SOLID ELECTROLYTE AND SEMICONDUCTOR
SO$_x$ AND NO$_x$ GAS SENSORS

PROEFSCHRIFT

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Ningling Rao

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Dit proefschrift is goedgekeurd door de promotoren,
Prof. Dr. J. Schoonman en Prof. Ir. C.M. van den Bleek.
To my parents and brother
To my grandparents
Preface

The thesis on the study of solid electrolyte and semiconductor based \( SO_x \) and \( NO_x \) sensors was started at the University of Science and Technology of China (USTC). It was continued at Ris\ø National Laboratories and finished at Delft University of Technology. During my research work in the three countries, many people have given me kindly help. Without their help, this thesis would have only been a nice dream. Here I would like to express my deep thanks to them.

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CHAPTER 1

SOLID STATE GAS SENSORS - GENERAL INTRODUCTION

1. STATE-OF-THE-ART OF CHEMICAL SENSORS

As environmental pollution has become a global concern, the demand for gas sensors is diversifying. Sensor systems for detecting minor noxious gases such as $\text{SO}_x \ (x=2,3)$, $\text{CO}$ and $\text{NO}_x \ (x=1,2)$ need to be developed urgently.

The requirement for the direct and fast detection of inflammable or toxic gases in industrial environments stimulated the research and development of solid state gas sensors. Chemical sensors, capable of detecting traces amounts of gases, have been applied in the chemical process and pharmaceutical industries and in fermentation processes in order to control the amount of harmful gaseous wastes emitted from industrial plants, or to avoid the explosion of flammable gases, and incomplete combustion processes, and to control the exhaust gases from automobiles[1].

A typical example of the application of chemical sensors in industrial areas is the monitoring of the concentration of the oxygen in molten steel and copper, and in fermentation at room temperature. At high temperatures the oxygen is detected by a chemical sensor based on stabilized $\text{ZrO}_2$ solid electrolyte, while the room temperature
detection of oxygen is performed using a sensor based on an organic-polymer selectively permeable membrane. A problem of this latter type of sensors is their limited life.

In any chemical sensor the sensing process can be devided into two parts, i.e. recognition which is based on the selective sensitivity of the sensor to a particular chemical species, and amplification which increases the usually weak signal to the level at which it can be conveniently handled by electronics. There are several physical property variations underlying chemical sensing, for example, electrochemical, optical, gravimetric, thermal, mechanical, and new types of sensors are being proposed every year. However, the general principle of these various types of sensors is invariably based on some selective chemical interaction of the species of interest with an active sensor material, which results in a change of some physical parameter such as electrical current, potential or conductivity, intensity of light, mass, temperature and pressure. By measuring the variation of this physical parameter, the concentration of the chemical species can be determined.

The main performance characteristics which determine whether or not a sensor system can be developed to a commercial state relate to sensitivity, selectivity, measurement range, response time, reproducibility and stability[2].

<table>
<thead>
<tr>
<th>Sensitivity</th>
<th>-</th>
<th>amount of substance adsorbed on sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>rate of reaction of substance</td>
</tr>
<tr>
<td>Selectivity</td>
<td>-</td>
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</tr>
</tbody>
</table>
ability of other substances to interfere with adsorption or reaction on sensor

Measurement range - ratio of substance adsorbed on sensor to substance in environment

Response time - rate of adsorption of substance on sensor
rate of reaction of substance on sensor

Reproducibility - Adsorption or reaction of substance is reversible
Reaction of substance is complete

Stability - Material in the sensor taking part in adsorption and/or reaction is unchanged by reaction, or by processes within it

When a sensor is combined with a microcomputer, a smart system results, which can be used to accomplish complicated work accurately, precisely and promptly, which was impossible before. Thus, the development of highly sensitive and reliable chemical sensors is an essential necessity for the smart system, and to date chemical sensors represent a high technology area in modern applied science.

2. SOLID ELECTROLYTE GAS SENSORS

Since 1913 when the unusual high ionic conductivity in $\alpha$-AgI (148-465°C) was discovered, solid state ionics as a novel branch of solid state chemistry and physics, has been studied and developed extensively and become an important and active research
area of modern chemistry and materials science. Solid electrolyte chemical gas sensors represent one of the significant applications of solid state ionics, and have attracted remarkably increasing interest because of their potential application in chemical technology, environmental monitoring and protection, automated control of industrial processes and in biochemistry.

The first commercially used solid electrolyte gas sensor was based on the partially stabilized zirconia oxygen sensor. To date, various kinds of solid electrolyte gas sensors are being studied, i.e. $\text{O}_2[3]$, $\text{H}_2[4,5]$, $\text{H}_2\text{O}[6]$, $\text{CO}_2[7,8]$, $\text{S}[9]$, $\text{SO}_x(x=2,3)[10-15]$, $\text{NO}_x(x=1,2)[16-20]$ and $\text{Cl}_2[21]$ sensors.

Solid electrolyte potentiometric gas sensors are Nernst-type electrochemical cells. Such galvanic cells are usually composed of two reversible electrodes separated by a solid electrolyte phase. Between the two electrodes, one can measure an equilibrium reversible electromotive force (EMF) at a constant temperature, as long as the local equilibrium is prevailing in the cell. The cell can be expressed as

\[ \text{I} \quad \text{Reference electrode / Solid electrolyte / Working electrode} \quad \text{II} \]

In this cell, the reference electrode can be a standard gas reference or solid reference, while porous platinum is generally employed as the working electrode, because of both its good stability and its high catalytic activity. From a practical point of view a solid reference electrode is preferred over a gaseous reference system, simply because with a solid reference electrode the sensor can be miniaturized, yet simple and cheap. The reversible electromotive force (EMF) of the cell can be given as[22]
\[ EMF = \sum_{i} \left( \frac{t_i}{Z_i^F} \right) d\mu_i \]  

(1)

where EMF is the electromotive force, \( F \) the Faraday constant, \( \mu_i \) the chemical potential of the ionic or electronic species \( i \) and \( t_i \) and \( Z_i \) the transference number and electrical charge of species \( i \), respectively. Eq.(1) is generally applicable, it can be analysed for special conditions of different gas sensors to gain further insight into the factors that control the operation of a sensor and to give a theoretical prediction for practical measurements.

Solid electrolyte gas sensors have some advantages over other analytical chemical methods[23], such as

(1) continuous quantitative measurement
(2) high selectivity and sensitivity
(3) easy operation and fast response
(4) simple construction and low price

In addition, there are some more requirements such as reproducibility, high mechanical and thermal strength, and slow aging which limit the commercial use of some solid electrolyte gas sensors.
3. SEMICONDUCTOR GAS SENSORS

Semiconductor materials for gas sensors have attracted wide spread attention in the past decades and gas sensors based on these materials and used for domestic gas alarms or combustion control systems have been rapidly developed and marketed[24] since the prototypes reported by Seiyama et al.[25,26] and Taguchi[27]. These semiconductor gas sensors include O\textsubscript{2} sensors for automobile engine management, H\textsubscript{2}S sensors in oil rigs, hydrocarbon sensors as domestic gas alarm, and CO sensors in underground car parks[28]. The first domestic gas leak detector using sintered SnO\textsubscript{2} as the active semiconductor sensor material was released in 1968, and to date, approximately five million tin oxide based semiconductor Taguchi-type gas sensors are used as domestic gas leak detectors in Japan[29].

