investigation on all the devices has been undertaken.

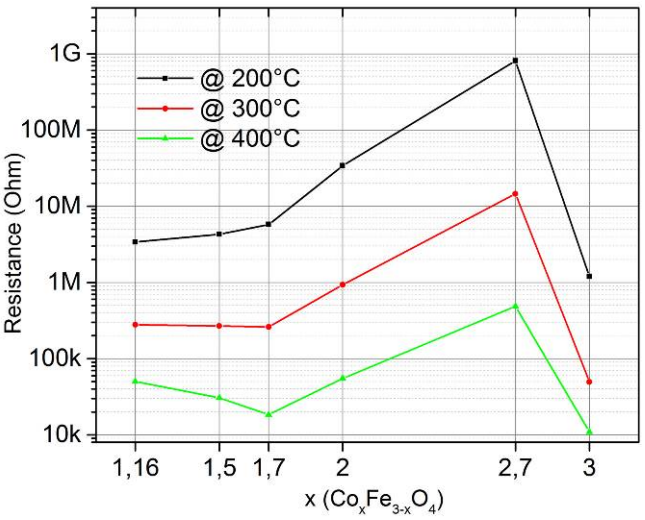

Figure 5: Baseline of the sample device at 200 °C, 300 °C and 400 °C.

Analysis of the baseline at different temperatures (Figure 5) shows again the MOS behaviour exposed before. However, the increase of cobalt content in the $Co_xFe_{3-x}O_4$ composition leads to the increase of the resistance baseline. It can be attributed to the decrease of Co^{2+}/Co^{3+} couples in octahedral sites. However the strong decrease of the resistivity observed for Co_3O_4 is unexpected as this oxide is known to have only Co^{3+} cations located in octahedral sites.

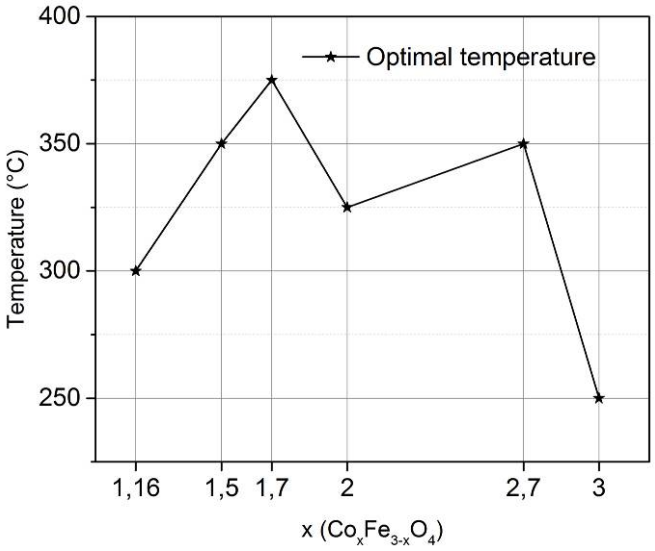

Figure 6: Optimal temperature of sensing for each composition

In the Figure 6 optimal temperature of each composition has been reported. Co_3O_4 appears to be more interesting with an optimum temperature much lower than the other oxides.

The responses of the samples have been plotted as a function of the temperature in the
Figure 7. Most optimal response values are between 4 and 15 %. However, the Co3 sample is clearly out of this trend. This result is particularly surprising when comparing the Co2.7 and Co3 compositions that are very close. It demonstrates that the presence of Fe^{3+} in the spinel structure strongly reduces the sensitivity to ethanol even for very small iron amount. Furthermore, samples Co1.7 and Co2 present negative

sensitivity at low temperatures performing like an n-type MOSs.

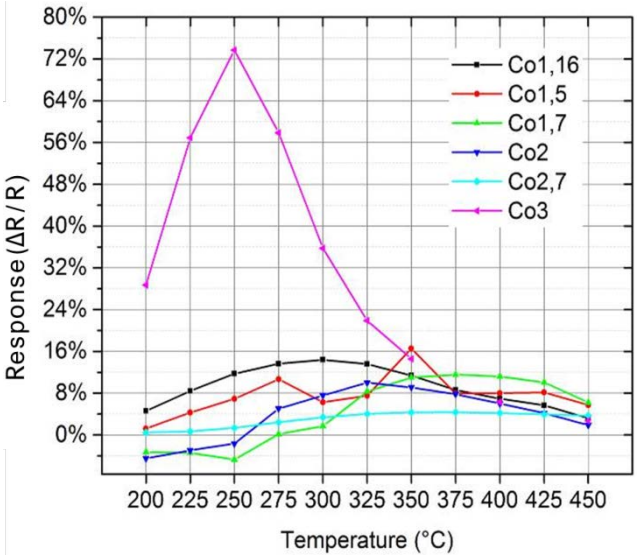

Figure 7: Comparison of the response toward 25 ppm of ethanol versus temperature for each composition.

Material and morphology	Synthesis Method	Concentration (ppm)	T (°C)	Response (Rg/Ra)	Ref
Co_3O_4 Nano-structures	Solvo-thermal	100	175	2	[10]
Co_3O_4 Microspheres	Solvo-thermal	50	200	20	[11]
Co_3O_4 Nano-cubes	Microwave assisted solvo-thermal	20	200	2,25	[12]
Co_3O_4 Nanofibers	disintegration of nanofibers	100	250	20	[13]
Co_3O_4 Nano-sheets	hydrothermal	20	160	2,5	[14]
In this work					
Co_3O_4 Powder	Co-precipitation	25	250	1,73	This work

Table 3 Ethanol sensing performances of Co3O4 morphologies in the literature.

In the literature, it is hard to find studies on all the compositions used in this work. However, Co_3O_4 is a well-studied material in the gas sensing field. Table 3 shows some studies close to the present work and for the ease of comparison, response previously presented as $(R_{gas}-R_{air})/R_{air}$ is presented as (R_{gas}/R_{air}). The response of the Co_3O_4 sample in the present study is lower than those found in the literature. This difference could be explained by the nano sized morphology of the samples measured in the literature compared with the large grain size of the annealed powders in this study with a mean diameter of 500nm determined by Scanning Electron Microscopy (not shown here).

IV. Conclusion

$Co_xFe_{3-x}O_4$ oxides powder were synthesised and coated onto alumina substrates in order to sense ethanol at 25 ppm concentration with 50 % humidity. Among all the sensitive samples, Co_3O_4 presents the highest sensitivity which makes it promising for further studies. The presence of iron in the cobaltite appeared to have a negative influence on the sensing properties.

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