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Nano-structured perovskite oxide electrodes for planar electrochemical sensors using tape casted YSZ layers

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Abstract

Solid-state NO_2 sensors based on yttria stabilized zirconia (YSZ), an O^{2-} conductor, combined either with an *n*- (WO_3), or a *p*-type semiconducting oxide ($LaFeO_3$), or a mixed electronic and ionic conductor ($La_{0.8}Sr_{0.2}FeO_3$) were investigated. Platinum parallel finger electrodes were applied on the surface of tape-casted YSZ layers and attached with gold wires for current collection. Nanocrystalline perovskite powders were prepared using different chemical methods: $LaFeO_3$ by the thermal decomposition of the LaFe–hexacyanide complex, and $La_{0.8}Sr_{0.2}FeO_3$ by a sol-gel route. A sub-micrometric commercial WO_3 powder was used. The oxide powders were mixed with a screen-printing oil and deposited on one Pt finger electrode. The presence of the oxide powder makes one of the electrodes different from the other in terms of catalytic activity, specific surface area, gas adsorption and reaction kinetics. Both electrodes were wholly exposed to the same gas atmosphere, without using reference air. The sensors were investigated at fixed temperature (450–700 °C) by measuring the electromotive force (EMF) at different concentrations of NO_2 and CO in air in the range 20–1000 ppm. A fast and stable response was measured for all the tested sensors. An EMF of opposite sign was measured for *p*- and *n*-type semiconducting based sensors upon exposure to the same gas. After increasing the grain size of the nano-structured $La_{0.8}Sr_{0.2}FeO_3$ powder by a heat treatment at 900 °C for 4 h, the response to NO_x became small, slow and unstable.

Keywords: Electrical properties; Perovskites; Sensors; ZrO_2

1. Introduction

At present, the control of the main pollutants in automotive emissions, such as NO_x, HCs and CO, is obtained through the on-board diagnostic (OBD) system. This is a quite complex and closed-loop system, mounted on each automobile, to continuously monitor the pollutant concentrations in the exhausts. It consists of two solid-state oxygen sensors (lambda sensors): one placed upstream the three-way catalytic converter (to control the fuel/air ratio), the second one located downstream in the exhaust to control, through an electronic unit, the efficiency of the catalytic converter. The availability of new, reliable and fast NO_x, HCs and CO solid-state sensors would allow a direct and fast analysis of the pollutants in the OBD system. Moreover, such new devices may allow to comply with much more strict standards on automobile emissions. Thus sensors able to operate at high temperatures and harsh environments are highly required. A way to improve the sensitivity, the stability and the selectivity of the sensors is to combine solid electrolyte and semiconducting oxide materials as sensing electrodes. This strategy is at the moment followed by few research groups with promising results.[1–4]

In this work, YSZ (8 wt.% of Y_2O_3) tape-casted layers as solid electrolyte were used with WO_3, $LaFeO_3$ and $La_{0.8}Sr_{0.2}FeO_3$ as semiconducting oxides. WO_3 and $LaFeO_3$ have been selected because of their excellent performance in bulk and thick-film form[5,6] as semiconductor NO_2 sensors. $La_{0.8}Sr_{0.2}FeO_3$ oxide was used to check whether the mixed conduction may improve the sensing response. The sensing performance to NO_2 and CO was investigated. The influence of the grain size of the $La_{0.8}Sr_{0.2}FeO_3$ electrode on the gas response was also studied. The sensing mechanism is also discussed.

2. Experimental

YSZ (8 wt.% of Y_2O_3) tape-casted layers of 150 μm in thickness, cut in rectangular shape of 8 mm×10 mm (width×length) in dimensions, were used as solid

