

Application of TiO₂ to amperometric NO_x sensors based on NASICON

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ABSTRACT

The work focused on improvement of the current response to NO and the reduction of response time of both NO and NO₂. By adding a layer of TiO₂ catalyst layer, the shortcoming of NO insensitivity of traditional NASICON based amperometric NO₂ sensor was solved. TiO₂ was known as an n-type semiconductor and a high-performance NO oxidation catalyst. We separately applied different types of TiO₂ (rutile and Degussa P25) on the device and compared the test results with the traditional type without a catalyst layer. The results showed that the TiO₂ attached device exhibited a significant improvement to NO response, and P25 was better than rutile TiO₂ on account of the higher activity of anatase TiO₂. In addition, TiO₂ also played a role of a semiconductor electrode, resulting in the increase of response to NO₂. The response time of NO and NO₂ was separately shrunk from 153 s, 70 s to 77 s, 43 s owing to the P25 layer. The current responses were found to be barely affected by the coexistence of CO₂.

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1. Introduction

Nitrogen oxide (NO_x: NO and NO₂) exhaust from combustion devices and vehicles causes acid rain and photochemical smog, both of which have a major impact on the environment [1–2]. Analytical instruments based on chemical luminescence and the Saltzman method has been used to detect NO_x, but they are either too expensive or too large, or not sufficiently sensitive to low concentrations of NO_x. Therefore, researchers have recently been paying considerable attention to the development of compact, low-priced, and high-sensitivity solid-state sensors which can detect in-situ NO₂ (or NO) in real-time. NO_x is emitted into the environment mostly as NO from combustion devices and automobile engines. In the atmosphere, some of the NO is gradually converted to NO₂ to establish a dynamic balance. The composition and concentration of NO and NO₂ in the air varies because of the differences in humidity, temperature, location, and weather conditions [3–9]. Thus, there is a need for a sensor capable of detecting NO₂ (or NO) in the parts-per-billion (ppb) range.

Yttria-stabilized zirconia (YSZ) [10–12] and sodium super ionic conductor (NASICON) [13–15] are solid-state electrolytes which are widely used in the field of gas sensors. Given that automobile emission standards continue to become stricter, mixed potential-type sensors based on YSZ have been the subject of intense research as such sensors can detect nitrogen dioxide in automobile exhaust [16–17]. Bosch in Germany and NGK in Japan have produced YSZ-based NO₂ sensors for automobile

applications. However, these products were designed to monitor parts per million (ppm) concentrations of NO₂. They are unable to measure ppb levels. To monitor these lower concentrations of NO₂, NASICON-based amperometric solid-electrolyte sensors [18] have been shown to be advantageous. This kind of sensor was first proposed by Miura et al. in 1997 [19]. The device could detect sub-ppm levels of NO₂ but could not detect NO. To enable the simultaneous detection of the concentration of NO₂ and NO, Miura et al. applied a layer of WO₃ oxidation catalyst to convert the NO to NO₂ [20]. Therefore, they successfully developed a device capable of detecting both NO and NO₂.

TiO₂ is widely applied to heterogeneous photo-catalytic oxidation because of its excellent photo-catalytic effect, and because it is an excellent n-type semiconductor [21–22]. Degussa P25 (20% rutile and 80% anatase) is a standard material in the field of catalytic reactions [23]. P25 has large specific surface area and crystalline imperfections, giving it the ability to capture O₂ from the air [24–26]. For this study, we employed Degussa P25 as a catalyst for amperometric NO_x sensors, which exhibit an excellent response to both NO and NO₂.

