NO$_2$ gas mixed-potential sensor based on positive temperature coefficient ceramics self-operated thermostatic controller

Zilong LIAN$^1$, Na ZHANG$^1$, Xiaohong ZHENG$^1$ and Cheng ZHANG$^{1,7}$

$^1$School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 201418, China

For a proper operation, conventional gas sensors based on solid electrolytes usually require complex heating elements and temperature control systems to ensure the transfer of ions inside a solid electrolyte substrate. In this study, a positive temperature coefficient (PTC) ceramic was used for the first time as a heating source to successfully compose a self-thermostatic potential NO$_2$ gas sensor. Powered by a 12-V multi-batteries, the PTC ceramic can be quickly heated to and stabilised at 250°C to provide the necessary working temperature to the sensor. It was proved that this self-thermostatic sensor displays a high NO$_2$ sensitivity (84.60 mV/decade) toward 5–150 ppm NO$_2$ at different ambient temperatures. Meanwhile, it exhibits a high NO$_2$ selectivity, along with excellent repeatability and stability. This simple and effective method is a solution to the significant obstruction of traditional gas sensors with burdensome heating structures, allowing a broad application to various types of on-site gas detection.

Key-words : NASICON, Self-thermostatic sensor, NO$_2$ potential sensor, Positive temperature coefficient ceramic

1. Introduction

The rapid development of industrial technology in recent decades has brought several environmental and health issues to the forefront, such as the emissions of poisonous and harmful gases. To expose these hazards, it is necessary to measure them in situ to optimise the combustion and exhaust gas aftertreatment processes. Nitrogen oxides are typical air-pollutants that cause acid rain and photochemical smog. Nitrogen oxides are emitted into the environment, mostly as NO gas from combustion furnaces and automobile engines, and will be gradually converted into NO$_2$, which is a more stable thermodynamic molecular structure at room temperature. In addition, NO$_2$ can easily cause serious consequences for human beings and natural environments, particularly when such dangerous gases are not monitored. Therefore, the development of NO$_2$ sensors has been the subject of intense research. Analytical instruments based on chemical luminescence and the Saltzman method are commonly used to detect NO$_2$, but they are either too expensive or too large. Even as the greatest disadvantage, they cannot be used in field tests. As a contrast, a solid-state electrolyte gas sensor has been acknowledged owing to its cost-effective performance and superior gas characteristics. Therefore, researchers have recently devoted themselves to the development of solid-state sensors that can detect in-situ NO$_2$ (or NO) in real-time.

Compared with solid electrolytes such as yttria stabilised zirconia and gadolinia-doped ceria, a sodium super ionic conductor (NASICON) has been recognised as the most promising electrolyte owing to its high conductivity at medium and low temperatures. Recently, many efforts have been devoted to developing NASICON-based gas sensors, which can detect various gases, such as CO$_2$, NH$_3$, SO$_2$, VOCs, and Cl$_2$. For example, Obata et al. discovered that a NASICON-based gas sensor using Na$_2$CO$_3$ as an auxiliary phase exhibits stable electromotive force (EMF) in a humid environment. Lu et al. reported that a NASICON-based gas sensor using Cr$_2$O$_3$ as a sensing-electrode material exhibits the highest sensitivity to Cl$_2$ gas in air at 300°C.

Positive temperature coefficient (PTC) ceramic is a typical temperature-sensitive semiconductor resistance. When the temperature exceeds a certain level (Curie temperature), its electrical resistance increases incrementally with an increase in temperature. PTC ceramic also has a fast heating speed and good surface thermal uniformity. In addition, it has a simple structure and can be customised in terms of shape and size. Moreover, the temperature of PTC ceramic can be easily determined by adjusting the resistance of the ceramic sheet or the supplied voltage. Owing to the maturity of the production level, PTC ceramic has been widely used in many fields. Common household appliances such as hair dryers, hair straighteners, and room heaters are typical applications of PTC materials.

