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Solid state ceramic gas sensors based on interfacing ionic conductors with semiconducting oxides

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Abstract

Solid-state ceramic NO_x sensors based on interfacing an ionic conductor (NASICON) with semiconducting oxides (rare earth perovskite-type oxides) were investigated. NASICON powders were pressed into thimbles 12 mm long with 3 mm inner diameter and 4 mm outer diameter, then sintered at 1270°C in air. A Pt wire was attached to the outer surface of the tubes using a platinum paste. A uniform Au/Pd (60 wt.%) coating, permeable to oxygen but not to NO_x, was sputtered for 40 min on the sensor external surface to allow the exposure of both electrodes to the gas atmosphere without using reference air. Windowless energy-dispersive spectroscopy (EDS) was used to evaluate the chemical composition of the Au–Pd layer before and after the performance of sensing tests. Sodalite powder as an auxiliary phase was tightly packed into the NASICON thimbles with a Pt lead for the electrical contact. To get an in-situ NO conversion to NO_2, a Pt-loaded alumina powder was used as a catalyst and incorporated with the sensor on the top of the auxiliary phase. Nano-sized and chemically-pure rare earth perovskite-type oxide ($LaFeO_3$, $SmFeO_3$, $NdFeO_3$ and $LaCoO_3$) powders, prepared by the thermal decomposition of the corresponding hexacyanocomplexes, were also used in the electrochemical cells. Each of the tested oxides was packed into the thimbles replacing the sodalite and the Pt-loaded alumina catalyst. Tests were performed also using only the perovskitic oxides. The microstructure of the materials tested was evaluated using scanning electron microscopy (SEM). The NO_2 sensing properties of the prototype sensors were investigated at controlled temperature (in the range 300–600°C) by measuring the electromotive force (EMF) at different NO_2 concentrations (in the range 2–2000 ppm in air). Some measurements were performed at various NO concentrations diluted with Ar. The results obtained showed a promising NO_2 sensing performance when ferrites were used. $SmFeO_3$ has a lower catalytic effect on NO oxidation than the Pt-loaded alumina catalyst, and has a similar effect to sodalite when used as auxiliary phase. The perovskite-type oxides are more preferable as auxiliary phase than sodalite because they improve the stability of the electrochemical sensor performances.

Keywords: Semiconducting oxides; Solid-state NO_x sensors; Perovskitic oxides

1. Introduction

The growing attention to environmental problems increases the need of reliable and selective solid-state NO_x sensors, both for air quality monitoring and automotive applications.[1,2] The requirements are different for each application; sensors able to selectively detect NO_2 in the concentration range 1 ppb–10 ppm are needed for environmental monitoring, while sensors are needed to detect NO_x in the concentration range 10–2000 ppm for combustion control and exhaust monitoring. At present, analytical techniques are approved by the environmental standards to monitor NO_x, which use very costly and bulky equipment.[3]

Therefore, the control and monitoring of pollutants for ambient air quality is limited by the high costs of the techniques at present accepted by regulations. The use of devices based on solid-state gas sensors would be enormously cheaper than the use of analytical techniques, and would lead to a wider distribution of environmental monitoring stations than exist at present with the same cost, resulting in an improved picture of air quality.[4] However, the performance of solid-state gas sensors is not satisfactory yet for this application.[5]

For automotive applications, NO_x sensors usually have to operate in harsh environments. The stability of sensing materials thus becomes of paramount importance. Ceramics appear to be more convenient as active elements for NO_x sensors, given their thermal and chemical stability, especially for the control of combustion exhausts.

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Solid-state sensors based on semiconducting oxides or electrolytes are currently studied for NO_x detection. Several *n*-type[6–15] and *p*-type[16–21] semiconducting oxides have been studied as NO_x sensors, mainly for applications at high temperatures. Few examples have been reported in the relevant literature for the use of semiconducting oxide NO_x sensors for indoor[22] and outdoor[23–25] air quality monitoring, and for the control of air quality inside passenger cars.[26] The main limitations of semiconductor NO_x sensors are the lack of selectivity and the inability to detect the very low gas concentrations as required by the environmental standards.[5]

Ceramic NO_x electrochemical sensors, mostly potentiometric and some amperometric, have been studied for use in combustion exhaust control systems.[27–31] In general, most of the equilibrium-potential sensors use oxyacid salts as auxiliary phases in combination with a solid electrolyte.[32] The auxiliary phases used for most of the solid electrolyte NO_x sensors so far studied are sodium nitrite or nitrate-based metal oxides.[33–35] These compounds have a low melting temperature and thus they show problems of thermal and chemical stability.