In addition to SnO\textsubscript{2}, several oxide semiconductor materials, such as TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3} and ZnO have been used for the detection of inflammable or noxious gases. They are all n-type oxide semiconductors. Also some p-type oxide semiconductors have been explored for use in gas sensors. The resistance of n-type oxide semiconductors decreases when reducing gas is adsorbed at the surface, and increases when exposed to oxidizing gas, whereas the p-type oxide semiconductor reveals the opposite effect of resistance change. Among these oxide semiconductor materials, tin oxide is still the most important material used for gas detection[30,31] and its electrical properties have long been studied[32].

Although hundreds of papers have been published about the gas-sensing mechanisms of the semiconductor materials, the detailed mechanism underlying the operation of semiconductor gas sensors still remains not clear. In fact, the variations in electrical
resistance of the material by gas adsorption are dependent on the surface properties of the sample[33], doping levels[30,34], temperature[35] and thermal history[36] and these parameters are considered to be the important factors determining the electrical response of these Taguchi-type sensors.

Metal oxide semiconductors offer the potential for developing portable, rugged and inexpensive chemical analysis devices. However, even though these materials are sensitive to many combustible gases in the ppm range, there are some important problems such as a poor selectivity, a non-linear response and a long-term drift which have prevented the use of these semiconductor gas sensors in the case that sensitive and precise detection of various gaseous components is required. Because the semiconductor gas sensors cannot discriminate gaseous components, they are hardly selective. For this reason, the commercially available gas detectors do not indicate the gas concentration, but only provide electrical output signals. The selectivity problem can be solved to a certain degree by doping with small amounts of the noble metals Pd, Pt or Ag as a catalyst[37-39], by applying a catalytic layer or filter on the surface of the sensor to eliminate impurity gases, or by employing a sensor array system using sensors with different gas selectivity[40]. Another major problem of semiconductor gas sensors is that the electrical resistance or the gas sensitivity of individual sensor elements, which have been produced according to the same procedure, can differ considerably from each other. Even though high gas sensitivity has been achieved, the variation in the gas sensitivity among the sensor elements in an array will become a serious problem, because calibration in order to establish the relationship between sensor output and gas concentration must be carried out for every sensor element. This means that the
detection circuit constant must be adjusted for each sensor so as to correspond to the
gas-sensing characteristics of each element when a direct measure of the gas
concentration is required. This makes the quantitative measurement very complicated,
and of course, is quite a serious problem from a practical point of view.

In order to fully characterize the response of semiconducting gas sensors, a quantitative
theoretical model for the behavior of wide bandgap metal oxide semiconductor gas
sensors was presented by Clifford[41]. In his work, an experimental and theoretical study
of the steady state and kinetic behavior of variously doped ZnO films and sputtered and
chemically deposited films of SnO₂ was undertaken. In addition, the popular
commercially available Taguchi Gas Sensor (TGS), which exemplifies the state-of-the-art
in metal oxide gas sensors, was extensively studied. It was concluded that a model based
on a three step process, i.e. physisorption of oxygen on disordered surfaces, reactive
desorption of physically adsorbed oxygen by the action of inflammable or combustible
gases, and barrier layer limited chemisorption of oxygen, accounts for the essential
features of the gas response of homogeneous semiconductor sensors based on SnO₂.

4. SCOPE OF THE THESIS

In this thesis, the preparation, structure and the thermal, chemical and electric properties
of the solid electrolyte materials Na₂SO₄, Nasicon, Na⁺-β"-alumina and Ag⁺-β"-alumina
are studied. The electrochemical SOₓ (x=2,3) gas sensors based on these solid
electrolytes have been fabricated and tested as the main object of the thesis. Research
of the solid electrolyte and semiconductor \( \text{NO}_x \) (\( x=1,2 \)) gas sensors has also been performed, using \( \text{Ag}^+ - \beta^\text{a}-\text{alumina} \) as the solid electrolyte and \( \text{Al}_2\text{O}_3 - \text{ZnO} - \text{V}_2\text{O}_5 \) mixed oxide semiconductors as the gas-sensing materials, respectively.

After a preliminary introduction of solid electrolyte and semiconductor gas sensors in Chapter 1, a theoretical consideration for Nernst-type \( \text{SO}_x \) and \( \text{NO}_x \) gas sensors is presented in Chapter 2. The operation principle is discussed and the thermodynamical prediction of the electromotive force (EMF) is given. They are the fundamental aspects for understanding the sensor performance.

Chapter 3 deals with the preparation, phase transition and electrical properties of \( \text{Na}_2\text{SO}_4 \)-based solid electrolyte materials. Yttrium and lanthanum sulfate are employed as dopants to enhance the ionic conductivity of \( \text{Na}_2\text{SO}_4 \)-I and to stabilize this high temperature, fast-ion conducting phase. \( \text{Na}_2\text{WO}_4 \) is also used to stabilize \( \text{Na}_2\text{SO}_4 \)-I down to room temperature and to improve the mechanical properties of \( \text{Na}_2\text{SO}_4 \)-based materials.

Potentiometric \( \text{SO}_x \) gas sensors based on a tubular Nasicon solid electrolyte are described in Chapter 4. A temperature gradient between the two electrodes of the sensor has been found to be the reason for the deviation of the experimental EMF response from the Nernstian response. This deviation can be eliminated to a degree by using the new thermodynamic calculations for the non-isothermal systems presented in Chapter 2.
Chapter 5 describes a novel Temperature Gradient Na⁺-Beta"-alumina (TGNB) SOₓ sensor without reference gas electrode, using a tubular Na⁺-β"-alumina solid electrolyte and tested under non-isothermal conditions. The same gas mixture was supplied over the two electrodes of the sensor as both sample gas and reference gas under non-isothermal conditions. The potential commercial application of the TGNB SOₓ sensors is evident from the good agreement of the sensor response with the theoretical calculations. In addition, the sensor’s configuration is simple.

Planar and tubular Ag⁺-β"-alumina based SOₓ gas sensors using silver metal as solid reference electrode are discussed in Chapter 6. The preparation, structure and properties of Ag⁺-β"-alumina are studied. The planar and tubular Ag⁺-β"-alumina SOₓ sensors are assembled and examined, indicating a Nernstian response to 10 to 1000 ppm SO₂ in the temperature region of 500 to 700°C.

