Characterization of a NASICON based potentiometric CO_2 sensor

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Abstract

Open CO_2 sensors work in a differential mode and the response must only depend on the CO_2 pressure. To obtain a more stable response, the O_2 reference electrode consists of a material which can exchange oxygen with gas and sodium ions (Na^+) with the NASICON membrane. Such an electrode is composed of a mixture of sodium titanates $Na_2Ti_3O_7$–$Na_2Ti_6O_{13}$ and $La_{1-x}Sr_xMnO_3$ (LSM). This latter compound is added to improve the oxygen electrode reaction. The sensing electrode is composed of gold and a mixture of sodium and barium carbonates (Na_2CO_3 and $BaCO_3$). Different compositions of the two electrodes are investigated in a large range of CO_2 pressure. Sensors with a weight composition of carbonates about 3:1 in sodium and barium for the sensing electrode show a nernstian response in the 385–668 °C temperature range. In this range, the experimental slopes are about 90% of the theoretical value. Below 385 °C, a logarithmic function of the CO_2 pressure is still observed but deviations from the Nernst behaviour occur. A thermodynamic approach based on the standard potential E° point of view reveals a good agreement between theory and experiments.
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1. Introduction

With the increasing gas pollution in the atmosphere (SO_x, NO_x, CO and CO_2), a monitoring and controling system is becoming more and more important. In this field, many studies were investigated on solid state potentiometric sensors. In the case of CO_2 pollution, the first device based on K_2CO_3 electrolyte and carbonates as sensing electrode was proposed by Gauthier et al.[1] Several types of CO_2 sensors used carbonate phase with solid electrolyte like β-alumina or NASICON.[2–5] In the literature, it was proposed to replace Na_2CO_3 by a carbonate systems such as Na_2CO_3–$MeCO_3$,[6–9] Li_2CO_3 or Li_2CO_3–$MeCO_3$[10] (Me = Ba, Ca, Sr...). These changes improved the stability and the resistance of water effect on the sensor. NASICON electrolyte have been chosen for its high Na^+ conductivity allowing fast Na^+ exchange at the interfaces.

A sensor needs a constant reference electrode, so many devices were tested in chemical cell with two different gas compositions at the reference (air) and sensing (air + CO_2) electrodes. Holzinger et al.[5] proposed a mixture of materials for the reference electrode: $Na_2Ti_3O_7$–$Na_2Ti_6O_{13}$ or $Na_2Ti_6O_{13}$–TiO_2 which were sensitive to O_2. These materials allowed the fabrication of "open sensors" without separation gas between the reference and the sensing electrodes. Many investigations were performed to improve the sensor stability, for example Pasierb et al.[11] have studied the effect of the composition of such materials and Ramirez et al.[12] added $La_{1-x}Sr_xMnO_3$ (LSM) for its well known catalytic properties towards the oxygen reaction. However, the mechanism between the different interfaces is not very well understood: Kida et al. observed an interfacial corrosion layer (Li_2ZrO_3) between NASICON and the lithium carbonate layer.[13]

In this paper, sensors based on NASICON are studied in large ranges of temperature and CO_2 pressure. The influence of the electrode composition was approached on the $Na_2Ti_3O_7$–$Na_2Ti_6O_{13}$|NASICON| Na_2CO_3–$BaCO_3$ electrochemical cell.

2. Experimental

The NASICON ($Na_3Zr_2Si_2PO_{12}$) was prepared by sol–gel method as described elsewhere.[14] The powder obtained was heat-treated at 750 °C to eliminate the solvent. Pellet with

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1 cm diameter was pressed uniaxially at 100 MPa and isostatically at 300 MPa and then sintered at 1000 °C for 2 h. A X-ray diffraction pattern confirmed the NASICON phase.

$Na_2Ti_3O_7$–$Na_2Ti_6O_{13}$ was also prepared by sol–gel reaction as described by Ramirez et al.[12] This preparation led to a powder of sodium titanates with different mass compositions. This powder was sintered at 800 °C for 4 h and the structures were confirmed by X-ray diffraction pattern.

The mixture of carbonates Na_2CO_3–$BaCO_3$ was prepared by mixing the two powders in the good proportion, heating above the melting point, cooling down and milling.

Different deposition methods for the electrodes were investigated:

1. Painting: an ink was realized by mixing the sodium titanates and LSM (1:1 in mass), terpineol, polyvinylpyrrolidon (PVP) and polyvinylbutanal (PVB) for the reference electrode. The same preparation was made for the sensing materials with a mixture of sodium and barium carbonates and gold paint (1:1 in mass). Firstly, the reference electrode ink was deposited on one side of the NASICON pellet and sintered at 800 °C during 2 h. Secondly, the sensing electrode ink was pasted on the other side and fired at 750 °C during 1 h.
2. Melting: the powder of carbonates was deposited on one side of the pellet upon a gold grid by the melting and quenching method. The reference electrode was formed with the painting method described in (1).
3. Screen-printing (realised at "Ecole des Mines de Saint-Etienne" with M. Pijolat and M. Viricelle): in this case, both electrodes were deposited by screen-printing method in the same mass ratios than in (1). The reference was sintered at 800 °C and on the other side of the pellet, the sensing electrode was sintered at 750 °C. Then, a gold grid was screen-printed on the carbonate layer and fired at 750 °C.

