Potentiometric NO$_x$ ($x=1, 2$) sensors with Ag$^+\beta^\text{--}$-alumina as solid electrolyte and Ag metal as solid reference

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A new Nernst-type NO$_x$ ($x=1, 2$) sensor was designed with Ag$^+\beta^\text{--}$-alumina as the solid electrolyte, porous platinum together with AgNO$_3$ as the gas-sensing working electrode, and silver metal as the solid reference electrode. Both planar and tubular Ag$^+\beta^\text{--}$-alumina based NO$_x$ sensors have been prepared and tested in a simple configuration which allows these sensors to be commercially developed. The planar NO$_x$ sensors with a thin sputtered platinum electrode are sensitive to a variation in the NO concentration at a fixed temperature around 200°C, but a difference between the experimental and theoretical EMF response was observed, due to a poor catalytic activity of the working electrode. However, the tubular sensor with a thicker painted platinum electrode revealed experimental EMF values close to the theoretical values in the NO concentration range of 10$^5$ to 10$^6$ ppm. The EMF response of the tubular sensors to lower NO concentrations of 50 to 1000 ppm is affected by the thickness of the silver nitrate formed at the platinum working electrode. The EMF response of a tubular sensor shows a temperature dependence in agreement with the theoretical dependence for temperatures at the working electrode. SEM pictures of the platinum working electrode reveal before testing a porous structure, while after testing several AgNO$_3$ crystalline particles were observed, due to the formation of the electrochemically active AgNO$_3$ solid electrolyte layer at the working electrode.

I. Introduction

In recent years, many efforts have been focussed on the development of technologies to detect the NO$_x$ content in industrial exhaust gases, such as chemoluminescence methods [1], ion selective electrodes [2,3], biochemical sensors [4,5], semiconductor sensors [6] and solid electrolyte sensors [7–10].

Chemoluminescence methods are affected by sample turbidity, color and the presence of metal ions. They also require a long response time and additional reagents.

Ion-selective electrodes have been commercially available since 1974. They have the advantage of simple design, rapid response, possible interfacing with automatic and computerized systems and can be applied in case of turbidity, and colored samples. However, they can only be used in aqueous solutions, and the cross-sensitivity to CO$_2$ poses also a problem.

Biochemical sensors using a gas-permeable membrane with immobilized nitrite oxidizing bacteria can detect NO$_2$ in the range of 0.5 to 260 ppm within 3 min and 4% of relative error. The selectivity of this microbial sensor is also satisfactory. However, biochemical sensors can not be applied for NO$_2$ detection in industrial exhaust gases at elevated temperatures.

Semiconductor sensors are the most widely developed and commercially applied NO$_x$ sensors during the last decades. In principle there are two types of semiconductor sensors. One type is either based on semiconducting metal oxide films, or a mixture of semiconducting oxides, while the other type is based on metal phthalocyanine organic semiconductors. The poor selectivity to different gaseous species remains a serious problem in the utilization of semiconductor gas sensors.

Solid electrolyte sensors for NO$_x$ detection were not investigated as extensively as SO$_x$ ($x=2, 3$) solid electrolyte sensors in the last decade because of the lack of suitable solid electrolytes. However, sodium conducting solid electrolytes provided with a gas-sensitive nitrate layer can be used to develop a NO$_x$ sensor, and this concept is attracting an increasing research interest. The solid electrolyte sensor is one
of the most promising gas sensors for commercial application because of its high selectivity and sensitivity, ease of operation, fast response, and simple construction.

Several univalent and divalent metal nitrates have been explored for use as solid electrolyte in NO$_x$ sensors, but the results were far from satisfactory because of the low values of ionic conductivity and the poor thermal and mechanical strength of these nitrate materials. The lack of a suitable solid electrolyte was overcome to a certain degree by Weppner et al. [9], who used the Na$^{+}$-β$^{-}$-alumina solid electrolyte and NaN$_2$O as the gas-sensing layer. Na$^{+}$-β$^{-}$-alumina is one of the best sodium ionic conductors with quite a high ionic conductivity, even at room temperature. Furthermore it exhibits very good thermal and mechanical strength and is commercially available to date. However, in the case of applying Na$^{+}$-β$^{-}$-alumina as solid electrolyte, either a standard NO–O$_2$–NO$_2$ gas system has to be used as reference gas at the reference electrode, or metallic sodium which is one of the most chemically active materials has to be employed as solid reference electrode.