2. Experimental

2.1. Materials synthesis

NASICON was synthesized by means of a high-temperature solid-state method using Na₂CO₃, SiO₂, ZrO₂, and NH₄H₂PO₄ powders, which were commercially sourced from Sinopharm Chemical Reagent Co., Ltd. The substrates were weighed and mixed according to the mole ratio of the Na₃Zr₂Si₂PO₁₂, and then heated in air to 1125 °C for

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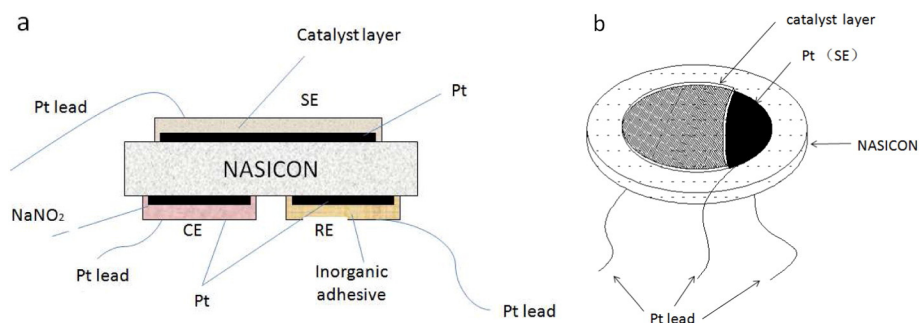


Fig. 1. Schematic view of sensor with TiO_2 oxidation layer: side view (a) and cross-sectional view (b).

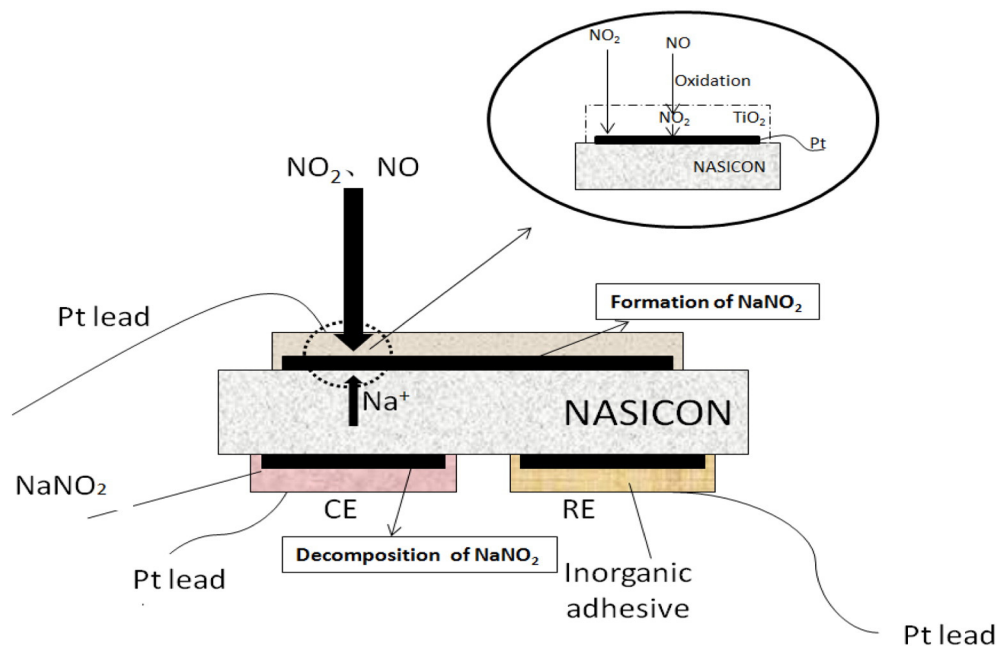


Fig. 2. Schematic sensing model of amperometric NO_x sensor.

12 h. Owing to the volatility of the phosphorus, a 5 wt.% excess of $\text{NH}_4\text{H}_2\text{PO}_4$ was applied. The resulting material was then ground in a mortar to identify the NASICON phase, which was then further milled for 24 h with zirconia balls in anhydrous ethanol to produce a fine powder. A certain amount of powder was cold-isostatic pressed at 160 MPa into 12-mm diameter uniaxial pellets. Finally, NASICON disks were produced by sintering these pellets at 1175 °C for 12 h. The SE oxidation

catalyst was obtained by mixing TiO_2 powder with terpineol and ethyl cellulose, then ball-milling for 1 h in a vibratory mill.