All screen-printed sensors were tested in a large range of CO_2 pressure (25–150,000 ppm) and for different temperatures. The other sensors were only tested in a 250–2400 ppm range of CO_2 pressure. It is important to note that all sensors were exposed to a constant partial oxygen pressure (20%) by fixing a constant flow rate of the different gas. The CO_2 partial pressures were obtained by using flow controllers to dilute CO_2 in Ar and to keep a constant gas flow ($d = 5$ L/h).

Voltage (EMF) was measured by a multimeter HP 34401A® and all data were exported to a computer.

3. Results and discussion

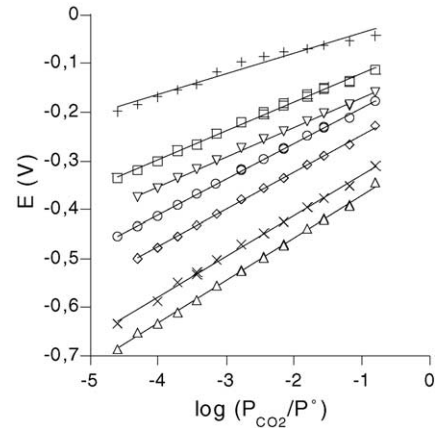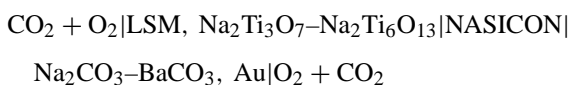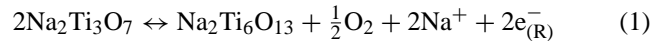The CO_2 sensors investigated in this work are defined by the following electrochemical cell:

$$CO_2 + O_2 | LSM, \ Na_2Ti_3O_7–Na_2Ti_6O_{13} | NASICON |$$

$$Na_2CO_3–BaCO_3, \ Au | O_2 + CO_2$$

Fig. 1. EMF measurements as a function of log $P(CO_2)$ at different temperatures: 280 °C (+), 385 °C (□), 436 °C (▽), 485 °C (○), 532 °C (◇), 579 °C (×) and 668 °C (△).
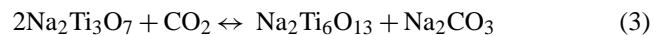
The reference electrode reaction (R) is:

$$2Na_2Ti_3O_7 \leftrightarrow Na_2Ti_6O_{13} + \tfrac{1}{2}O_2 + 2Na^+ + 2e^-_{(R)} \qquad (1)$$

At the sensing electrode (S), with a binary carbonate, only the Na^+ exchange is usually considered [7,9] and the reaction is:

$$2Na^+ + 2e^-_{(S)} + \tfrac{1}{2}O_2 + CO_2 \leftrightarrow Na_2CO_3 \qquad (2)$$
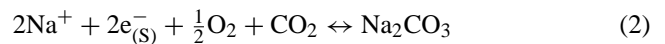
Finally, the overall reaction is:

$$2Na_2Ti_3O_7 + CO_2 \leftrightarrow Na_2Ti_6O_{13} + Na_2CO_3 \qquad (3)$$

The EMF (ΔE) of the cell is described by the Nernst equation:

$$\Delta E = \phi_S - \phi_R = E^\circ + \frac{RT}{2F} \ln \left(\frac{P_{CO_2}}{P^\circ} \right) \qquad (4)$$

The standard potential E° is related to Eq. (3) if the activities of components are supposed equal to one.

$$E^\circ = \frac{-\Delta_r G^\circ}{2F} = \frac{1}{2F}(2\mu^\circ(Na_2Ti_3O_7) + \mu^\circ(CO_2)$$
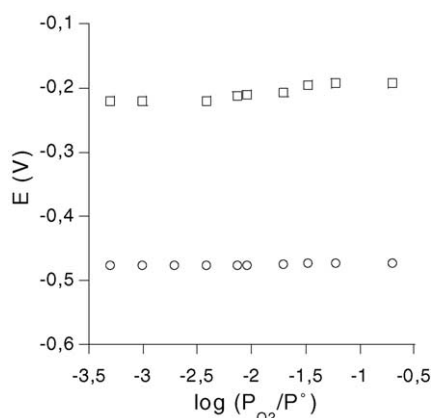$$- \mu^\circ(Na_2Ti_6O_{13}) - \mu^\circ(Na_2CO_3)) \qquad (5)$$

The tests with painted and melted electrodes in the ranges 380–700 °C and 250–2400 ppm of CO_2 gave responses close to the theoretical slope, unfortunately short life times were observed (about 10 days). Moreover, the melting method did not lead to good reproducibility on elaboration of several sensors.