As described above, different NASICON-based sensors for detecting various gases have been investigated. To the best of author’s knowledge, owing to the ordinary electro-
chemical properties at room temperature, most NASICON-based sensors require a certain high temperature to work properly. Therefore, it is often necessary to equip complex heating and temperature control devices to achieve a stable temperature for the substrate. This therefore severely limits the application range of a sensor, such as in field detection.\textsuperscript{6,11-19} To date, few researchers have devoted themselves to developing simple and efficient heating methods based on NASICON gas sensors. Therefore, in this study, we took a NASICON-based potential sensor as an example to prove the reliability of the PTC ceramic sheet. PTC ceramic was first used in gas sensors and as the heating source to provide the necessary working temperature for ion transport in the electrolyte. This is a new heating method for a sensor operation, and vastly simplifies the structure of the sensor. At different ambient temperatures, the temperature of PTC ceramic is stable, and the response signal of the sensor is less affected by the ambient temperature.

2. Experimental

2.1 Materials synthesis and fabrication of sensors

All reagents applied in this experiment were of analytical-grade purity (Shanghai Macklin Biochemical Co. Ltd.) and used as-received without any further purification. NASICON was prepared using a high-temperature solid state method with Na\textsubscript{2}CO\textsubscript{3}, SiO\textsubscript{2}, ZrO\textsubscript{2}, and (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4} powders.\textsuperscript{20} A schematic of the NASICON-based sensor is displayed in Fig. 1. The sensor was fabricated by screen-printing Pt pasted onto one side of the plate to form a sensing electrode (SE) and a reference electrode (RE). The platinum wire was bonded to the two electrodes with the same platinum paste, and then heated for 2 h at 800°C. Next, the PTC (Forrester Heat Flow Systems Manufacturing Co., Ltd.) ceramic sheets were bonded to the other side of the substrate using an inorganic binder (HR-8767, Huirui Electronic Co., Ltd.), and the PTC ceramic was connected with a 12 V multi-layer battery through wires.

The P25 [TiO\textsubscript{2}, 20\% rutile phase, 80\% anatase phase, Evonik Degussa (China) Co., Ltd.] layer was screen-printed on the SE, followed by calcinating at 600°C for 2 h.

2.2 Characterization method and gas sensing measurement

The crystal and phase identifications of the products were achieved using X-ray diffraction (XRD Rigaku Miniflex 600, Japan) with a monochromatized source of Cu Kα radiation (\(\lambda = 0.15405 \text{ nm}\)) at 1.6 kW (40 kV, 40 mA) with a step of 0.02°/s. After polishing, the morphology and microstructure were observed by scanning electron microscopy (SEM Hitachi S-4100, Japan). Test gas mixtures containing different concentrations of NO\textsubscript{2} were prepared by diluting the NO\textsubscript{2} (500 ppm in N\textsubscript{2}) with O\textsubscript{2} (21\%) and N\textsubscript{2} (79\%). The total flow rate was fixed at 100 cm\textsuperscript{3}/min, which was controlled using computer-controlled gas mass flow controllers. The voltage between the two electrodes was measured using a digital multimeter (34972 A multimeter, Agilent, USA) and the results obtained were registered with a computer connected to an electrometer. When the sensitivity of the sensor was defined as the slope of the working curve, a linear relationship was demonstrated between \(\Delta V\) and the logarithm of the NO\textsubscript{2} concentration.

3. Results and discussion

Figure 1 shows a structural diagram of the self-thermostatic potential NO\textsubscript{2} sensor. When the sensor is in an NO\textsubscript{2} atmosphere, the electrochemical reactions (1) and (2) described below take place at the same time and consequently form a local cell at the SE. The NO\textsubscript{2} concentration directly determines the speed of reaction (1). When the reaction rates are equal to each other, the SE potential is acquired. The difference in values between the SE potential and the RE potential is regarded as the response signal. The catalytic layer of P25 promotes the reduction of NO\textsubscript{2} to NO\textsubscript{2}–, and improves the sensitivity of the sensors.\textsuperscript{6}
NO₂ + O₂, TiO₂, Pt[NASICON]Pt, NO₂ + O₂
SE: NO₂ + Na⁺ + e⁻ → NaNO₂
(1)
RE: Na₂O (in NASICON) → 2Na⁺ + 2e⁻ + \frac{1}{2} O₂
(2)

