Characterization of a NASICON based potentiometric CO_2 sensor

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Abstract

In open devices, 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.

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 way, 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 carbonates phase with solid electrolyte like β-alumina or NASICON [2-5]. In the literature, it was proposed to replace the carbonate phase Na_2CO_3 by a binary carbonate system such as Na_2CO_3-$MeCO_3$ [6-8], Li_2CO_3 or Li_2CO_3-$MeCO_3$ [9-10] (Me = Ba, Ca, Sr…). This change ameliorated the stability and the resistance of water effect on the sensor.

Sensors based on NASICON electrolyte have been well studied in these last years. Indeed, an advantage of NASICON is its high conductivity at low temperature.

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. In this way, Holzinger *et al.* [5] proposed a mix of materials $Na_2Ti_3O_7$-$Na_2Ti_6O_{13}$ or $Na_2Ti_6O_{13}$-TiO_2. These materials have allowed the fabrication of "open sensors" with no separation gas between the reference and the sensing electrodes. With the same materials, many investigations were performed to improve the sensor stability. Pasierb *et al.* [11] have studied the effect of the composition and Ramirez *et al.* [12] have chosen $La_{1-x}Sr_xMnO_3$ (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.* have shown an interfacial layer between NASICON and the carbonate layer [13].

In this paper, sensors based on NASICON are studied in a large range of temperature and carbon dioxide pressure. The influence of composition of the electrode material was approached on the $Na_2Ti_3O_7$-$Na_2Ti_6O_{13}$|NASICON| Na_2CO_3-$BaCO_3$ electrochemical cell.

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 1 cm in diameter was pressed uniaxially at 100 MPa and isostastically at 300 MPa and sintered at 1000°C during 2 hours. A X-ray diffraction pattern confirmed the NASICON phase.

The reference electrode material $Na_2Ti_3O_7$-$Na_2Ti_6O_{13}$ was also prepared by sol-gel reaction as described by Ramirez *et al.* [12]. This preparation gave a mix of the two sodium titanates with different mass compositions. This powder was sintered at 800°C during 4 hours to obtain the two well defined structures 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.

Sensors were fabricated on NASICON pellet by different methods:

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 mix 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 hours. Secondly, the sensing electrode ink was pasted on the other side and fired at 750°C during 1 hour.

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: in this case, both electrodes were deposited by screen-printing method in the same mass ratios than in 1. On the first side, the reference was sintered at

800°C. On the other side, 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 carbon dioxide pressure (25 ppm to 150000 ppm) and for different temperatures. Instead of this, 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 five flow controllers: two controllers were used to dilute CO_2 in Ar and the three others to keep a constant gas flow (d = 5 L/h).
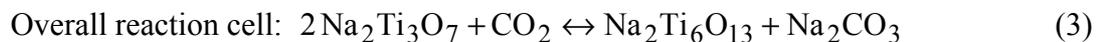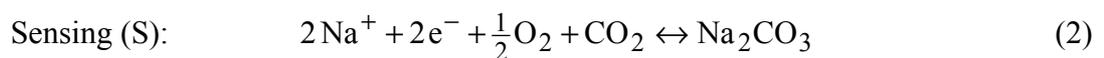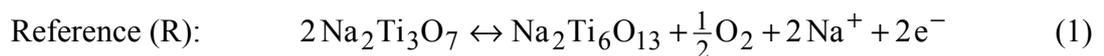
Voltage (EMF) was measured by a multimeter HP 34401A$^\circledR$ and all data were exported to a computer.

Results and discussion

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

$$CO_2 + O_2 \,|\, LSM, Na_2Ti_3O_7 - Na_2Ti_6O_{13} \,|\, NASICON \,|\, Na_2CO_3 - BaCO_3, Au \,|\, O_2 + CO_2$$

The electrode reactions are expressed in equations (1), (2) and (3):

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

$$\text{Sensing (S):} \qquad 2\,Na^+ + 2\,e^- + \tfrac{1}{2}O_2 + CO_2 \leftrightarrow Na_2CO_3 \qquad (2)$$

$$\text{Overall reaction cell:} \quad 2\,Na_2Ti_3O_7 + CO_2 \leftrightarrow Na_2Ti_6O_{13} + Na_2CO_3 \qquad (3)$$

The EMF ΔE of the cell is described by the Nernst Equation:

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

Where the number of electrons involved in the sensing reaction is equal to the theoretical value (n = 2).