2.2. Fabrication of sensors

As shown in Fig. 1, the sensor was fabricated by screen-printing Pt paste (Pt 7850, Sino-platinum Metals Co., Ltd.) on both sides of the

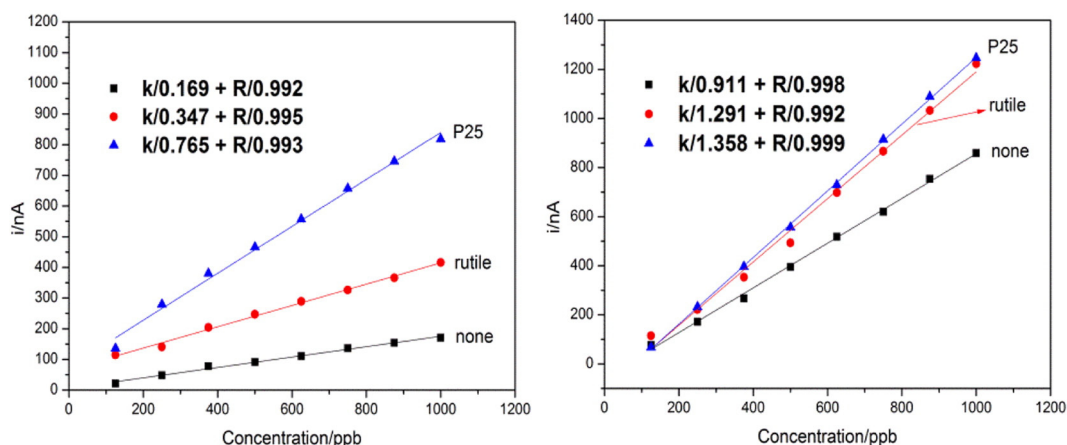


Fig. 3. Calibration curves for NO (a) and NO_2 (b) for three devices either with or without catalyst layers (−200 mV, 150 °C).

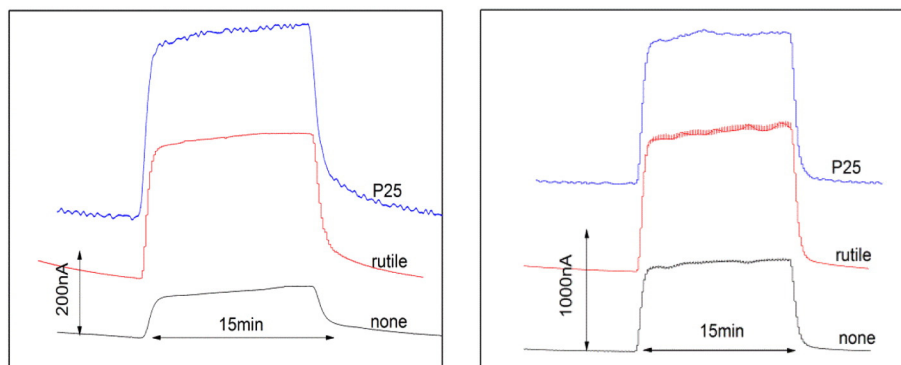


Fig. 4. Enlarged view of transient current for detecting 1 ppm (a) NO (b) NO₂ (−200 mV, 150 °C).

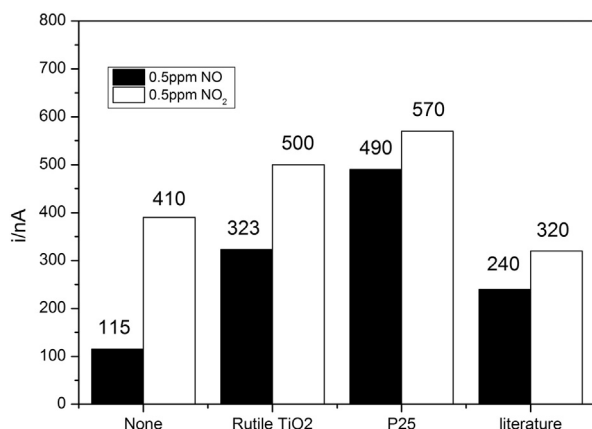


Fig. 5. Current produced in response to NO and NO₂ by the three devices (−200 mV, 150 °C).