**Figure 2** shows the XRD pattern of the prepared material. The NASICON phase \((Na_3Zr_2Si_2PO_12)\) was successfully prepared according to the peak intensity and peak position characteristics shown in Fig. 2, and matched with the JCPDS PDF No. 35-0412. Trace amounts of a monoclinic ZrO₂ phase are caused by a volatilisation of the P element at high temperature. This is inevitable in the preparation process of the high-temperature solid phase method.

According to the SEM image in **Fig. 3(a)**, a dense ceramic disk was attained and grain growth occurred in certain regions. The same result is shown in **Fig. 3(b)**, and the grain microstructure demonstrates a three-dimensional morphology with a size of approximately 2 μm.

**Figure 4** shows the infrared images of PTC at different ambient temperatures. It can be seen from the figure that the PTC sheet heats up rapidly and stabilises at 250°C, independent of the environmental temperature. At the beginning of the heating stage, the temperature of NASICON chip is slightly lower. However, as the temperature continues to increase, the temperature of NASICON remains consistent with that of the PTC sheet. Moreover, the surface temperature of PTC is uniform, and thus has the potential to provide a fixed working temperature for the sensor.

Due to the resistance of the NASICON disk is significantly affected by the operation temperature, hence, the relationship between resistance and temperature of
NASICON disk has been studied [Fig. 5(a)]. During the whole temperature changing period, the NASICON disk resistance decreases rapidly from 25 to 100°C [Fig. 5(a)], while the resistance drops tardily from 100 to 250°C [inset of Fig. 5(a)]. At 250°C, the substrate resistance is 0.115 kΩ, and the conductivity is \(8.7 \times 10^{-2}\) S/cm. The working curve at different operating temperatures for a NO\(_2\) concentration range of 5–150 ppm was measured, as shown in Fig. 5(b). The response value (\(\Delta V\)) of the sensor is linearly changed with the logarithm of the NO\(_2\) concentrations. The gas response values of the sensor are relatively low at both the lower and higher operating temperatures. The reasons for this phenomenon are as follows: When the temperature is below 250°C, although there are sufficient NO\(_2\) molecules adsorbed on the surface of a sensitive electrode, the activation energy can only partially satisfy the reaction.\(^2\) With the increase in temperature, more and more gas molecules are involved in the reaction, and thus the response signal continuously increases.

However, when the temperature exceeds 250°C, although there is sufficient activation energy for the gas to participate in the reaction, the desorption rate of the gas exceeds the adsorption rate and the high desorption ability leads to the gas quantity taking part in the reaction being less than the amount at 250°C.\(^2\) The higher the temperature, the greater the decrease in the gas response. Therefore, 250°C is thought as the optimal operation temperature and PTC ceramic plate with 250°C heating temperature is used to fabricate the sensor for further sensing property measurement.

At different ambient temperatures (50, 25, and –30°C), the self-thermostatic potential sensor response and recovery transient for different concentrations (5–150 ppm) of NO\(_2\) was measured, and the results are shown in Fig. 5(c). The gas response value increases with the NO\(_2\) gas concentration. In addition, the response value of the sensor toward 150 ppm NO\(_2\) is as large as 180.9 mV. At different ambient temperatures, the three response and recovery

![Fig. 5.](image-url)
transient curves are basically the same. This indicates that the self-stability of the self-thermostatic potential sensor is excellent, which is also demonstrated in Fig. 5(d). In other words, the performance of the sensor does not change under different ambient temperatures, and regardless of the season, the sensor can obtain the same potential signal.