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electrolyte for sensor fabrication. Pt paste was used for metallic electrodes and deposited on one side of the layers in two parallel fingers. Thin gold wires were connected for current collection. The firing temperature of Pt paste was 800 °C for 10 min. For the fabrication of the sensing electrode, commercial WO_3 powders (99.995% purity), $LaFeO_3$, and $La_{0.8}Sr_{0.2}FeO_3$ perovskite oxides were mixed with a screen-printing oil. The slurry thus obtained was painted on one metallic electrode and fired at 750 °C for 3 h. Nano-sized $LaFeO_3$ powders were prepared by the thermal decomposition of a LaFe–hexacyanide complex at 700 °C for 1 h.[7] $La_{0.8}Sr_{0.2}FeO_3$ was prepared by a sol-gel route. The precursors used were: $La(NO_3)_2$, $Sr(NO_3)_2$, $Fe(NO_3)_3$, citric acid, ethylene glycol. The nitrates and the citric acid were mixed in the following molar ratios: La:Sr:Fe:citric acid = 0.8:0.2:1:2, while the citric acid:ethylene glycol weight ratio was 40:60. Stoichiometric amounts of salts were first dissolved into ethylene glycol. When the precursors were completely dissolved, a controlled amount of citric acid was added. A complete dissolution of precursors resulted in a clear red-brown solution. The gel formation occurred at 120 °C, its transparency giving an indication of an homogeneous system. The samples were dried at 120–130 °C for a few hours and then heated at 700 °C for 3 h. To check the influence of the electrode grain size on the sensing response of the devices, the $La_{0.8}Sr_{0.2}FeO_3$ oxide was also heated at 900 °C for 4 h.

X-ray diffraction (XRD) analysis was conducted for phase identification. Microstructures of the powders were observed by scanning electron microscopy (SEM).

Sensing experiments were carried out in a conventional gas-flow apparatus equipped with a controlled heating facility. The sensor was alternatively exposed to air and NO_2 or CO (20–1000 ppm in air) at a total flow rate of 100 ml/min in the temperature range between 550 and 700 °C. Electromotive force (EMF) measurements were performed between the two electrodes of the sensors using a digital electrometer.

3. Results and discussion

From XRD patterns of oxide powders only the peaks of orthorhombic perovskite-type $LaFeO_3$ and $La_{0.8}Sr_{0.2}FeO_3$ structure were found, showing a good crystallinity and purity of the powders.

SEM observations were performed on the different powders used for the sensing electrode. WO_3 powders showed a porous structure made of grains of submicrometric dimension of about 200–250 nm. The $LaFeO_3$ observations were in agreement with what has been previously reported for these perovskite-type oxides.[7] The powder calcined at 700 °C was highly porous and consisted of large grains 2–10 μm in size. Each of these $LaFeO_3$ grains was made of soft agglomerates of homogeneous nanometric particles of 50–100 nm.

The grain size of $La_{0.8}Sr_{0.2}FeO_3$ powders decomposed at 700 °C was smaller than 50 nm as shown in Fig. 1. The $La_{0.8}Sr_{0.2}FeO_3$ powder calcined at 900 °C for 4 h showed an increase in the grain size up to about 150 nm (Fig. 2).

The EMF response, performed on WO_3 based sensors at fixed temperature (550–700 °C), was in opposite direction upon exposure to NO_2 and CO. Positive EMF values were measured at different NO_2 concentrations and negative EMF values at different CO concentrations. The response was stable and reproducible. At 600 °C the EMF magnitude was 25 and 17 mV upon exposure to 1000 ppm of NO_2 and CO, respectively. The response (20 s) and recovery (40 s) times were quite fast for both gas mixtures. A linear correlation was observed between the EMF values and the NO_2 and CO concentrations in logarithmic scale. The best sensitivity to both NO_2 and CO gases was observed at 600 °C, as shown in Fig. 3.

The EMF responses of $LaFeO_3$- and $La_{0.8}Sr_{0.2}FeO_3$-based sensors were found in opposite directions with respect to the WO_3-based sensors response: negative EMF values upon NO_2 exposure, positive values upon CO exposure. Figs. 4 and 5 show the EMF response of $La_{0.8}Sr_{0.2}FeO_3$-based sensors to NO_2 and CO at 550 °C, respectively. At a given gas concentration, the EMF

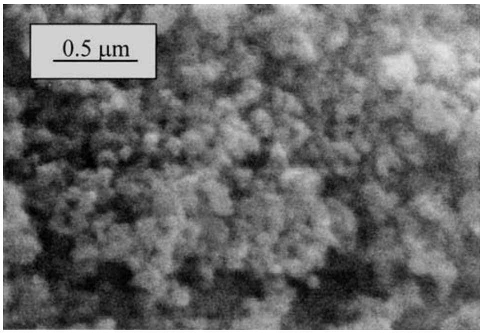

Fig. 1. SEM micrograph of the $La_{0.8}Sr_{0.2}FeO_3$ powder heated at 700 °C for 3 h.