A more stable compound, nitrited sodalite, has been used as an auxiliary phase.[36] Sodalite belongs to the zeolite family and contains NO_2 in its formula $Na_8[Al_6Si_6O_{24}](NO_2)_2{\cdot}xH_2O$, which makes it sensitive to gaseous NO_2 permitting its use as auxiliary phase. Given that it is an ionic conductor with Na^+ ions as charge carriers, nitrited sodalite has been also used as a solid electrolyte for NO_x electrochemical sensors.[37,38] However, stable operating conditions have been obtained at maximum 400°C.

A new approach to improve the stability and the selectivity of the NO_x devices is to combine a solid electrolyte with an electrode of semiconducting oxides, substituting the auxiliary phase of the electrochemical sensor with a metal oxide.[39] This approach has been proposed to improve thermal and chemical stability of CO, CO_2, H_2S and hydrocarbon sensors,[40–44] though one of the most appealing application of these concepts is in the study of NO_x sensors.[45,46] The oxide electrode used as auxiliary phase can act as an electrode catalyst increasing the selectivity of the device. The design of sensors based on the integration of materials with different electrical properties is an alternative way of producing devices with improved performance and novel functions.[47] The better sensing performance to NO and/or NO_2 as well as the stability at higher temperatures can be due to novel detection mechanisms, probably based on changes of mixed potential at the electrode interface.[48,49] Another possible working method for the detection of NO_x of such ionic conductor/semiconductor structures is the amperometric one,[50,51] which can have advantages for the detection of low gas concentrations.[46]

In this work, an investigation on solid-state ceramic NO_x sensors based on interfacing an ionic conductor (NASICON) with semiconducting oxides (rare earth perovskite-type oxides) is reported. NASICON is a sodium conductor with a very high ionic conductivity at relatively low (< 400°C) temperatures. It has been used for NO_x electrochemical sensors using mixtures of nitrites and nitrates as auxiliary phases.[32] Nano-sized and chemically-pure rare earth perovskite-type oxide powders were used as electrodes. These powders were prepared by the thermal decomposition of the corresponding hexacyanocomplexes,[52–56] according to a procedure well investigated by one of the authors of this paper.[57] Some of the perovskite oxide powders, in thick film form, have been already successfully tested as semiconductor NO_2 sensors.[58,59]

2. Experimental procedure

2.1. Materials

NASICON powders with the formula $Na_3Zr_2Si_2PO_{12}$ were prepared by solid-state reaction.[60] Nitrited sodalite with $Na_8[Al_6Si_6O_{24}](NO_2)_2{\cdot}xH_2O$ formula was synthesized using the method reported by Hund.[61] Rare earth perovskite-type oxides ($LaFeO_3$, $SmFeO_3$, $NdFeO_3$ and $LaCoO_3$) were prepared by the thermal decomposition at low temperatures of the corresponding heteronuclear hexacyanocomplexes.[52,53] The phases present were confirmed by X-ray diffraction (XRD) analysis.

2.2. Prototype sensors

Fig. 1 shows a schematic diagram of a prototype sensor. NASICON powders, containing 0.5 wt.% of an organic sintering aid, were isostatically pressed at 250 MPa into thimbles 12 mm long with 3 mm inner diameter and 4 mm outer diameter. The thimbles were then sintered at 1270°C in air. A platinum wire was attached to the outer surface of the tubes using a platinum paste that was fired at 1000°C for 5 min.