Chapter 7 presents the Nernst-type NOₓ gas sensor using Ag⁺-β"-alumina as the solid electrolyte, Ag as the solid reference electrode and porous Pt together with the gas-sensing AgNO₃ thin layer as the working electrode. The performance of the planar and tubular sensors is investigated in the temperature range of 150 to 220°C, when the NO concentration is in the region of 50 to 10,000 ppm. The microstructure of the working electrode is examined by SEM, providing information about the mechanism underlying the electrochemical reactions at the interface of the electrolyte and the gas-sensing electrode.
Semiconductor NO$_x$ sensors are studied in Chapter 8. Al$_2$O$_3$-ZnO-V$_2$O$_5$ oxide mixtures are applied as the gas-sensing semiconductor materials. The sensor elements based on Al$_2$O$_3$-ZnO-V$_2$O$_5$ with different compositions are fabricated and tested in order to find the optimal composition of the respective oxides for which a high sensitivity and selectivity to NO$_x$ gases can be achieved.

REFERENCES


12


[38] T. Seiyama, H.Futada, F. Era and N.Yamazoe, Denki Kagaku, 40, (1972) 244
CHAPTER 2

THEORETICAL CONSIDERATIONS FOR NERNST TYPE GAS SENSORS

I. A New Theoretical EMF Expression for SO$_x$ (x=2,3) Sensors with Solid Electrolyte Concentration Cells

ABSTRACT

Potentiometric SO$_x$ (x=2,3) gas sensors comprising Na$_2$SO$_4$-based solid electrolyte concentration cells have been developed and studied in recent years. However, for the theoretical EMF prediction, a universal expression is lacking in the literature which also covers non-isothermal systems.

In this paper, a new EMF equation was derived for non-isothermal solid electrolyte SO$_x$ sensors of the type

$$\text{Pt} (\text{SO}_2, \text{SO}_3, \text{O}_2) / \text{Na}^+ \text{ ion conductor} / (\text{SO}_2, \text{SO}_3, \text{O}_2) \text{II} \text{Pt}$$

$$(\text{Na}_2\text{SO}_4, \text{Nasicon, Na}^+-$\beta$,$\beta''$-alumina, etc.)$$

$T_1 - \delta T - T_2$
This expression differs from the simple Nernst equation usually employed for the isothermal response, and can be widely used to predict theoretical EMF values of $SO_x$ sensors for both isothermal and non-isothermal conditions. According to the present theoretical considerations, a new type of $SO_x$ sensor without a gaseous reference electrode could be designed.
I-1. INTRODUCTION

Since the 1970s many attempts have been made to utilize alkali sulfates, including Na$_2$SO$_4$[1-3], K$_2$SO$_4$[4,5], Li$_2$SO$_4$[6,7] and some Na$^+$ ion conductors such as Nasicon[8,9], β- and β'-alumina[10,11] as solid electrolyte in concentration cell SO$_x$ (x=2,3) sensors of the type

$$\text{Pt (SO}_2\text{SO}_3\text{O}_2)^I / \text{alkali sulfate} / (\text{SO}_2\text{SO}_3\text{O}_2)^{II} \text{ Pt}$$  (1)

The electromotive force (EMF) values of these cells were essentially consistent with the values theoretically calculated using the Nernst equation:

$$\text{EMF} = \frac{RT}{2F} \ln \frac{p^{II}(\text{SO}_2)}{p^{I}(\text{SO}_2)}$$  (2)

under the assumption that the temperatures of both reference and working electrode are the same, and that the activity of A$_2$SO$_4$ (A=Li,Na,K) formed by the electrochemical reaction at both electrodes is equal to 1. This assumption is reasonable if the sensor has the form of a thin disk, and is kept in the isothermal circumstances. But for practical use, however, a small and simple sensor system is required. For that purpose, sensors in a tubular form for which only a small furnace would be required, have attracted attention in recent years. In this case, a temperature difference between the two electrodes can easily exist. To date, a theoretical derivation of the EMF expression for non-isothermal systems has not been reported in the literature. Wagner[12] first derived the equation
relating the EMF of a concentration cell to the difference in chemical potential between the two electrodes. Weppner[13] described the basic relations governing the generation of potentials by ionic and mixed conducting solids in potentiometric gas sensors. Saito et al.[8] derived the Nernst equation for sulfur dioxide sensors. Recently, Schoonman[14] presented a review of the derivation of the EMF expressions for different gas sensors. However, this derivation was based on the assumption of isothermal conditions. In this work we will derive a more general equation that also covers the non-isothermal case for the solid electrolyte concentration cell $\text{SO}_x$ gas sensors.

1-2. THEORETICAL DERIVATION OF EMF EQUATION

Solid electrolyte gas sensors based on electrochemical cells consist of a solid ionic conductor as electrolyte, and two mixed conducting electrodes, one being the working electrode which is exposed to a gas phase containing the chemical species to be detected, the other is the reference electrode at which the chemical potential of the mobile species is kept constant at a certain temperature by using either a gas flow or a solid mixture which provide a known partial pressure or chemical activity of the chemical species to be measured, respectively. The theory underlying the measuring principle is a Nernst-type expression for the electromotive force (EMF) or the open circuit potential (OCV) of the electrochemical cell.

For instance, a $\text{SO}_x$ sensor based on a concentration cell using a sodium ion conducting solid electrolyte can be represented as
Pt \((SO_2SO_3O_2)^I\) / Na\(^+\) ion conductor / \((SO_2SO_3O_2)^{II}\) Pt \((3)\)

In case that the sodium ion conducting solid electrolyte is not a sulfate-based material, there should always be a Na\(_2\)SO\(_4\) layer formed on both sides of the solid electrolyte before constructing the sensor. Then the cell may be represented by

\[\text{Pt}(SO_2SO_3O_2)^I/Na_2SO_4/Na^+ \text{ ion conductor}/Na_2SO_4/(SO_2SO_3O_2)^{II}\text{Pt}\] \((4)\)

Dekker\(^{[15]}\) derived the theoretical EMF expression for this kind of SO\(_x\) sensor to be

\[EMF = \frac{\mu^{II}(SO_2) - \mu^I(SO_3)}{2q} + \frac{\mu^{II}(O_2) - \mu^I(O_2)}{4q}\] \((5)\)

with the assumption \(\mu^{II}(Na_2SO_4) = \mu^I(Na_2SO_4)\). Here \(\mu(i)\) represents the chemical potential of species \(i\). This assumption holds true when the sensor is operated under isothermal conditions, i.e. both electrodes have the same temperature. For this isothermal system, one obtains from Eq.(5)

\[EMF = \frac{RT}{2F} \ln\frac{p^{II}(SO_x)}{p^I(SO_x)}\] \((6)\)

where \(p(SO_x)\) is referring to the introduced SO\(_x\) (\(x=2,3\)) partial pressures under the assumption that the oxygen partial pressures are equal in both electrode compartments. Eq.(6) was used in most papers on solid state electrochemical SO\(_x\) gas sensors. However, when the temperatures and/or oxygen partial pressures at both electrodes are different, we have to deal with
\[
EMF = \frac{\mu^{II}(SO_3) - \mu^{I}(SO_3)}{2q} + \frac{\mu^{II}(O_2) - \mu^{I}(O_2)}{4q} - \frac{\mu^{II}(Na_2SO_4) - \mu^{I}(Na_2SO_4)}{2q} 
\]

(7)