Because the stability and reproducibility are important parameters that may affect the actual application of the sensor, the repeatability for both the short and long term were investigated, as shown in Figs. 6(a) and 6(b). Figure 6(a) shows the repeatable response-recovery transient of the present sensor toward 80 ppm of NO$_2$. In the six continuous test cycles, the response curves change only slightly. In Fig. 6(b), the sensitivity ranges from 83.11 mV/decade to 84.60 mV/decade for three working curves measured after 1, 7 and 14 days, with an error of $\leq$2%.

The response and recovery times of the sensor are significant parameters. The response time is defined as time for reaching the 90% of the maximum response potential change and the recovery time is defined as time attaining within 10% of the response potential change. As shown in Fig. 6(c), a gas response time of 37 s and a recovery time of 44 s were observed for 10 ppm NO$_2$. We compared the response and recovery times of sensors reported in the references,$^{11,18,23,24}$ as shown in Table 1. The comparison tells us that our work has obvious advantages over their results. In addition, the response time characteristic is sufficient indeed for NO$_2$ sensors.

In addition, the selectivity is also an important evaluation criterion of the sensor. Hence, as a contrast, we chose the response value of the present sensor toward three other interfering gases at 100 ppm. As observed from Fig. 6(d), the NO, NH$_3$ and CO$_2$ contents do make very little influence on the EMF of the sensor, and the response value of the sensor to NO$_2$ is much higher than those of any other interfering gases, including NO at 250°C. Thus, the sensor exhibits a rather high selectivity toward NO$_2$.

![Figure 6](image_url)

**Table 1. Comparison of response and recovery time**

| Response (sec) | Recovery (sec) | Reference |
|---------------|----------------|-----------|
| 57            | 65             | 11)       |
| 40            | 100            | 18)       |
| 200           | 520            | 23)       |
| 135           | 200            | 24)       |
| 37            | 44             | this work |

Fig. 6. (a) Repeatability of the sensor to 80 ppm NO$_2$. (b) Sensor repeatability for 14 days at 250°C. (c) The response and recovery rates at 10 ppm NO$_2$. (d) The cross-sensitivities of the self-thermostatic potential sensor toward various interfering gases at 250°C.
Table 2. Comparison of the heating methods of the present sensor and that of other devices reported in the literature

| Gas     | Heating method     | Volume of equipment | Temperature regulating device | Reference |
|---------|--------------------|---------------------|-------------------------------|-----------|
| NO₂     | tube furnace       | large               | needless                      | 6)        |
| Cl₂     | resistance wire    | little              | need                          | 16)       |
| NO₂     | tube furnace       | large               | needless                      | 17)       |
| NO      | resistance wire    | little              | need                          | 18)       |
| NO₂     | tube furnace       | large               | needless                      | 19)       |
| NO₂     | PTC ceramic        | little              | needless                      | this work |

Table 3. Our work contrasts with those in literatures

| Basis material | Preparation method | ∆V (mV) | Reference |
|----------------|--------------------|---------|-----------|
| NASICON        | sol-gel method     | 29 (5 ppm) | 17)       |
| NASICON        | solid state method | 6 (5 ppm)  | 20)       |
| NASICON        | sol-gel method     | 8 (5 ppm)  | 22)       |
| NASICON        | solid state method | 47.7 (5 ppm) | this work |

Furthermore, the heating methods of the existing sensors and reported devices are compared, as tabulated in Table 2. Most provide a temperature environment for the sensor through a tubular furnace. The others generate heat by feeding the resistance wire with electricity, which requires additional temperature measuring devices. However, we creatively used PTC ceramic sheets powered by 12-V multi-batteries as the heating source. The temperature control system, supplying electricity, is simple and can replace an ordinary complex heating and temperature control system, supplying efficient and reliable essential working conditions for the sensor. Gas sensing studies reveal that such sensors exhibit the best response at 250°C, and achieve a high NO₂ sensitivity (84.60 mV/decade) toward 5–150 ppm NO₂. Meanwhile, a response time of 37 s and a recovery time of 44 s toward 10 ppm NO₂ gas at 250°C were shown. In addition, the self-thermostatic potential NO₂ gas sensor also exhibits good repeatability and long-term stability for 14 days, with excellent selectivity to NO₂ in the presence of interference gases such as NO, CO₂, and NH₃. Benefitting from such a feasible heating mode, more portable gas sensors are expected to be fabricated for various gas sensing applications, as long as suitable PTC materials are selected to maintain the required temperatures for certain solid electrolytes.