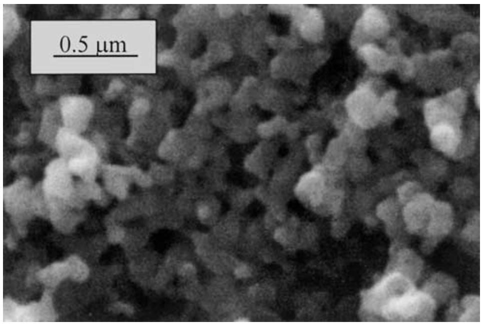

Fig. 2. SEM micrograph of the $La_{0.8}Sr_{0.2}FeO_3$ powder heated at 900 °C for 4 h.

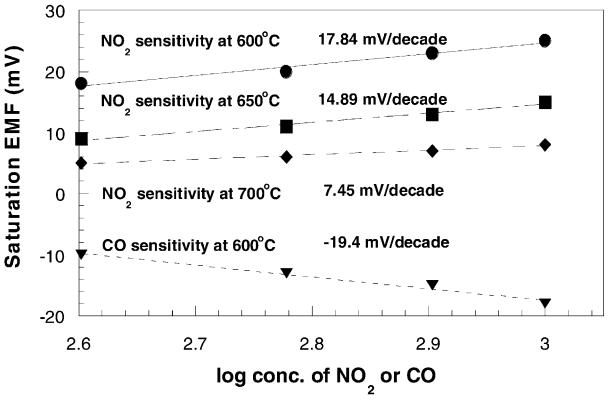

Fig. 3. EMF values of WO_3 based sensors vs. the concentrations of NO_2 and CO in logarithmic scale at different operating temperatures.

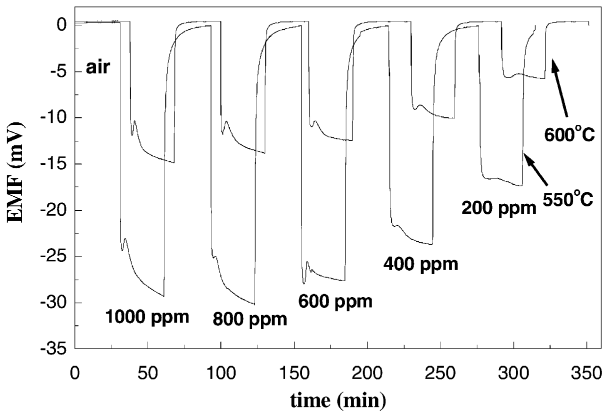

Fig. 4. EMF response of $La_{0.8}Sr_{0.2}FeO_3$ (700 °C) based sensors to different concentrations of NO_2 at 550 °C.

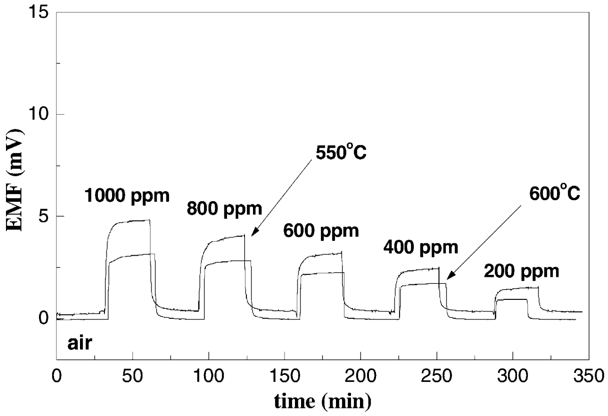

Fig. 5. EMF response of $La_{0.8}Sr_{0.2}FeO_3$ (700 °C) based sensors to different concentrations of CO at 550 °C.