Thus we can express the EMF as

\[
EMF = \frac{RT_2}{2F} \ln \frac{K_2p^{II}(SO_3)p^{II}(O_2)}{1+K_2[p^{II}(O_2)]} - \frac{RT_1}{2F} \ln \frac{K_1p^{I}(SO_3)p^{I}(O_2)}{1+K_1[p^{I}(O_2)]} + \frac{G^o(SO_3) - G^o(SO_3)}{2F} + \frac{G^o(O_2) - G^o(O_2)}{4F} - \frac{G^o(Na_2SO_4) - G^o(Na_2SO_4)}{2F} 
\]

(8)

where \(G^o(i)\) is the molar free energy of the corresponding species, and \(K\) represents the equilibrium constant of the \(SO_2\) oxidation reaction. In Eq.(8), the summation of the last three terms is the thermoelectrical power between the two electrodes. Using the thermodynamic data at different temperatures for \(SO_3\), \(O_2\) and \(Na_2SO_4\cdot I\) (conducting crystallographic phase of \(Na_2SO_4\)) from ref.[16], we have

\[
G^o(SO_3) = -362.743 - 0.3198T \quad \text{kJ/mol} 
\]

(9)

\[
G^o(O_2) = -375.356 - 0.2364T \quad \text{kJ/mol} 
\]

(10)

\[
G^o(Na_2SO_4\cdot I) = -1291.02 - 0.3324T \quad \text{kJ/mol} 
\]

(11)
with correlation factors of 0.9998, 0.9999 and 0.9990, respectively. Then the thermoelectrical power, \( E_t \), can be calculated using

\[
E_t = -0.5472(T_2 - T_1) \\
= 0.5472(T_{\text{ref.}} - T_{\text{work.}}) \quad (\text{mV}) \tag{12}
\]

Here \( T_{\text{ref.}} \) and \( T_{\text{work.}} \) denote the temperature of the reference and working electrode, respectively. Combining Eqs.(8) to (12), we can get the theoretical EMF equation for a non-isothermal system

\[
\text{EMF} = 10 \cdot 10^{\frac{RT_2}{2F} \ln \frac{K_2 p^{II}(SO_x)p^{II}(O_2)}{1 + K_2[\sqrt{p^{II}(O_2)}]} - \frac{RT_1}{2F} \ln \frac{K_1 p^{II}(SO_x)p^{II}(O_2)}{1 + K_1[\sqrt{p^{II}(O_2)}]} + 0.5472(T_{\text{ref.}} - T_{\text{work.}})(mV) \tag{13}
\]

It can be seen from Eq.(6) and Eq.(13) that the isothermal and non-isothermal concentration cells yield quite different EMF values. These two equations should fit the experimental data under the different conditions employed, provided that electrochemical equilibrium is reached.

I-3. THEORETICAL MODELLING AND DISCUSSION

In the following discussion, the two kinds of sensors are assumed to be at the same \( SO_2 \) and \( O_2 \) partial pressures on both the reference and working electrodes in order to
compare with each other. The only difference is that the temperature of the reference and working electrode are the same in the isothermal system, but in the non-isothermal system the temperature of the reference electrode is 50 K higher than that of the working electrode.

I-3.1 EMF of the SO\textsubscript{x} sensors as a function of temperature

Figs. 2.1 and 2.2 represent the theoretical EMF responses of the SO\textsubscript{x} sensor as a function of temperature for isothermal and non-isothermal systems, respectively.

Fig. 2.1  Theoretical EMF of the isothermal SO\textsubscript{x} sensor as a function of temperature. \(p_{\text{ref.}}(\text{SO}_2) = 100 \text{ ppm, } p_{\text{ref.}}(\text{O}_2) = p_{\text{work.}}(\text{O}_2) = 0.21 \text{ atm.} \) \(p_{\text{work.}}\) (ppm) values are given in the figure.
Fig. 2.2  Theoretical EMF of the non-isothermal SO\textsubscript{x} sensor as a function of temperature. \( p_{\text{ref}}(\text{SO}_2) = 100 \ \text{ppm}, \ p_{\text{ref}}(\text{O}_2) = p_{\text{work}}(\text{O}_2) = 0.21 \ \text{atm} \).

\( p_{\text{work}} \) (ppm) values are given in the figure.

Comparing Fig. 2.1 and Fig. 2.2, we can see that they are different in three aspects: 1) The curves in Fig. 2.1 are exactly straight lines, but not in Fig. 2.2; 2) The slopes of the curves in Fig. 2.2 are higher than the corresponding ones in Fig. 2.1; 3) The EMF values for the non-isothermal sensor are also higher than those for the isothermal sensor.
I-3.2 EMF of the SO$_x$ sensors as a function of SO$_2$ partial pressure

Fig. 2.3 gives a series of curves of the EMF response of the isothermal SO$_x$ sensor to the SO$_2$ partial pressure at different temperatures, whereas Fig. 2.4 shows the corresponding curves for a non-isothermal system under the same conditions. It can be seen that the curves in these two figures are all straight lines. However, the EMF response values of the non-isothermal sensor are obviously higher than that of the isothermal sensor because of the temperature difference between the reference and working electrode in the non-isothermal system.

![Graph showing EMF vs. logp(SO$_x$) ppm](image)

**Fig. 2.3** Theoretical EMF of the isothermal SO$_x$ sensor as a function of the SO$_2$ partial pressure. $p_{\text{ref.}}$(SO$_2$) = 100 ppm, $p_{\text{ref.}}$(O$_2$) = $p_{\text{work.}}$(O$_2$) = 0.21 atm. Temperatures (K) are given in the figure.
Fig. 2.4  Theoretical EMF of the non-isothermal SO$_x$ sensor as a function of the SO$_2$ partial pressure. $p_{\text{ref}}(\text{SO}_2)=100$ ppm, $p_{\text{ref}}(\text{O}_2)=p_{\text{work}}(\text{O}_2)=0.21$ atm. Temperatures (K) are given in the figure.

Another difference is that all the curves in Fig. 2.3 cross over at the same point where the EMF is equal to zero when the SO$_2$ partial pressures at both electrodes are the same. The curves in Fig. 2.4 on the contrary do not have such a common point due to the complicated relation between EMF, temperature and ln$p($SO$_x)$ as described in Eq.(13).
I-3.3 Effect of a temperature difference on the EMF response

As shown in Fig. 2.5, the effect of the temperature difference between the reference and the working electrode on the EMF response values of the non-isothermal SO\textsubscript{x} sensor can be expressed by linear curves having all the same value of 0.5472 for the slope as predicted by Eq.(13), since the EMF values from the thermoelectrical power due to the temperature difference are independent of the SO\textsubscript{2} partial pressure.