plates to form a sensing electrode (SE), counting electrode (CE), and reference electrode (RE). After drying at 80 °C for 1 h, current-collector electrodes were formed by attaching Pt wires to the ends of each electrode using the same Pt paste, followed by sintering of the plates at 800 °C for 2 h. Then, an inorganic binder (HR-8767, Huirui Electronic Co., Ltd.) was used to seal the platinum to the reference electrode to avoid interference from the surrounding atmosphere during NO₂ gas measurement. A layer of rutile TiO₂ (Sinopharm Chemical Reagent Co., Ltd.) or a P25 (Evonik Degussa (China) Co., Ltd.) TiO₂ layer was screen-printed onto the SE to produce a device with an oxidation catalyst, followed by calcining at 500 °C for 2 h. The counter electrode was covered with a layer of NaNO₂ and then dried at 80 °C for 0.5 h.

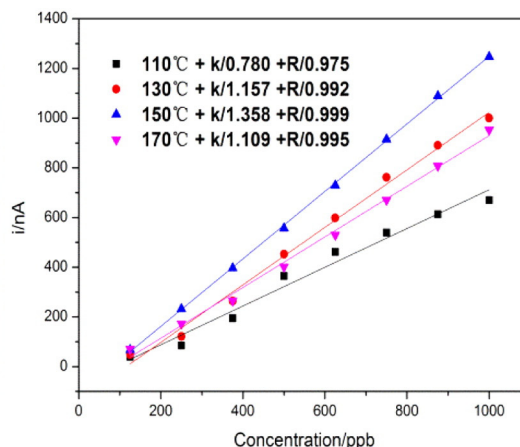
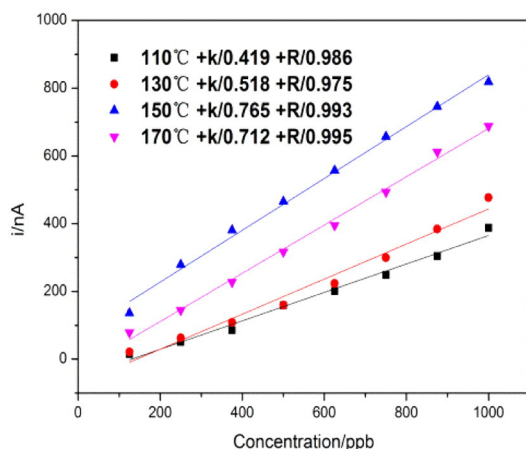


Fig. 6. Calibration curves for (a) NO (b) NO₂ at −200 mV for a device with P25 at different temperatures.

2.3. Gas sensing measurement

Gas sensing experiments were performed within a quartz tube placed inside a tube furnace (KSG30-10, Wuxi Allfine Electric Furnaces Co., Ltd.). A computer-controlled gas delivery system with calibrated mass flow controllers (MFCs) was used to introduce the test gas stream. Test gas mixtures containing different concentrations of NO were prepared by diluting the NO (10.5 ppm in N₂) in oxygen (O₂, 5 vol.%, held constant) and nitrogen (N₂). The total flow rate was fixed to 100 cm³/min. The Pt wires attached to each electrode were connected to the outer leads. The gases from the MFCs were introduced into a mixing device. The current signal from the sensor was measured with an electrochemical workstation (CHI660D, Shanghai Chenhua Instrument Co., Ltd.). The voltage between the SE and RE was varied from −150 mV to −400 mV.