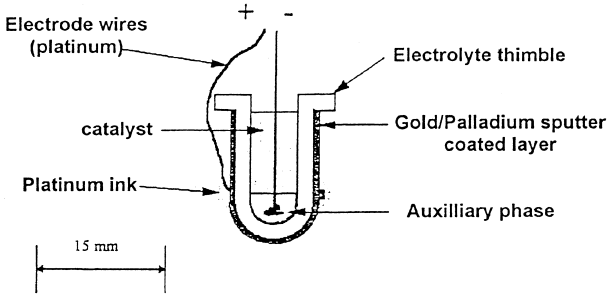

Fig. 1. Schematic diagram of NO_x sensor device using NASICON thimble with auxiliary phase and Pt-catalyst inside.

The need for a reference atmosphere would make the sensing device complicated and impractical. To simplify the operation, both electrodes should be exposed to the analyte. Thin electrodes layers of Au–Pd have been demonstrated to be blocking to all gases and vapours but oxygen.[62] Therefore, an uniform Au/Pd (60 wt.%) coating, permeable to oxygen but not to NO_x, was sputtered for 40 min on the sensor external surface.[62] Thus, during testing the sensors were wholly exposed to NO_x atmosphere without using reference air for the reference electrode.

A solid-electrolyte NO_x electrochemical cell developed in Cambridge was used as standard comparison. Sodalite as auxiliary phase was tightly packed into the NASICON tubes with a platinum lead for the electrical contact. To get an in-situ NO conversion to NO_2, a Pt-loaded alumina powder was used as a catalyst and incorporated with the sensor on the top of the auxiliary phase. The sensors described can be represented by the following electrochemical cell:

$$(-)O_2,NO_x||\text{Pt-alumina catalyst}|\text{sodalite}|\text{NASICON}||\text{Au}-\text{Pd}||\text{Pt},\ O_2(+). \quad (1)$$

To evaluate the effect of the rare-earth perovskite-type oxides on the performance of the electrochemical sensors, each of the tested oxides was packed into the thimbles instead of sodalite and of the Pt-loaded alumina catalyst. Tests were performed also using only the perovskitic oxides into the NASICON thimbles. The resulting electrochemical cells were:

$$(-)O_2,NO_x||\text{RE perovskite oxide}|\text{sodalite}|\text{NASICON}||\text{Au}-\text{Pd}||\text{Pt},\ O_2(+) \quad (2)$$

$$(-)O_2,NO_x||\text{Pt catalyst}|\text{RE perovskite}|\text{NASICON}||\text{Au}-\text{Pd}||\text{Pt},\ O_2(+) \quad (3)$$

$$(-)O_2,NO_x||\text{RE perovskite oxide}|\text{NASICON}||\text{Au}-\text{Pd}||\text{Pt},\ O_2(+) \quad (4)$$

2.3. Characterization

The microstructure of the materials tested was evaluated using scanning electron microscopy (SEM). Windowless energy-dispersive spectroscopy (EDS) was used to evaluate the chemical composition of the Au–Pd layer before and after the performance of sensing tests.

NO_x sensing experiments were carried out at controlled temperatures in the 300–600°C range in a conventional flow apparatus equipped with a heating facility. The sensor response, expressed as electromotive force (EMF), was measured with a digital multimeter at a total flow rate of 100 ml/min and at different NO_2 concentrations (in the range 2–2000 ppm) obtained by mixing NO_2 in air with dry synthetic air. Some measurements were performed at various NO concentrations diluted with Argon, in the 2–1000 ppm range.

3. Results and discussion

3.1. Materials analysis

Fig. 2 shows a SEM micrograph of the $SmFeO_3$ powder prepared by the thermal decomposition of the hexacyanoferrite complex at 700°C for 1 h. SEM observations showed that the morphology of $SmFeO_3$ powders consisted of large agglomerates (in the size range of micrometers) made of nano-sized particles of about 50–80 nm.[21] Some non-agglomerated nanometric particles are also visible in the micrograph. Similar morphologies were observed for the other ferrite oxides. In the case of $LaCoO_3$, the presence of the micron-sized agglomerates was not observed and the formation of nanometric particles occurred already at 700°C.[57]

SEM observations with EDS analysis were performed on the sputtered Au/Pd coating on as-sputtered samples and after exposure to NO_2 gas. After gas testing, the sample surface became darker. SEM observations showed that the Au/Pd coating became more continuous after gas exposure. Fig. 3 shows the EDS spectra for the as-sputtered sample (Fig. 3a) and for the sample after gas exposure (Fig. 3b). The significant difference between the EDS plots is the presence of the oxygen peak on the sample after gas exposure. This can be interpreted as a partial oxidation of the metallic coating.