![Graph showing EMF response as a function of temperature difference and SO\textsubscript{x} concentration](image)

\[ T_{\text{ref}} - T_{\text{work}} \quad (K) \]

**Fig. 2.5** Theoretical EMF of the non-isothermal SO\textsubscript{x} sensor as a function of temperature difference between the two electrodes.

\[ p_{\text{ref.}(SO_2)} = 100 \text{ ppm}, \quad p_{\text{ref.}(O_2)} = p_{\text{work.}(O_2)} = 0.21 \text{ atm.} \]

\[ p_{\text{work.}} \text{ (ppm) are given in the figure.} \]
I-3.4 A new type of \( \text{SO}_x \) sensor utilizing a temperature gradient

Since the 1970s, when electrochemical \( \text{SO}_x \) sensors comprising solid electrolyte concentration cells were first studied, many attempts have been made to apply new types of reference electrodes, including some metals, oxides and/or sulfates instead of the usual \( \text{SO}_2 \) standard gas, because reference gas systems usually make gas sensor devices complicated, and expensive, which may hamper commercial application. On the basis of the above theoretical considerations for non-isothermal effects, a new type of \( \text{SO}_x \) sensor without reference gas system has been designed. The fundamental of this new type of sensor is that upon application of a temperature gradient between the reference and working electrode, it is possible to apply the same \( \text{SO}_2 \) and \( \text{O}_2 \) partial pressures at both electrodes. This means that a very simple \( \text{SO}_x \) sensor can be developed, for example, a disk of Nasicon or other \( \text{Na}^+ \) ion conductor provided with two Pt electrodes and placed in a small furnace which provides a well-defined temperature gradient between the two electrodes and is then exposed to the sample gas. Hence there is no need to construct gas-tight seals at the solid electrolyte in order to separate the sample and reference gas, or to apply a suitable solid reference electrode.

Fig. 2.6 shows the theoretical EMF response of this new type of \( \text{SO}_x \) sensor to the \( \text{SO}_2 \) partial pressure at different temperatures. We can see that higher \( \text{SO}_2 \) concentrations yield lower EMF values. This observation differs from that in Fig. 2.4, which is attributed to the different reference gas concentrations.
Fig. 2.6  Theoretical EMF as a function of SO$_2$ partial pressure for the non-isothermal SO$_x$ sensor without reference gas system.

$p_{\text{ref.}}$(SO$_2$) = $p_{\text{work.}}$(SO$_2$), $p_{\text{ref.}}$(O$_2$) = $p_{\text{work.}}$(O$_2$) = 0.21 atm.

Temperatures (K) are given in the figures.

Fig. 2.7 gives the EMF response of this new type of SO$_x$ sensor as a function of the temperature of the working electrode. It is clear that the curves in Fig. 2.7 have the same slope for the different SO$_2$ partial pressures, while in Fig. 2.2 the slopes of the EMF
response curves vary substantially with the different SO$_2$ partial pressures. Fig. 2.8 shows that the EMF response values of this type of SO$_x$ sensor increase proportionally with the temperature difference between the two electrodes.

![Graph showing EMF response vs. temperature]

$T_{\text{work.}}$ (K)

Fig. 2.7 Theoretical EMF of the non-isothermal SO$_x$ sensor as a function of temperature.

$p_{\text{ref.}}(\text{SO}_2) = p_{\text{work.}}(\text{SO}_2)$, $p_{\text{ref.}}(\text{O}_2) = p_{\text{work.}}(\text{O}_2) = 0.21$ atm.

$p_{\text{work.}}$ (ppm) values are given in the figure.
Fig. 2.8  Theoretical EMF of the $\text{SO}_x$ sensor as a function of the temperature gradient between the two electrodes.

\[ p_{\text{ref}}(\text{SO}_2) = p_{\text{work}}(\text{SO}_2), \quad p_{\text{ref}}(\text{O}_2) = p_{\text{work}}(\text{O}_2) = 0.21 \text{ atm}. \]

I-4. SUMMARY AND FURTHER REMARKS

A new theoretical EMF expression for $\text{SO}_x$ sensors based on a $\text{Na}^+$ ion conducting solid electrolyte has been derived, i.e. Eq.(13) and EMF values were calculated,
\[ \text{EMF} = 10^3 \left[ \frac{RT_2}{2F} \ln \frac{K_p^{II}(SO_x)p^{II}(O_2)}{1 + K_1^{II}(O_2)} - \frac{RT_1}{2F} \ln \frac{K_p^{I}(SO_x)p^{I}(O_2)}{1 + K_1^{I}(O_2)} \right] + 0.5472(T_{ref} - T_{work})(mV) \] (13)

This expression covers both the isothermal and non-isothermal systems and differs from the simple Nernst equation usually employed in the literature, i.e.

\[ \text{EMF} = \frac{RT}{2F} \ln \frac{p^{II}(SO_x)}{p^{I}(SO_2)} \] (6)

On the basis of these two expressions, the theoretical modelling and discussion have been presented for the EMF responses of both the isothermal and non-isothermal SO\textsubscript{x} sensor as a function of SO\textsubscript{2} partial pressure and of temperature. Eq.(13) will be employed to calculate the theoretical EMF values for the SO\textsubscript{x} sensors based on Nasicon and Na\textsuperscript{+}-β\textsuperscript{-}-alumina solid electrolyte as discussed in Chapter 4 and Chapter 5, respectively.
II. Theoretical EMF Expression for Ag\textsuperscript{+}-β'-alumina Based SO\textsubscript{x} Sensors with Silver Metal as Solid Reference

In principle, a solid state SO\textsubscript{x} sensor with Ag\textsuperscript{+}-β'-alumina as solid electrolyte and Ag metal as solid reference can be expressed as,

\[ \text{Pt, Ag / Ag}^{+}\text{-β'-alumina / Ag}_2\text{SO}_4 / (\text{SO}_2, \text{SO}_3, \text{O}_2) \text{ Pt} \] \hspace{1cm} \text{(14)}

The anodic reaction at the silver electrode reads,

\[ \text{Ag} = \text{Ag}^{+} + e^- \] \hspace{1cm} \text{(15)}

while at the cathode the following reactions occur,

\[ \text{SO}_2 + 1/2 \text{O}_2 = \text{SO}_3 \] \hspace{1cm} \text{(16)}
\[ \text{SO}_3 + 1/2 \text{O}_2 + 2e^- = \text{SO}_4^{2-} \] \hspace{1cm} \text{(17)}
\[ \text{SO}_4^{2-} + 2 \text{Ag}^{+} = \text{Ag}_2\text{SO}_4 \] \hspace{1cm} \text{(18)}

Therefore, the total electrochemical reaction of this SO\textsubscript{x} sensor is

\[ \text{SO}_3 + 1/2 \text{O}_2 + 2 \text{Ag} = \text{Ag}_2\text{SO}_4 \] \hspace{1cm} \text{(19)}
When these reactions are at equilibrium, the following equations hold,

\[ \mu^I(\text{Ag}) = \eta^I(\text{Ag}^+) + \eta^I(e^-,\text{Pt}) \quad (20) \]
\[ \mu(\text{SO}_2) + \frac{1}{2} \mu(\text{O}_2) = \mu(\text{SO}_3) \quad (21) \]
\[ \mu(\text{SO}_3) + \frac{1}{2} \mu(\text{O}_2) + 2 \eta^{II}(e^-,\text{Pt}) = \eta(\text{SO}_4^{2-}) \quad (22) \]
\[ \eta(\text{SO}_4^{2-}) + 2 \eta^{II}(\text{Ag}^+) = \mu(\text{Ag}_2\text{SO}_4) \quad (23) \]
\[ \eta^I(e^-,\text{Pt}) = \mu^I(e^-,\text{Pt}) - F\phi_I \quad (24) \]
\[ \eta^{II}(e^-,\text{Pt}) = \mu^{II}(e^-,\text{Pt}) - F\phi_{II} \quad (25) \]
\[ \eta^I(\text{Ag}^+) = \eta^{II}(\text{Ag}^+) \quad (26) \]
\[ \mu_i = \mu_i^\circ + RT\ln a_i \quad (27) \]
\[ \mu^{II}(e^-,\text{Pt}) = \mu^I(e^-,\text{Pt}) \quad (28) \]