3. Results and discussion

3.1. Sensing mechanism

As shown in Fig. 2, when the sensing electrode is polarized at an appropriate voltage relative to the Pt reference electrode, electrochemical reactions will occur on the electrodes, as follows:



Reaction (1) takes place upon exposure to NO₂, while reverse Reaction (2) takes place at the counter electrode, such that the NaNO₂ decomposes to produce Na⁺, e[−], and NO₂. The generated Na⁺ passes

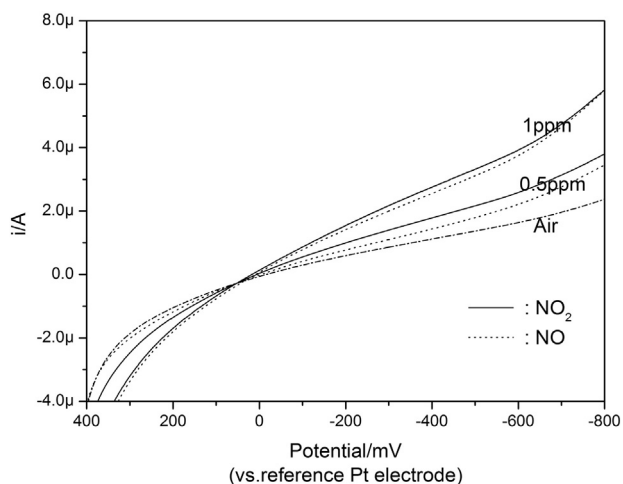


Fig. 7. Polarization curves for device with P25 in air and in the sample gases containing different concentrations of NO or NO₂ at 150 °C.

through the NASICON disks to arrive at the sensing electrode under the influence of the applied electric field. The generated e[−], on the other hand, flows through the open circuit under the influence of the same electric field, with the electrochemical workstation recording the current resulting from this movement. Finally, once both the Na⁺ and e[−] arrive at the working electrode, they interact with the surrounding NO₂ to produce electrochemical reactions. The NO₂ concentration directly determines the speed of Reaction (1) and ultimately influences the response current. On the other hand, the recorded current reflects the NO₂ concentration.

The metal oxides are mostly n-type semiconductors with a donor density N_D that is equal to 10¹⁷ to 10²⁰ cm^{−3} [27]. When a polycrystalline TiO₂ layer is exposed to the air, the O₂ molecules from the air diffuse into the layer along the inter-grain boundaries and eventually cover the surface of each grain. At temperatures above 25 °C, these O₂ molecules react with the conduction electrons [28–29], where e[−] is a conduction electron and O₂[−] is a molecule with a negative charge due to the bound electron [30], which will react with NO₂. These reactions occur as follows:



The adsorption of O₂[−] onto the surface of TiO₂ will accelerate the formation of NO₂[−], which will react with the Na⁺ that migrates from the

counter electrode. Meanwhile, the consumption of Na⁺ consequently enhances the current produced by the device.

Electrons and holes (h⁺) are generated, and they migrate to the surface of the catalyst. In high temperature, electrons in the valence band are stimulated and transition to conduction band. The electron was captured by oxygen molecules while water molecules were oxidized to •OH by electron holes. Followed by capturing •OH and •O^{2−}, NO will convert to NO₂.

3.2. NO_x sensing performance of devices with attached catalysts

The current output by the devices in response to NO and NO₂ were measured under a sensing-electrode potential of −200 mV at 150 °C. Fig. 3 shows the transient current of each device at corresponding NO (or NO₂) concentrations. The definition of sensitivity (k) and linearity (R) was introduced to evaluate the performance of the devices, where k is the slope of the line and R is the degree of fitting. According to Fig. 3a, the devices produced a linear correlation between the NO concentration and the response current, with the response current of the catalyst-free device being nonzero as a result of the spontaneous oxidation of NO in the O₂ environment and the catalytic performance of the Pt paste. The response current increased with the NO concentration while the device with P25 produced the highest current for a given concentration of NO, indicating that the device with P25 exhibits the best NO catalytic oxidation performance. The holes of anatase TiO₂ are easier to be captured, resulting in the higher NO oxidation performance of P25. Without the TiO₂ to act as an NO conversion catalyst, the sensor exhibits poor sensitivity to NO.

From Fig. 3b, it can be seen that the current produced by a catalyst-free device was lower than that produced by the other two devices. The two devices with attached catalyst exhibited very similar response currents, proving that both the rutile TiO₂ and P25 exhibit similar catalytic activity and improve the sensitivity of the sensors. This can be explained that both TiO₂ are n-type semiconductor, the capturing of O₂ is barely affected by the structure of TiO₂.