The standard potential E° is defined in eq. (5) by the electrochemical cell where the activity of components is supposed equal to one.

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

The tests of painted and melted sensors in the ranges 380-700°C and 250-2400 ppm of CO_2 gave responses close to the theoretical value (n = 2) but short life times were observed (about ten days). Moreover, the melting method did not lead to good reproducibility on elaboration of several sensors.

These problems were solved with the screen-printed sensors. Indeed, this deposit method ensured a good control of the layer thickness of the electrode. Several compositions of reference and sensing electrodes were tested. We have observed generally long life times. In the present paper, we present only the best results obtained with the composition 55:45 in mass for the sodium titanates and 3:1 for the carbonates. The measurements of EMF *vs.* log (P_{CO2}/P^o) 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 this temperature, n is deviating from the theoretical value. In these cases, curves are always straight lines but sub-nernstian slopes appear. In the table 1, the experimental slopes, values of standard potential E° and the electron number n are reported.

Figure 2 illustrates the influence of oxygen pressure at a constant CO_2 pressure for two temperatures (385°C and 668°C). The O_2 pressure had no significant effect on the EMF according to the electrochemical reaction cell (eq. 4). There is a good agreement for the highest temperature and in all the tested range of O_2 pressure. A shift of 30 mV of EMF was observed at low temperature as Holzinger *et al.* [15] showed in their work. Such shifts could be due to different kinetics of O_2 reaction at both electrodes.

Figure 3 shows the transient response of this sensor. Each step represents a change in the CO_2 pressure. In this case, a good reproducibility of the EMF is observed for the CO_2 pressure

cycle. The response time was about a few minutes essentially due to the high delay of the atmosphere change.

Figure 4 displays the standard potential E° value as a function of the temperature. On this graph, two theoretical curves obtained with the thermodynamic database [16-18] are presented. To plot this curve, the free reaction enthalpy was calculated for each component and reported in eq. 5 to obtain the overall reaction enthalpy. As can be seen, the E° values of this sensor are very close to the thermodynamic values calculated via Fact-web [18]. A slight discrepancy appears when E° is calculated with the different data taken in the literature. The uncertainties on the formation free enthalpies are relatively low (a few kJ), nevertheless they lead to an important uncertainty on the overall reaction enthalpy (10 to 50 kJ). This could be an explanation of the difference between the two theoretical curves.

A study is in progress to understand the difference observed between the thermodynamic databases.

Conclusion

In this work, the effect of deposition was investigated. As a result, all sensors were linear with the logarithm of CO_2 pressure and in good agreement with the theory. Screen-printing process has ameliorated the control of the deposit and led to sensors which could be tested in a range 385-668°C and in a large range of CO_2 pressure. In a first approach, the best composition of sodium titanates is 55:45 in mass and the standard potential E° is in good agreement with the thermodynamical value.

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Table

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

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

Figures captions

Figure 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 (Δ).

Figure 2: EMF dependence of log P(O_2) at: 385°C (⊠) and 668°C (▨).

Figure 3: Transient response for CO_2 partial pressure at T = 668°C.