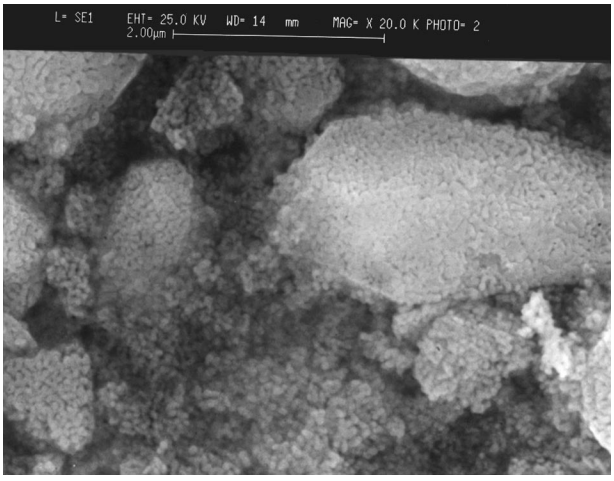

Fig. 2. SEM micrograph of $SmFeO_3$ powder fired at 700°C.

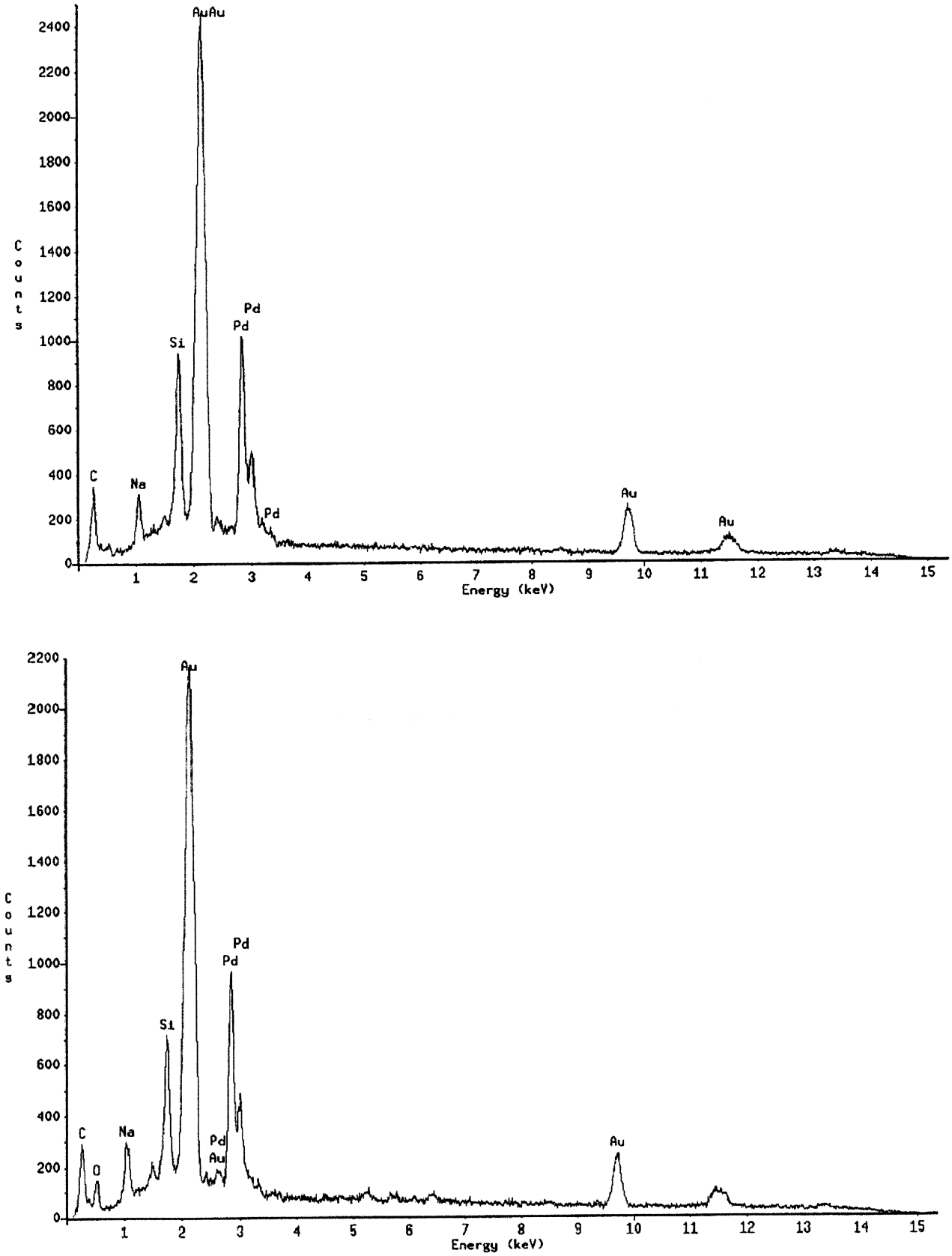

Fig. 3. EDS spectra for (a) the as-sputtered sample and (b) for the sample after gas exposure.

3.2. Electrical analysis of the prototype sensors

Fig. 4 shows the EMF response to various concentrations of NO_2 for the electrochemical cell (1), i.e. the comparison sensor, measured at 400°C. This prototype sensor was sensitive to NO_2 and its response time, which is the time to get the 90% of the stable EMF value in presence of NO_2, was within few minutes. However, the response at each gas concentration tested was not stable. Moreover, the EMF base-line in air decreased significantly during the tests.

Gas sensing measurements were performed on the electrochemical cells (2), (3), and (4), where sodalite, or catalyst, or both sodalite and catalyst were substituted with a rare-earth perovskite-type oxide. The results obtained using $SmFeO_3$ as perovskitic oxide are shown here below. The results obtained using the other rare-earth orthoferrites ($LaFeO_3$ and $NdFeO_3$) were similar to the results obtained with $SmFeO_3$, while the EMF gas response for the sensors using $LaCoO_3$ was worst. The EMF measured at each NO_2 concentration for all the sensors based on the orthoferrites was larger than the corresponding EMF measured for the cell (1). The