The response time was acquired by determining the difference between the corresponding times at 10% and 90% of the response value. Fig. 4a reveals that the response time for 1-ppm NO was 153 s for a device with no catalyst layer at −200 mV. In contrast, the response time of the devices with the rutile TiO₂ and P25 were 81 s and 77 s. In Fig. 4b, the response time of the three devices was 70 s, 48 s, and 43 s. The device with the P25 exhibited the fastest response to the 1-ppm NO₂ while the response of the catalyst-free device was the slowest. The response time for NO or NO₂ showed that catalyst layers can accelerate the electrode reactions of NO and NO₂. The slower response to a concentration of NO than to the corresponding concentration of NO₂ under the same

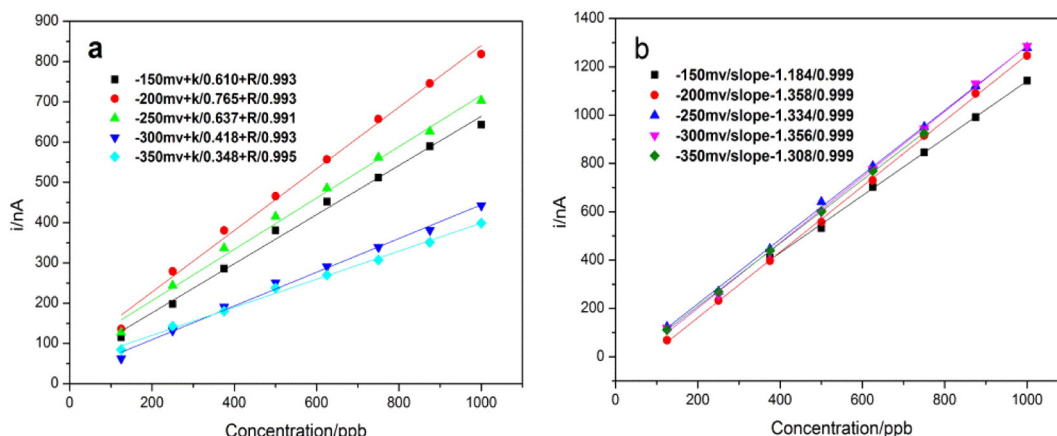


Fig. 8. Calibration curves for NO and NO₂ for device with P25 layers at different applied voltages (a) NO, (b) NO₂ (150 °C).

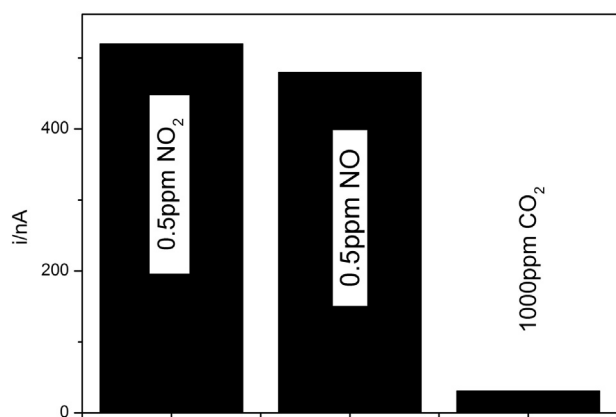


Fig. 9. Cross-sensitivities to various gases at 150 °C for device with a layer of P25 TiO₂.

conditions may be due to the additive oxidation reaction of NO in the sensing electrode.

Fig. 5 compares the response current for NO₂ and NO (0.5 ppm each), produced by each of the three devices. The catalyst-free device was much more sensitive to NO₂ than to NO. The devices with rutile TiO₂ and P25 produced a larger current in response to both NO and NO₂ than the catalyst-free device. This suggests that TiO₂ successfully converts NO into NO₂ and that it plays the role of an electrode catalyst for the electrochemical reaction of NO₂. The fact that the currents produced by the device with P25 in response to NO and NO₂ are much larger than those produced by the device with rutile showed that the anatase structure of P25 exhibits a greater reactivity than the rutile structure. Compared to the results of Miura et al. [20], the current response of NO and NO₂ is 240 nA and 320 nA separately.