Acknowledgements This work was financially supported by the “Foundation of Science and Technology Commission of Shanghai Municipality (No.18090503600)”.

References

1) N. Docquier and S. Candel, *Prog. Energ. Combust.*, 28, 107–150 (2002).
2) S. Marini, C. Strada, M. Villa, M. Berretttonic and T. Zerla, *Energ. Convers. Manage.*, 87, 1134–1140 (2014).
3) D. Popp, *J. Environ. Econ. Manag.*, 51, 46–71 (2006).
4) Y. Sun, L. Wang, Y. Wang, L. Quan and L. Zi, *Sci. Total Environ.*, 409, 933–940 (2011).
5) J. M. Godowitch, G. A. Pouliot and S. T. Rao, *Atmos. Environ.*, 44, 2894–2901 (2010).
6) J. Wu, C. Zhang and Q. Li, *Solid State Ionics*, 292, 32–37 (2016).
7) B. Xie, Y. Xu, J. Sun, D. Jiang and T. Feng, *Adv. Mat. Res.*, 1058, 140–144 (2014).
8) T. Zhong, W. Zhao, F. Jiang and X. Liang, *Sensor. Actuat. B-Chem.*, 202, 1103–1118 (2014).
9) F. Liu, Y. Guan, H. Sun, X. Xu, R. Sun and X. Liang, *Sensor. Actuat. B-Chem.*, 222, 698–706 (2016).
10) K. Mahendraprabhu and P. Elumalai, *Sensor. Actuat. B-Chem.*, 238, 105–110 (2017).
11) H. Dang and X. Guo, *Sensor. Actuat. B-Chem.*, 178, 163–168 (2013).
12) T. Hyodo, H. Inoue, H. Motomura, K. Matsuo, T. Hashishin, J. Tamaki, Y. Shimizu and M. Egashira, *Sensor. Actuat. B-Chem.*, 151, 265–273 (2010).
13) L. Wang, C. Gao, L. Dai and H. Zhou, *Ceram. Int.*, 44, 8983–8991 (2018).
14) X. Liang, T. Zhong, B. Quan, B. Wang and H. Guan, *Sensor. Actuat. B-Chem.*, 134, 25–30 (2008).
15) P. K. Jha, O. P. Pandey and K. Singh, *Silicon*, 9, 411–419 (2017).
16) H. Zhang, J. Li, H. Zhang, X. Liang, C. Yin, Q. Diao, J. Zheng and G. Lu, *Sensor. Actuat. B-Chem.*, 180, 66–70 (2013).
17) K. Obata and S. Matsushima, *Sensor. Actuat. B-Chem.*, 130, 269–276 (2008).
18) D. Chen, L. Yin, L. Ge, B. Fan, R. Zhang, J. Sun and G. Shao, *Sensor. Actuat. B-Chem.*, 185, 445–455 (2013).
19) X. Zheng, C. Zhang, J. Xia, G. Zhou and D. Jiang, *Sensor. Actuat. B-Chem.*, 284, 575–581 (2019).
20) G. Pascaiani, W. Mielcarek, K. Prociów and J. Warycha, *Ceram. Int.*, 40, 12783–12787 (2014).
21) C. Ma, L. Wang, Y. Zhang, X. Yang and X. Liang, *Sensor. Actuat. B-Chem.*, 284, 110–117 (2019).
22) Y. Shimizu, H. Nishi, H. Suzuki and K. Maeda, *Sensor. Actuat. B-Chem.*, 65, 141–143 (2000).
23) X. Liu, M. Hu and Y. Wang, *J. Alloy. Compd.*, 685, 364–369 (2016).
24) H. Zhang, J. Feng and T. Fei, *Sensor. Actuat. B-Chem.*, 190, 472–478 (2014).