Here \( \eta(i) \) represents the electrochemical potential of species \( i \), and \( \phi \) the electrostatic potential. Combining these equations with

\[ \text{EMF} = \phi_{II} - \phi_I \quad (29) \]

yields for the EMF the following expression,

\[ \text{EMF} = \frac{RT}{2F} \ln p(\text{SO}_3) + \frac{RT}{4F} \ln p(\text{O}_2) - \frac{\Delta G^\circ}{2F} \quad (30) \]
assuming \(a(\text{Ag}) = 1\) and \(a(\text{Ag}_2\text{SO}_4) = 1\). Here \(\Delta G^0\) refers to the standard free energy change for reaction (19) and numerical values have been calculated using data from reference[16],

\[
\begin{align*}
\Delta G^0(600-703\text{K}) &= 227.36T-312148 \quad \text{J/mol} \\
\Delta G^0(703-933\text{K}) &= 196.10T-290016 \quad \text{J/mol} \\
\Delta G^0(933-1100\text{K}) &= 165.52T-261600 \quad \text{J/mol}
\end{align*}
\]  

(31) (32) (33)

The equilibrium constant \(K\) of reaction (16) is calculated from reference [16] as

\[K = \exp(-11.15 + 11783/T) \quad (600-1100\text{K})\]  

(34)

the equilibrium \(\text{SO}_3\) partial pressure in Eq.(30) can be expressed as a function of the introduced \(\text{SO}_x\) \((x=2,3)\) partial pressure \(p(\text{SO}_x)\) from the following equations,

\[
p(\text{SO}_x) = p(\text{SO}_2) + p(\text{SO}_3) \\
K = \frac{p(\text{SO}_3)}{p(\text{SO}_2)p(\text{O}_2)}
\]

(35) (36)

Combining Eqs.(35) and (36) yields

\[
p(\text{SO}_3) = \frac{K\sqrt{p(\text{O}_2)}}{1 + K\sqrt{p(\text{O}_2)}}p(\text{SO}_x)
\]

(37)

Combining this equation with Eq.(30) to eliminate \(p(\text{SO}_3)\), one obtains
\[ EMF = E^\circ + \frac{RT}{2F} \ln p(SO_x) \quad (38) \]

with

\[ E^\circ = \frac{RT}{2F} \ln \frac{K_p(O_2)}{1 + K_p(O_2)} - \frac{\Delta G^\circ}{2F} \quad (39) \]

Therefore, according to Eqs.(31) to (34) and Eqs.(38) and (39), the theoretical EMF values for this Ag\(^+\)-\(\beta\)"-alumina SO\(_x\) sensor can be calculated for given temperature and SO\(_x\) partial pressure.

Itoh et al.[10] have reported the theoretical response of a similar type of Ag\(^+\)-\(\beta\)"-alumina based SO\(_x\) sensor. For reaction (16) they obtained

\[ \Delta G^\circ = -97960 + 92.73T \quad \text{J/mol} \quad (600-1100K) \quad (40) \]

and for reaction (19)

\[ \Delta G^\circ = 227.18T - 312000 \quad \text{J/mol} \quad (600-703K) \quad (41) \]
\[ \Delta G^\circ = 195.02T - 289310 \quad \text{J/mol} \quad (703-933K) \quad (42) \]
\[ \Delta G^\circ = 167.46T - 263740 \quad \text{J/mol} \quad (933-1100K) \quad (43) \]

Comparing Eqs.(40) to (43) with Eqs.(31) to (34) reveals good agreement.

Considering the possible interference of CO\(_2\) and NO\(_x\) with the sensor's response to SO\(_x\), we have to investigate the formation of Ag\(_2\)CO\(_3\) and AgNO\(_3\) on the surface of the
present solid electrolyte. Literature data[16] reveal that $\text{Ag}_2\text{CO}_3$ will decompose at $220^\circ\text{C}$, and $\text{AgNO}_3$ at about $330^\circ\text{C}$. The $\text{SO}_x$ sensor usually has to be used at temperatures higher than $450^\circ\text{C}$, because it is difficult for $\text{SO}_2$ and $\text{SO}_3$ to establish the oxidation equilibrium at lower temperatures even in the presence of an efficient catalyst. Therefore, in principle, this $\text{SO}_x$ sensor is expected to exhibit good selectivity to $\text{SO}_x$ against $\text{CO}_2$ and $\text{NO}_x$. 


III. Theoretical EMF Expression for NO$_x$ Sensors

III-1. DERIVATION OF EMF EQUATION FOR CONCENTRATION CELLS

Dekker[15] has derived a theoretical derivation of the EMF-NO$_x$ concentration relation for solid state NO$_x$ concentration cells with Ba(NO$_3$)$_2$ as solid electrolyte and NO$_2$ standard gas or a Pb(NO$_3$)$_2$/PbO two-phase mixture as the gaseous or solid reference electrode. The expression for the EMF reads,

$$EMF = \frac{RT}{F} \ln \frac{p^{I}(NO_2)}{P^{I}(NO_2)} + \frac{RT}{2F} \ln \frac{p^{II}(O_2)}{p^{I}(O_2)}$$  \tag{44}$$

with the assumption that

$$\mu^{II}(Ba(NO_3)_2) = \mu^{I}(Ba(NO_3)_2)$$  \tag{45}$$

In the case of a NO$_x$ sensor using Na$^+$-β"-alumina as the solid electrolyte, the sensor can be represented by

I Pt,NO$_x$O$_2$/NaNO$_3$/Na$^+$-β"-alumina/NaNO$_3$/O$_2$/NO$_x$ Pt  II  \tag{46}$$
The NaNO$_3$ layers on the solid electrolyte are obtained by a thermal treatment of Na$^+$-$\beta^n$-alumina in NO$_x$ ambients. The redox reactions for this NO$_x$ sensor are the same as those used to derive expression (44), i.e.

\[
\text{NO}_2 + \frac{1}{2} \text{O}_2 + e^- = \text{NO}_3^-
\]  

(47)

while the subsequent reaction with the solid electrolyte is given by

\[
\text{Na}^+ + \text{NO}_3^- \rightarrow \text{NaNO}_3
\]  

(48)

instead of

\[
\text{Ba}^{2+} + 2\text{NO}_3^- \rightarrow \text{Ba(NO}_3)_2
\]  