In the present study, Ag$^{+}$-β$^{-}$-alumina has been selected as the solid electrolyte. It can be easily prepared from Na$^{+}$-β$^{-}$-alumina by ion exchange. Then, silver metal can be applied as solid reference electrode. Ag$^{+}$-β$^{-}$-alumina is a pure silver ion conductor with a high conductivity comparable to Na$^{+}$-β$^{-}$-alumina. Its thermal and chemical stability are also satisfactory.

The solid electrolyte Ag$^{+}$-β$^{-}$-alumina based NO$_x$ sensor

I Pt, Ag/Ag$^{+}$-β$^{-}$-alumina/AgNO$_3$/(NO, O$_2$, NO$_2$),

Pt II

(1)

where AgNO$_3$ is formed by the reaction between Ag$^{+}$-β$^{-}$-alumina and the NO–O$_2$–NO$_2$ ambient at the platinum working electrode, has been studied for the detection of 10$^3$ to 10$^9$ ppm of NO$_2$ industrial exhaust gases for a temperature range of 150 to 220°C. The detailed theoretical calculation of the sensor EMF and the discussion of the measurement limit and working temperature as well as the selectivity of the sensor have been described in ref. [11].

2. Experimental aspects

Polycrystalline Na$^{+}$-β$^{-}$-alumina tubes with a length of 40 mm, a diameter of 11 mm, and a wall thickness of 1.5 mm, and pellets with diameter of 10 and 16 mm and thickness of 1 and 1.5 mm as used in this work were supplied by the Shanghai Institute of Ceramics of the Chinese Academy of Sciences. The preparation and characterization of the Ag$^{+}$-β$^{-}$-alumina solid electrolyte have been described in detail in ref. [11]. With these solid electrolytes, Ag as solid reference electrode, and porous Pt as working electrode both tubular and planar NO$_x$ sensors were fabricated. For tubular sensors, platinum and silver paste were painted on the outer and inner surface of the sensor tube, respectively, followed by a heat treatment to obtain a high ohmic conductance and a porous platinum structure. The latter has a high catalytic activity for the NO/NO$_2$ conversion. For planar sensors, both platinum and silver paste, or sputtered platinum and silver thin layers can be used as electrodes. The silver reference electrode has to be protected from the NO$_2$ containing ambient. Fig. 1 shows the schematics of the tubular and planar NO$_x$ sensors. The sensors are tested in a system shown in fig. 2. The sample gas mixtures with different NO and O$_2$ partial pressures were made by introducing pure argon, oxygen in argon and NO in argon into the reactor at different ratios controlled by three mass flow meters. The Nernst response and working temperature of the sensor were recorded. The EMF response

![Fig. 1. Schematic configuration of Ag$^{+}$-β$^{-}$-alumina based NO$_x$ sensors: (a) tubular sensor: 1. Ag$^{+}$-β$^{-}$-alumina solid electrolyte, 2. porous platinum working electrode, 3. platinum lead of Ag reference electrode, 4. platinum lead of working electrode; (b) planar sensor: 1. platinum lead of reference electrode, 2. platinum lead of working electrode, 3. cement, 4. metal Ag reference electrode, 5. alumina tube, 6. Ag$^{+}$-β$^{-}$-alumina electrolyte, 7. porous platinum working electrode, 8. platinum mesh.](image-url)
of the sensor was obtained as a function of operating time, NO and O₂ partial pressure as well as the working temperature.

3. Results and discussion

3.2. EMF response to variations in the NO partial pressure

Fig. 3 presents the theoretical and experimental EMF values as a function of NO partial pressure at a fixed temperature of 200°C and an oxygen partial pressure of 0.011 atm. This result was obtained for the planar sensor AgBNSp2 constructed according to the schematics given in fig. 1b. There is a substantial difference between the theoretical and experimental EMF values. Considering the use of a thin layer of sputtered platinum as the gas sensing electrode, the observation of lower experimental EMF values is assumed to be due to a lack of catalytic activity of the porous platinum sensing electrode, which will result in NO₂ concentrations which are lower than the equilibrium values. Fig. 4 shows the percentage of NO in equilibrium with NO₂ in the total gas flux as a function of the NO concentration. The data were calculated from fig. 3. With increasing NO concentration the efficiency of NO conversion to NO₂ is decreasing. For a NO concentration of 4500 ppm, only 50% of NO is in equilibrium with NO₂. Improved results, as presented in figs. 5 and 6, were obtained.

Fig. 4. Conversion efficiency of NO to NO₂ in a planar sensor as calculated from the data in fig. 3 at $T_{\text{work}} = 200^\circ\text{C}$ and $P_{\text{O}_2} = 0.011$ atm.

Fig. 5. EMF response of a tubular sensor to NO concentration at $T_{\text{work}} = 197^\circ\text{C}$ and $P_{\text{O}_2} = 0.016$ atm. (+) theoretical data, (Δ) experimental data.