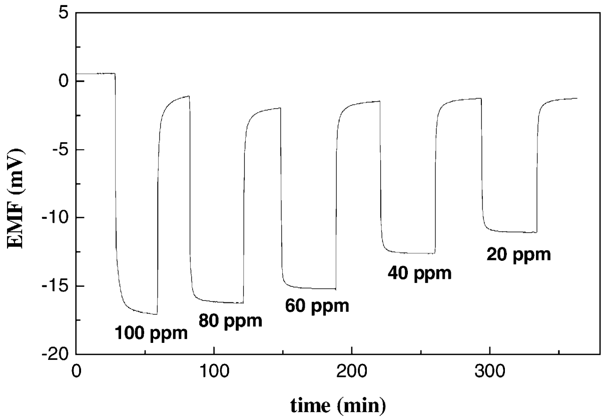

Fig. 6. EMF response of $La_{0.8}Sr_{0.2}FeO_3$ based sensors, prepared with powders heated at 700 °C, at different concentrations of NO_2 at 450 °C.

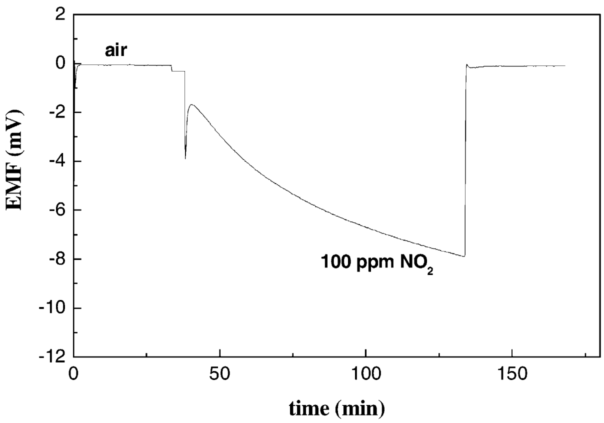

Fig. 7. EMF response of $La_{0.8}Sr_{0.2}FeO_3$ based sensors, prepared with powders heated at 900 °C, at 100 ppm of NO_2 at 450 °C.

values decreased with increasing the operating temperature. At 550 °C the EMF magnitude at 1000 ppm of NO_2 in air was about 30 mV, while the EMF value at the same concentration of CO was only 5 mV. The $La_{0.8}Sr_{0.2}FeO_3$-based sensors showed a reduced cross-sensitivity to CO in comparison to WO_3 and $LaFeO_3$-based sensors. This might be due to the mixed ionic and electronic conduction mechanism. Some oxygen ions adsorbed on the surface can migrate inside the grains and so a reduced number of adsorbed oxygen ions is available for the reaction with CO. For NO_2, this mechanism does not apply given that it adsorbs competitively with O_2. For both perovskite oxide-based sensors the best sensitivity was observed at 550 °C (from the slope of the linear fit of the measured curves).

Fig. 6 shows the EMF of $La_{0.8}Sr_{0.2}FeO_3$-based sensors with powders decomposed at 700 °C, measured at 450 °C with different concentrations of NO_2. The response is fast and stable. Fig. 7 shows the EMF of $La_{0.8}Sr_{0.2}FeO_3$-based sensors, prepared with powders heated at 900 °C for 4 h, measured at 100 ppm of NO_2 at 450 °C. The larger the grain size of the powders, the smaller, slower and more unstable the response of the sensors. According to what has been previously reported,[8] the grain size of the sensing electrode strongly affects the sensor performance.

The results obtained from the EMF measurements (different sign of EMF for *p*- and *n*-type oxide-based sensors) cannot be explained by the occurrence of the electrochemical reactions at the three phase boundary (solid electrolyte/electrode/gas).[9] Because of the electrode design, close finger-electrodes exposed to the same gas atmosphere, the electrochemical reactions take place with the same rate at both the electrodes and thus the chemical adsorption mechanism of gases on the semiconducting oxide is believed to be the predominant factor for the gas sensing mechanism.

4. Conclusions

Electrochemical sensors obtained combining YSZ with WO_3, $LaFeO_3$, $La_{0.8}Sr_{0.2}FeO_3$ semiconducting oxides as sensing electrodes are promising candidates for pollutant detection at high temperatures. The sensors show fast and stable response without the use of reference air. The sensor response was found to be strongly affected by the grain size of the powder used for the preparation of the sensing electrode: the gas response is much larger when the grain size is reduced to nano-sized dimensions. When using oxide electrodes in planar-type sensors, changes in EMF upon exposure to NO_2 and CO cannot simply be explained by means of electrochemical reactions, but mainly by a different chemical sorption–desorption behaviour at the two electrodes.

Acknowledgements

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