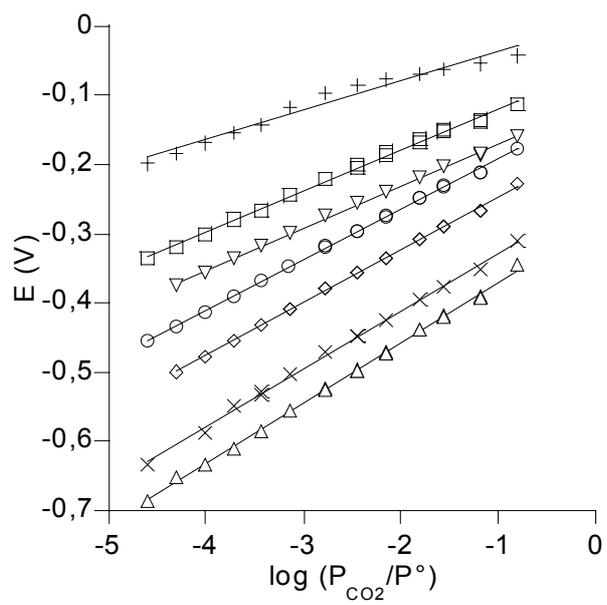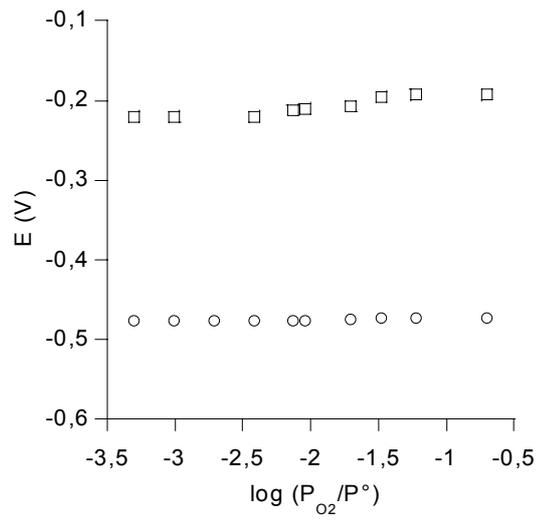Figure 4: Standard potential of sensor as a function of temperature: data form Fact-web [18] (⊠) data from Kubaschewski [16] and Pelton [17] (▨) and experimental values (▤).
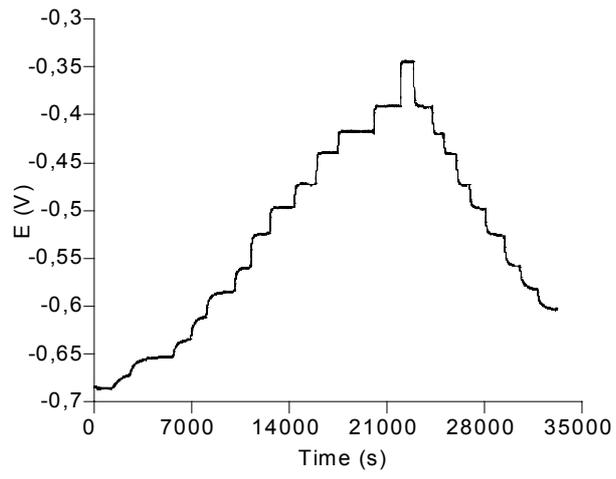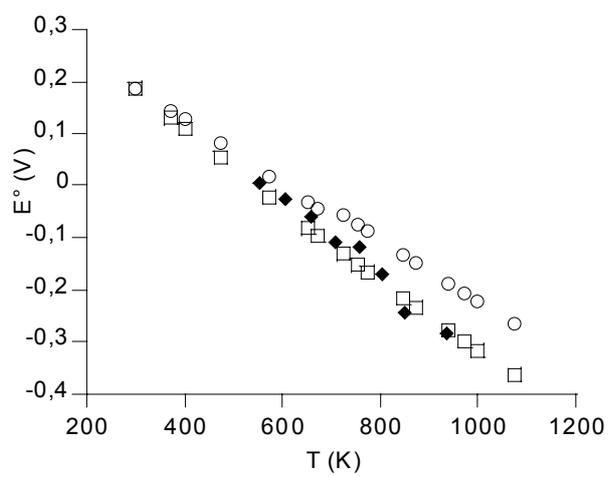
Figure 1

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Figure 4