Fig. 3. EMF response of a planar sensor as a function of the NO concentration at $T_{\text{work}} = 200^\circ\text{C}$ and $P_{\text{O}_2} = 0.011$ atm. (+) theoretical values, (Δ) experimental values.
with a tubular sensor AgBSNT1, where a platinum painted electrode was used.

From figs. 5 and 6 it is seen that at the fixed temperature of 197 °C and an O₂ concentration of 0.016 atm, the experimental EMF values are more in line with the theoretical values. The improvement of the sensor response is attributed to an enhanced catalytic activity of the sensing electrode, because in the tubular sensor the use of Pt paste leads to a thicker porous electrode structure.

If, however, the O₂ partial pressure is kept proportional to the NO concentration instead of constant, an excellent response to variations in the NO partial pressure in the range of 10³ to 8 x 10⁷ ppm, and O₂ partial pressures of 0.01 to 0.05 atm was obtained with the tubular sensor AgBSNT1. The agreement between the experimental EMF values and the theoretical values can be seen in fig. 7.

The EMF response of the tubular sensors in the low NO concentration regime has also been tested using the AgBSNT1 and AgBSNT2 sensors. Fig. 8 presents the response of sensor AgBSNT1 to NO variation in the range of 50 to 700 ppm. The O₂ concentration is kept in the range of 0.008 to 0.1 atm and proportional to the NO concentration. Below 200 ppm NO the deviation from the Nernst response becomes considerable.

An improved result is obtained for sensor AgBSNT2 as displayed in figs. 9 and 10. The better response of AgBSNT2 compared with AgBSNT1 can be explained by their testing history. Sensors AgBSNT1 and AgBSNT2 have exactly the same configuration, but AgBSNT1 had been exposed to very concentrated NO/NO₂ containing ambients and was tested for a long time before it was tested in the low NO concentration regime. It is expected that a thick layer of silver nitrate has been formed at the interface of the porous platinum working electrode and solid electrolyte, and impart into the porous platinum structure. This would limit the adsorption of NO and NO₂ on the platinum surface and hence the establishment of the NO to NO₂ conversion equilibrium.

However, AgBSNT2 was a newly fabricated sensor, which was first tested in this low NO concentration
Fig. 9. EMF response of AgBNSt2 as a function of NO partial pressure at 187°C and \( P_{o_{2}} = c \cdot P_{NO} \) with \( P_{o_{2}} \) in the range of 0.008 to 0.1 atm: (+) theoretical data, (△) experimental data.

Fig. 10. Conversion efficiency of NO to NO₂ in sensor AgBNSt2 as calculated from the data in Fig. 9.

The region of 50 to 700 ppm. In this sensor the Pt electrode morphology is more porous, and provides a higher catalytic activity for the NO to NO₂ conversion. Therefore, the experimental response is more close to the theoretical value. This difference in response between the two tubular sensors raises the problem concerning the control of the thickness of the AgNO₃ gas-sensing layer formed at the interface of the Ag⁺-β⁺-alumina electrolyte and the platinum electrode.

3.2. Temperature dependence of the sensor EMF response

The temperature dependence of the EMF of the tubular sensors at fixed NO and O₂ concentrations was investigated, and results are presented in Fig. 11. The experimental temperature dependence fits the theoretical values reasonably well.

3.3. SEM analysis of Pt electrode

In order to obtain more information about the interfacial reactions at the working electrode, SEM analysis was applied to study the microstructure of the electrode. The SEM picture in Fig. 12 shows the porous structure of the working electrode of a planar sensor before testing. For comparison, Fig. 13 presents a picture of the platinum working electrode of the same sensor after a long period of testing. Fig. 13 reveals that many crystalline particles have been formed at the platinum working electrode, and these particles represent the formed electroactive layer of AgNO₃.

3.4. Reproducibility of the sensor response

Reproducibility is one of the most important factors which determines the operation and applicability of a gas sensor. If a sensor exhibits a good reproducibility, even though the experimental results are not able to reach the theoretical values because of, for instance kinetic reasons, the sensor can still be of practical use, provided that the sensor has been calibrated before use.

Fig. 13 shows the result of a preliminary study of the reproducibility of tubular sensor AgBNSt1. The
duration of the test was three weeks with the sensor at 197°C and $P_{\text{NO}}$ being 1120 ppm, and $P_{\text{O}_2}$ being 0.016 atm. It is observed that the experimental EMF response is reasonably constant and that the deviation of the measured EMF values from the theoretical values is not too large and remains virtually constant. This result as well as the simple configuration make the Ag $\cdot$ $\beta$-alumina based NO$_x$ sensor to be a promising candidate sensor for development for commercial application.