(49)

as used by Dekker[15]. However, we can still use the same derivation and obtain the same EMF expression as Eq.(44), assuming

\[
\mu^\Pi(\text{NaNO}_3) = \mu^I(\text{NaNO}_3)
\]  

(50)

In fact, the change of solid electrolyte does not change the Nernst equation of the NO$_x$ sensor. In the case of Na$^+-$-$\beta^n$-alumina provided with surface layers of NaNO$_3$ the electrolyte behaves as pure NaNO$_3$. The temperature, NO$_2$ and O$_2$ partial pressures determine the EMF expression.
III-2. EMF CALCULATION FOR A Ag⁺-β"'-ALUMINA BASED NOₓ SENSOR

Similar to Ag⁺-β'-alumina based SOₓ sensors, a solid state NOₓ sensor with Ag⁺-β"'-alumina as solid electrolyte and Ag metal as solid reference electrode can be designed,

\[ \text{I Pt, Ag / Ag}^{+}\text{-β}'\text{-alumina / AgNO}_3 / (\text{NO, O}_2, \text{NO}_2) \text{ Pt II} \]  \hspace{1cm} (51)

At the silver electrode the anodic reaction reads,

\[ \text{Ag} = \text{Ag}^{+} + e^- \]  \hspace{1cm} (52)

while at the porous Pt II electrode the cathodic reaction is given by,

\[ \text{NO}_2 + 1/2 \text{O}_2 + e^- = \text{NO}_3^- \]  \hspace{1cm} (53)

\text{NO}_3^- \text{ reacts with the solid electrolyte to form silver nitrate according to the reaction,}

\[ \text{NO}_3^- + \text{Ag}^+ = \text{AgNO}_3 \] \hspace{1cm} (54)

The total redox reaction of this NOₓ sensor, therefore, reads

\[ \text{NO}_2 + 1/2 \text{O}_2 + \text{Ag} = \text{AgNO}_3 \]  \hspace{1cm} (55)
At equilibrium, the undermentioned equations hold true:

\[ \mu^I(\text{Ag}) = \eta^I(\text{Ag}^+) + \eta^I(e^-,\text{Pt}) \]  
(56)

\[ \mu(\text{NO}_2) + 1/2 \mu(\text{O}_2) + \eta^{II}(e^-,\text{Pt}) = \eta(\text{NO}_3^-) \]  
(57)

\[ \eta(\text{NO}_3^-) + \eta^{II}(\text{Ag}^+) = \mu(\text{AgNO}_3) \]  
(58)

\[ \eta^I(e^-,\text{Pt}) = \mu^I(e^-,\text{Pt}) - F\phi_I \]  
(59)

\[ \eta^{II}(e^-,\text{Pt}) = \mu^{II}(e^-,\text{Pt}) - F\phi_{II} \]  
(60)

\[ \eta^I(\text{Ag}^+) = \eta^{II}(\text{Ag}^+) \]  
(61)

Upon combining these equations with the relation between the chemical potential of species \( i \) and its activity \( a_i \),

\[ \mu_i = \mu^i_\circ + RT\ln a_i \]  
(62)

and the electrostatic potential difference

\[ \text{EMF} = \phi_{II} - \phi_I \]  
(63)

one obtains

\[ \text{EMF} = \frac{RT}{F} \ln p(\text{NO})_2 + \frac{RT}{2F} \ln p(\text{O}_2) - \frac{\Delta G^\circ}{F} \]  
(64)
assuming $a(\text{Ag}) = 1$ and $a(\text{AgNO}_3) = 1$. Here $\Delta G^\circ$ refers to the standard free energy change for reaction (55), and the numerical values have been calculated using the data in reference [16], i.e.

\[
\Delta G^\circ(298-433K) = 239.6T-152130 \quad \text{J/mol} \quad (65)
\]
\[
\Delta G^\circ(433-483K) = 224.5T-145578 \quad \text{J/mol} \quad (66)
\]
\[
\Delta G^\circ(483-600K) = 196.4T-131871 \quad \text{J/mol} \quad (67)
\]

Considering the conversion of NO to NO$_2$ one has

\[
\text{NO} + \frac{1}{2} \text{O}_2 = \text{NO}_2 \quad (68)
\]
\[
\ln K = -9.15 + 6993/T \quad (69)
\]

\[
p(\text{NO}_2) = \frac{K\sqrt{p(\text{O}_2)}}{1+K\sqrt{p(\text{O}_2)}} \quad (70)
\]

Combining Eqs.(64) and (70) to eliminate $p(\text{NO}_2)$, we obtain

\[
EMF = \frac{RT}{F} \ln p(\text{NO}_x) + \frac{RT}{F} \ln \frac{Kp(\text{O}_2)}{1+K\sqrt{p(\text{O}_2)}} - \frac{\Delta G^\circ}{F} \quad (71)
\]

According to Eqs.(65) to (67), (69) and (71), the theoretical EMF values can be calculated at fixed temperatures with the introduced NO$_x$ and O$_2$ partial pressures.
III-3. DISCUSSION AND FURTHER REMARKS

In order to know the relation between the sensor operating temperature and the lowest limit of the NO\textsubscript{x} (x=1,2) concentration which can be detected by this sensor, and to check our aim to monitor NO\textsubscript{x} in the range of 10 to 10,000 ppm with the sensor operating at temperatures above 100°C, we present here the equations calculated from the last section showing the relations of the sensor EMF in terms of operating temperature and NO\textsubscript{x} (x=1,2) concentration to be measured:

\[ EMF(25-160^\circ C) = 1576.7 - 2.483T + 0.086T ln(p(NO_x)) + \]
\[ 0.086T ln \frac{Kp(O_2)}{1+Kp(O_2)} (mV) \]  
\[ (72) \]

\[ EMF(160-210^\circ C) = 1508.8 - 2.327T + 0.086T ln(p(NO_x)) + \]
\[ 0.086T ln \frac{Kp(O_2)}{1+Kp(O_2)} (mV) \]  
\[ (73) \]

\[ EMF(210-327^\circ C) = 1366.8 - 2.036T + 0.086T ln(p(NO_x)) + \]
\[ 0.086T ln \frac{Kp(O_2)}{1+Kp(O_2)} (mV) \]  
\[ (74) \]

Table 2.1 gives the relation between the operating temperature and the detection limit of the NO\textsubscript{x} concentrations as calculated from Eqs.(72) to (74) with p(O\textsubscript{2})=0.21 atm.
Table 2.1. Relation between temperature and NO\textsubscript{x} detection limit

<table>
<thead>
<tr>
<th>Temp.(°C)</th>
<th>100</th>
<th>150</th>
<th>170</th>
<th>200</th>
<th>210</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x} (ppm)</td>
<td>0.004</td>
<td>1.17</td>
<td>8</td>
<td>98</td>
<td>212</td>
<td>2760</td>
<td>41580</td>
</tr>
</tbody>
</table>

For instance, if we choose 150°C as the operating temperature for 10 to 200 ppm NO\textsubscript{x}, we obtain an EMF of the sensor in the range of 70 to 190 mV as indicated in Table 2.2.