response time of the sensors was in most of the cases about one minute for all the samples tested. The response time decreased with increasing the NO_2 concentration. The recovery time in air was in the range of 4–10 min, and it was the slowest for the type (3) cells, and the fastest for the type (4) cells that used only rare-earth ferrites.

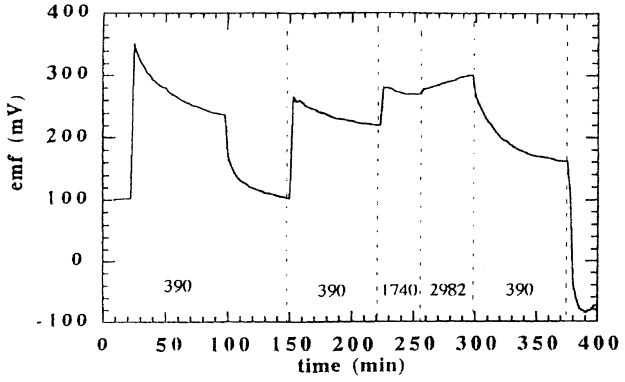

Fig. 4. EMF response to various NO_2 concentrations (ppm in air) for the electrochemical cell (1), i.e. the comparison sensor using sodalite and Pt-loaded alumina catalyst, measured at 400°C.

Fig. 5 shows the EMF response to various concentrations of NO_2 for the electrochemical cell (2), where $SmFeO_3$ was used as a catalyst together with the sodalite auxiliary phase, measured at 400°C. The NO_2 response was fast but the stability of the results was not satisfactory. Moreover, the base-line in air increased by more than 100 mV during the test period.

Fig. 6 shows the EMF response to various concentrations of NO_2 for the electrochemical cell (3), where $SmFeO_3$ was used as auxiliary phase together with the Pt-loaded alumina catalyst, measured at 400°C. Also this sensor was quickly responding to NO_2, though its response was the slowest, but its performance was the less adequate, even though its EMF values were the largest measured. In fact, the EMF values were scattered as a function of the NO_2 concentration.