3.3. Effects of different working temperatures on the sensing performance

Given the results described above, we chose P25 as the catalyst to be applied to the sensing electrode. Subsequently, we investigated the optimum working temperature for NO_x detection. For a working temperature range of 110 to 170 °C and a voltage of −200 mV, the calibration curves were as shown in Fig. 6. The catalytic performance and adsorption action of the P25 improved with an increase in the temperature, but as shown in Fig. 6, the maximum sensitivity is obtained at 150 °C, i.e., the response performance was not only determined by the catalyst layers, but was also influenced by the status of the NaNO₂. The as-milled NaNO₂ was easy to form into cakes and was not active above 170 °C, which influenced the movement of the Na⁺ ions.

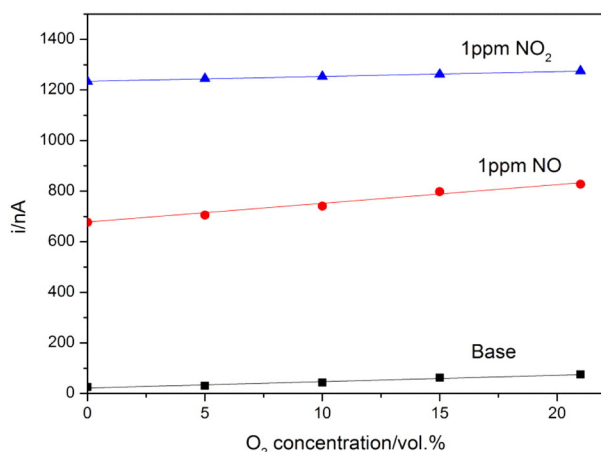


Fig. 10. Dependence of current produced in response to 1-ppm NO₂ and NO on the concentration of coexistent O₂ (−200 mV, 150 °C).

3.4. NO_x sensing properties of device using P25

Based on the results presented above, the device with P25 was selected to test the current produced in response to NO_x at different voltages. To explore the optimal applied voltage for the resulting device with P25 catalyst layers, polarization curves were measured in the presence of 0, 0.5, and 1 ppm NO₂ (or NO) in air at 150 °C. From Fig. 7, it can be seen that the cathodic current increases with an increase in the NO₂ or NO concentration, and a limiting-like current is observed in the sample gases when the sensing electrode is polarized at around −150 to −400 mV relative to the reference electrode, this range being selected on the basis that the transient signal could only reach a stable plateau within this applied voltage range.

As shown in Fig. 8, the sensitivity of the sensor was significantly influenced by the voltage applied at a given temperature. When the voltage was between −150 mV and −400 mV, the highest sensitivity of the device was obtained at −200 mV. From this, it was evident that both the working temperature and the applied voltage can influence the movement of Na⁺. Thus, −200 mV was chosen as the optimum bias voltage.

3.5. Influence of interference gas

The device with the P25 was subjected to further performance tests. It was also confirmed that the current produced in response (cross sensitivity) to 1000 ppm CO₂ was much lower than that to 0.5-ppm NO₂ (or NO), as shown in Fig. 9. Furthermore, the current produced in response to 1 ppm NO or NO₂ was almost independent of the oxygen concentration in the test range from 0 to 21 vol.%, as shown in Fig. 10. Given these sensing characteristics, the device appears promising for application to environmental testing.

4. Conclusion

An amperometric total NO_x sensor based on NASICON was obtained by applying a layer of TiO₂ catalyst paste to the sensing Pt electrode. The response current was found to be linear for NO and NO₂ concentrations of 0 to 1 ppm. A device with P25 was shown to exhibit the largest response current and the shortest response time among the three devices, indicating that it is an appropriate catalyst for the detection of both NO and NO₂. In light of this, −200 mV was deemed to be the optimal applied voltage, while the ideal working temperature was 150 °C.

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