3.5. Selectivity of the sensor to NO$_x$ against CO$_2$

According to the theoretical analysis in ref. [11], this type of NO$_x$ sensors should have excellent selectivity to NO$_x$ against CO$_2$. In the experimental EMF measurements, the response of 124.1 mV to 1000 ppm NO and 0.1 atm O$_2$ at 199°C (theoretical value is 128.6 mV) was not changed by the presence of 0.01 atm CO$_2$. This preliminary investigation of the selectivity of the sensor confirms that the interference of CO$_2$ in the NO$_x$ detection is not a problem for this type of NO$_x$ sensors.

3.6. Problem of oxygen partial pressure measurement

If in the practical use of NO$_x$ (and also SO$_x$) sensors the oxygen content in the sample gas is unknown, an oxygen sensor is required which can be operated in the same temperature region as the NO$_x$ sensor. However, the currently commercially available stabilized zirconia-based O$_2$ sensor is not suited,

Fig. 12. SEM picture of the porous Pt working electrode of a planar sensor (a) before and (b) after testing.

Fig. 13. Reproducibility of tubular sensor AgBNS1 at 197°C, $P_{\text{NO}}$ = 1120 ppm, and $P_{\text{O}_2}$ = 0.016 atm. (+) theoretical values, (△) experimental data.
firstly because of its high operating temperature, and secondly, due to the multiple charge-transfer reactions at the zirconia–platinum interface in the presence of NOx as suggested by Michaels et al. [12]. Multiple charge-transfer processes result in mixed potentials, which fall between the thermodynamical potentials of the individual charge-transfer reactions [13]. This signal will thus lead to invalid oxygen partial pressure data in the gas system. According to this multiple charge-transfer mechanism, we also have to take into account the possible \( \text{O}_2/\text{O}^{2-} \) charge transfer reaction on the platinum electrode of the NOx (SOx) sensors. Therefore, the measurement of an unknown \( \text{O}_2 \) partial pressure will remain a problem in the practical use of NOx and SOx sensors.

In addition, it is well known that a porous platinum electrode does not fulfill entirely the long term stability requirement, gauge response time and accuracy requirements for high temperature oxygen sensors [14]. To overcome these problems, the use of metal oxides and mixed metal oxides as electrode materials was proposed [15,16]. However, more research has to be done before a proper oxide electrode material can be applied, and a smart multiple sensor system for the detection of SOx, NOx, and \( \text{O}_2 \) is commercially available.

4. Conclusions

1. A new Nernst-type NOx (\( x=1, 2 \)) sensor was designed with surface modified Ag\(^+\)-\( \beta \)-alumina as the solid electrolyte, porous platinum together with AgNO3 as the gas-sensing working electrode and metallic silver as the solid reference electrode. Both planar and tubular Ag\(^+\)-\( \beta \)-alumina based NOx sensors have been fabricated and tested. Theoretical considerations reveal that this sensor may give a Nernstian EMF response of hundreds of millivolts to NO concentrations in the range of \( 10^2 \) to \( 10^4 \) ppm and in the temperature region of 150 to 220°C.

2. SEM analysis of the platinum working electrode before testing reveals a porous structure, while after testing, some crystalline particles are observed, most probably due to the reaction of Ag\(^+\)-\( \beta \)-alumina with NOx in the presence of oxygen to form AgNO3.

3. The planar NOx sensors with a thin sputtered platinum electrode are sensitive to a change in NO concentration at a fixed temperature around 200°C, but a difference between the experimental and theoretical EMF response was observed, and attributed to the insufficient catalytic activity of the sputtered platinum working electrode.

4. A tubular NOx sensor AgBNSt1 with a thicker painted Pt electrode exhibits an experimental EMF response close to the theoretical values. The conversion efficiency of NO to NO2 calculated from the experimental data is about 80% for the NO gas at concentrations in the range of \( 10^3 \) to \( 10^4 \) ppm, if the \( \text{O}_2 \) partial pressure is fixed. The EMF response of sensor AgBNSt1 is in good agreement with the theoretical value, if the oxygen concentration is kept proportional to the NO partial pressure.

5. The EMF response of the tubular sensors to NO concentration in the range of 50 to 700 ppm is affected by the thickness of the gas-sensing silver nitrate formed at the platinum working electrode.

6. The EMF response of a tubular sensor showed a temperature dependence in agreement with the theoretical calculation.

7. A preliminary investigation indicated the good selectivity of this type of NOx sensor to NOx against CO2 gas.

References