Fig. 7 shows the EMF response to various concentrations of NO_2 for the electrochemical cell (4), where only $SmFeO_3$ was used inside the NASICON thimble, measured at 400°C. This sensor showed the best overall performance, because the sensor answer was the most stable. The EMF base-line values in air increased by about 40 mV during the tests.

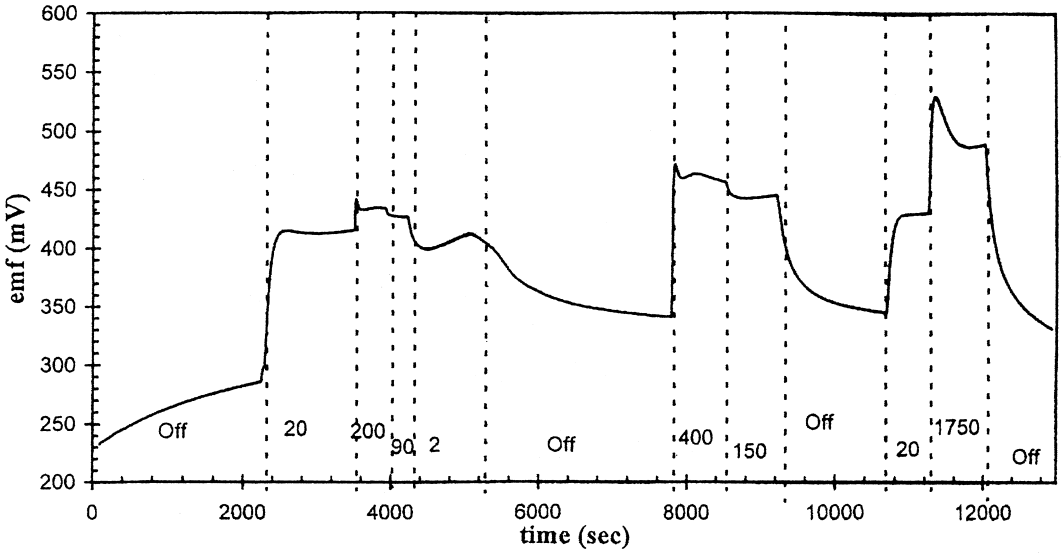

Fig. 5. EMF response to various NO_2 concentrations (ppm in air) for the electrochemical cell (2), where $SmFeO_3$ was used as a catalyst together with the sodalite auxiliary phase, measured at 400°C.

These findings showed that the perovskite-type oxides can be used as auxiliary phase in the NO_2 electrochemical sensors. The NO_2 response of the devices based on interfacing the ionic conductor with a semiconducting oxide is larger than the gas response of the electrochemical cell based on sodalite as an auxiliary phase. It is possible to say that the perovskite materials might be effective also if used as in-situ catalyst for NO oxidation.

Fig. 8 shows that the EMF responses of $SmFeO_3$-based sensors were linear when plotted against the logarithm of NO_2 concentration ($\log P_{NO_2}$), with positive slopes. The NO_2 sensitivity was the largest for the type (3), using $SmFeO_3$ and Pt-alumina catalyst, though the data were largely scattered. The NO_2 sensitivity for the type (2), using $SmFeO_3$ and sodalite, and (4), using only $SmFeO_3$, was almost the same. Therefore, one can infer that while $SmFeO_3$ has a lower catalytic effect on NO oxidation than the Pt-loaded alumina catalyst, it has a similar effect as sodalite when used as auxiliary phase. Therefore, the perovskite-type oxides are more preferable than sodalite because they improve the stability of the electrochemical sensor performances.

From these plots, using the Nernst equation, the number of electrons involved in the electrochemical reactions were evaluated to be between 1.3 and 1.5. These findings allowed us to infer that the sensing mechanism for these devices was non-Nernstian, and probably mixed potential behaviour should be postulated as their sensing mechanism.[32] Moreover, it should be kept in mind that both electrodes of the sensors were exposed to the same atmosphere.