Best results were obtained with the screen-printed method. This could be due to a good control of the electrode thickness. Several compositions of reference and sensing electrodes were tested. We have observed generally long life times. In the present paper, only the best results were presented which were obtained with the composition 55:45 in mass for the sodium titanates and 3:1 for the carbonates. The measurements of EMF versus log (P_{CO_2}/P°) are plotted in Fig. 1. This figure shows straight lines with slopes in good agreement with the Nernst equation for the temperature above 485 °C. Below

Table 1
Values of the theoretical and experimental slopes, the electron number and the standard potential $E°$ for different temperatures

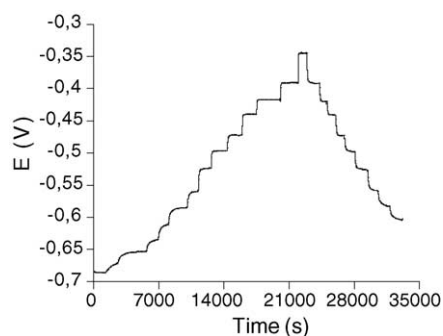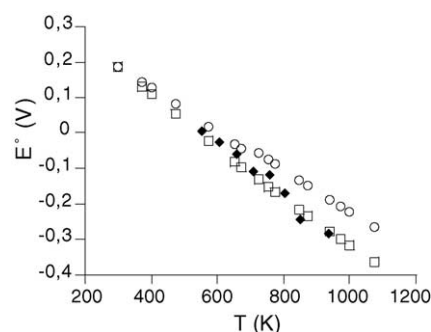| Temperature (°C)	Theoretical slope (mV/dec)	Exp. slope (mV/dec)	Electron number (*n*)	$E°$ (mV)
280	54.86	42.3 ± 2.3	2.59 ± 0.14	5 ± 7
385	65.29	58.6 ± 1.0	2.23 ± 0.04	−61 ± 3
436	70.35	61.2 ± 0.7	2.30 ± 0.03	−108 ± 2
485	75.21	72.7 ± 0.5	2.07 ± 0.01	−119 ± 1
532	79.88	76.3 ± 0.6	2.09 ± 0.02	−170 ± 2
579	84.54	83.6 ± 1.2	2.02 ± 0.03	−244 ± 3
668	93.37	87.1 ± 0.7	2.14 ± 0.02	−283 ± 2

Fig. 2. EMF dependence of log P(O_2) at: 385 °C (□) and 668 °C (○).

Fig. 4. Standard potential of sensor as a function of temperature: data form Fact-web[18] (□), data from Kubaschewski[16] and Pelton[17] (○) and experimental values (♦).

this temperature, slope is deviating from the theoretical one, curves are always straight lines but sub-nernstian slopes appear. Experimental values (slopes, $E°$ and *n*) are reported in the Table 1.

Fig. 2 illustrates the influence of oxygen pressure at a constant CO_2 pressure for two temperatures (385 °C and 668 °C). According to the electrochemical reaction cell (Eq. (4)), no significant effect of O_2 pressure must be observed on the EMF. Our results are in good agreement for the highest temperature and in all the tested range of O_2 pressure. Only a shift of 30 mV of EMF is observed at low temperature, like Holzinger et al.[15] showed in their work using β-alumina and pure Na_2CO_3. Such shifts could be due to different kinetics of O_2 reaction at both electrodes.

Fig. 3 shows the transient response of this sensor. In this case, a good reproducibility of the EMF is observed for

the CO_2 pressure cycle. The response time is about a few minutes.

The standard potential $E°$ calculated from Eq. (4) are plotted in Fig. 4 as a function of the temperature. Theoretical values were calculated from differents thermodynamical databases[16–18] according to Eq. (5) and are plotted in Fig. 4. As can be seen, the $E°$ values of this sensor are close to the thermodynamical values, more especially those extracted from Fact-web database.[18] A slight discrepancy between $E°$ calculated from the databases is due to the uncertainties on the formation free enthalpies for each component which are relatively high compared to the final values.

In comparison with the sub-nernstian previous results on similar devices,[19] the present deposition method seems to improve significantly the response of open sensors using a binary carbonate system (Na_2CO_3–$BaCO_3$). In our case, the slope is nernstian and the $E°$ values correspond to the thermodynamical ones.

Fig. 3. Transient response for CO_2 partial pressure at $T = 668$ °C.

4. Conclusions

In this work, several deposition methods were investigated. All sensors were linear versus the logarithm of CO_2 pressure and in good agreement with the theory. The screen-printing process improved the control of the deposition and the life time of sensors. The sensors were tested in a range 385–668 °C and in a large range of CO_2 pressure. At high temperature, no significant effect of the O_2 pressure was observed, according to the theory. For the composition of sodium titanates 55:45 in mass, the standard po-

tential E° is in good agreement with the thermodynamical values.

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