The influence of the temperature on the EMF response to different NO_2 concentrations was also evaluated. Fig. 9 shows the dependence of EMF responses of type (4), $SmFeO_3$-based sensor on the

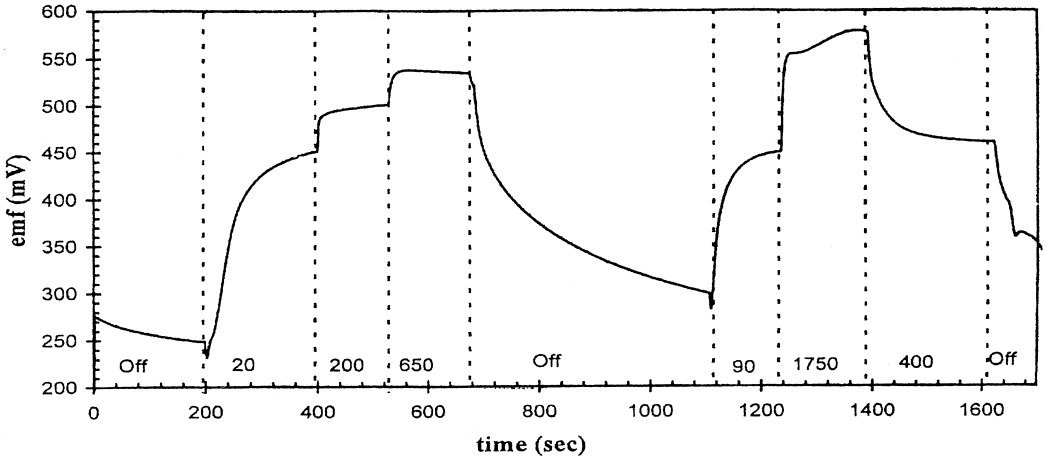

Fig. 6. EMF response to various NO_2 concentrations (ppm in air) for the electrochemical cell (3), where $SmFeO_3$ was used as auxiliary phase together with the Pt-loaded alumina catalyst, measured at 400°C.

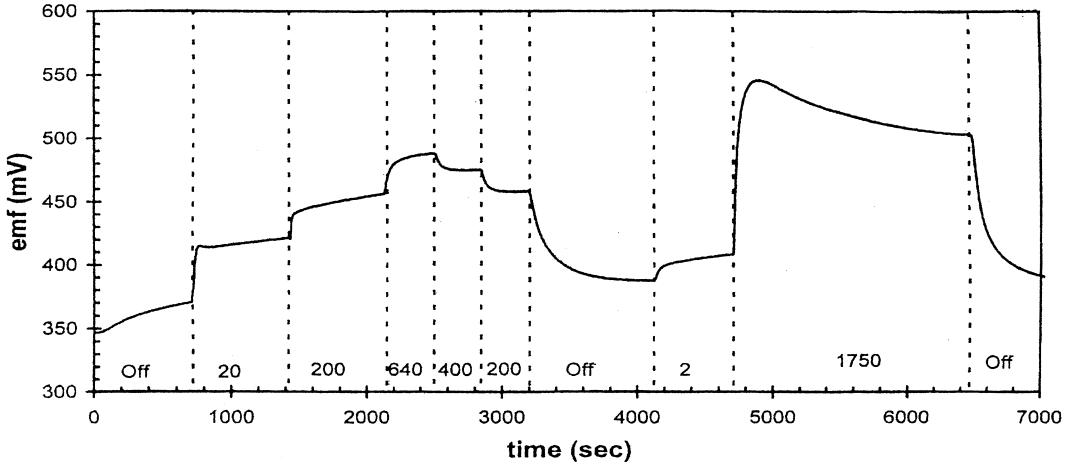

Fig. 7. EMF response to various NO_2 concentrations (ppm in air) for the electrochemical cell (4), where only $SmFeO_3$ was used inside the NASICON thimble, measured at 400°C.

logarithm of NO_2 concentration ($\log P_{NO_2}$), measured at different temperatures between 200 and 500°C. The EMF responses of these $SmFeO_3$-based sensors were linear, with a positive slope, to the logarithm of NO_2 concentrations at all the temperatures tested, and the EMF values increased with increasing the temperature.The NO_2 sensitivity was the largest at 400°C, while at 200 and 500°C the slope was almost flat.

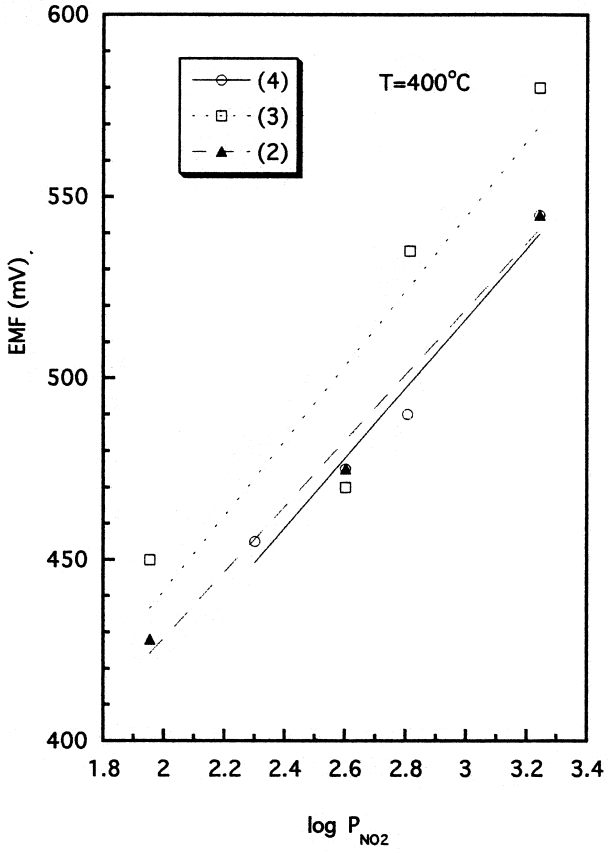

Fig. 8. Dependence of the EMF response for type (2), (3) and (4) $SmFeO_3$-based sensors on the logarithm of NO_2 concentration ($\log P_{NO_2}$, ppm in air), measured at 400°C.

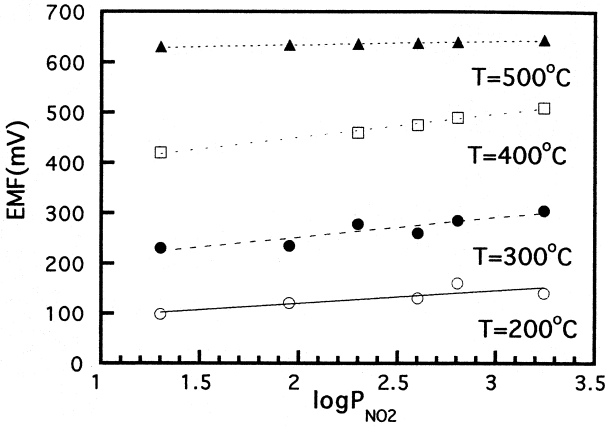

Fig. 9. Dependence of the EMF response for type (4) $SmFeO_3$-based sensors on the logarithm of NO_2 concentration ($\log P_{NO_2}$, ppm in air), measured at different temperatures.

EMF measurements were also performed at various NO concentrations at 400°C. The EMF values at each NO concentration for all the tested sensors were smaller than the corresponding EMF measured at the same NO_2 concentration and the response time was longer. EMF responses decreased with increasing NO concentration, being linear to $\log P_{NO}$ with negative slopes. These results are in agreement with the findings of other authors who used similar electrochemical systems.[33,46,48] In fact, the EMF in the presence of NO gas went always in the opposite direction with respect to the EMF in NO_2.

4. Conclusions

Solid-state ceramic sensors based on NASICON with rare-earth perovskite-type *ortho*ferrites as an auxiliary phase are promising candidates for the detection of NO_2. Their response time was fast and the EMF values increased when the ferrites were used as auxiliary phase. Moreover, the use of an oxide as auxiliary phase improves the stability of the gas sensing performance of the electrochemical cells, which is extremely important for automotive applications. Further studies are necessary to clarify of the sensing mechanism.

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