Table 2.2. Relation between NO\textsubscript{x} concentration and EMF at 150°C

<table>
<thead>
<tr>
<th>NO\textsubscript{x} (ppm)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>130</th>
<th>160</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMF (mV)</td>
<td>78.2</td>
<td>103.4</td>
<td>118.2</td>
<td>128.7</td>
<td>143.5</td>
<td>154.0</td>
<td>162.1</td>
<td>171.6</td>
<td>179.2</td>
<td>187.4</td>
</tr>
</tbody>
</table>

Similar data can be given for other operating temperatures and NO\textsubscript{x} concentrations.

In the case of practical measurements, one should also consider the role of the interfering gases such as CO and CO\textsubscript{2} on the sensor response. In the presence of CO\textsubscript{2}, the Ag\textsuperscript{+}-β\textsuperscript{-}-alumina solid electrolyte may react to form Ag\textsubscript{2}CO\textsubscript{3}. This leads to the following sensor configuration,
The redox reaction of this sensor is

$$2 \text{Ag} + \text{CO}_2 + 1/2 \text{O}_2 = \text{Ag}_2\text{CO}_3$$ (76)

For this reaction, the standard free energy change can be expressed as[16],

$$\Delta G^\circ(298-493\text{K}) = 110895-231.1T \quad \text{J/mol}$$ (77)

and the theoretical EMF of the sensor is given by

$$\text{EMF} = 574.7-1.198T + 0.022T\ln(p(\text{O}_2)) + 0.043T\ln(p(\text{CO}_2)) \quad \text{(mV)}$$ (78)

With this equation and Eqs.(72) to (74) we can discuss the interference of CO/CO$_2$ contaminations on the NO$_x$ sensor response. For instance, at 150°C and P(\text{O}_2)=0.21 atm with CO$_2$ in the concentration range of 10 to 200 ppm, Eq.(78) will give negative EMF values. This means that the sensor represented by (75) does not work under such conditions, hence the same concentration of CO$_2$ gas can not interfere with the NO$_x$ detection.

Furthermore, if we define the selectivity of the sensor to NO$_x$ against CO$_2$ as Eq.(79) where $p^\circ(\text{CO}_2)$ and $p^\circ(\text{NO}_x)$ stand for the CO$_2$ and NO$_x$ partial pressure for sensors (51) and (75) to have the same EMF value. This definition gives insight into the difference
in the interfering gas concentration and the measured gas concentration in order to lead for both species to the same EMF signal.

\[
Selectivity = \frac{P^0(CO_2)}{P^0(NO_x)}
\]  

(79)

Taking as an example \( T = 150^\circ C \), \( p(O_2) = 0.21 \text{ atm} \) and \( p(NO_x) = 10 \text{ ppm} \) one obtains a selectivity of \( 4 \times 10^5 \). Therefore, it is obvious that the selectivity of the Ag\(^+\)-\(\beta\)-alumina NO\(_x\) sensor to NO\(_x\) against CO\(_2\) is excellent. In general, combining Eqs.(72) to (74) with Eq.(78) yields

\[
Selectivity = C_1 p(NO_x)p(O_2)\ln\frac{C_2}{T}
\]  

(80)

Here \( C_1 \) and \( C_2 \) are two constants which can be calculated using the equations mentioned above. As can be seen from Eq.(80) the selectivity of the Ag\(^+\)-\(\beta\)-alumina NO\(_x\) sensor is better at higher concentrations of NO\(_x\) and O\(_2\) gases and at lower operating temperatures.

REFERENCES


CHAPTER 3

STUDY ON Na$_2$SO$_4$-BASED SOLID ELECTROLYTE MATERIALS

ABSTRACT

Na$_2$SO$_4$-based solid electrolyte with compositions Na$_2$SO$_4$ + x mol% Y$_2$(SO$_4$)$_3$ (x = 0, 3, 5, 6, 9, 12, 15) and Na$_2$SO$_4$ + y mol% La$_2$(SO$_4$)$_3$ (y = 0, 2, 4, 6, 8) were synthesized by a solid state reaction. The crystal structure, phases, and electrical conductivity of these solid electrolytes were studied by XRD, SEM, EDX, DTA, TGA and Impedance Spectroscopy. Upon doping with La$_2$(SO$_4$)$_3$ or Y$_2$(SO$_4$)$_3$ the high-temperature fast-ion conducting phase Na$_2$SO$_4$-I can be stabilized down to room temperature. Doping increases the ionic conductivity as well. Of these solid electrolytes the Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ and Na$_2$SO$_4$ + 4 mol% La$_2$(SO$_4$)$_3$ solid solutions exhibit the highest ionic conductivity values (at 400°C, 1.76x10$^{-2}$ S·cm$^{-1}$ and 2.95x10$^{-2}$ S·cm$^{-1}$, respectively) and lowest activation enthalpies (0.38 eV and 0.37 eV, respectively). When x≥12 or y≥8, the Na$_2$SO$_4$-I structure can be completely stabilized down to room temperature. For the solid electrolytes with x=5, Na$_2$WO$_4$ was used to further stabilize phase I, and to improve the mechanical properties. In the Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ + m mol% Na$_2$WO$_4$ (m = 5, 10, 15, 20) samples, XRD analysis reveals a Na$_2$SO$_4$-I structure to be stable at room
temperature as is illustrated by DTA. Impedance measurements show that doping these solid solutions with Na$_2$WO$_4$ decreases the ionic conductivity. However, their conductivity is still higher than that of undoped Na$_2$SO$_4$. From a point of view of practical application as SO$_x$ sensor material, the Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ + Na$_2$WO$_4$ materials are better than undoped Na$_2$SO$_4$ because of their higher conductivity, and absence of a phase transition.
1. INTRODUCTION

Sulfur oxides (SO₂ and SO₃) are widely emitted in many industrial combustion processes and the detection of these gases has attracted widespread attention in recent years not only for the process control but also for the detection of air pollution. Since the early seventies, many efforts have been devoted to the development of potentiometric sensors based on SO₂-O₂-SO₃ concentration cells using alkali sulfates as solid electrolytes[1-4]. At elevated temperatures, alkali sulfates are alkali ion conductors. Gauthier et al.[1,2] first pointed out that K₂SO₄ can be used as a solid electrolyte for a SO₂ sensor. Following this study, Na₂SO₄ and Li₂SO₄ were examined by Jacob and Rao[3], and Worrell and Liu[4], respectively. In these studies, the EMF of the sensor agreed with the value calculated from the Nernst equation, if a small difference in SOₓ partial pressure between the reference and measuring electrode was applied. However, a large difference in SOₓ partial pressure yielded EMF values which were lower than the theoretical values. This deviation was due to the occurrence of a phase transition, poor sintering, and low values of the electrical conductivity[5-7].

Na₂SO₄ exhibits several phase transitions[8]. The room temperature phase V is orthorhombic in nature. When it is dried, a metastable phase III with a orthorhombic structure is resulted, and it takes some days to undergo a slow III → V phase transition. The prominent phase transition at 241°C results in the hexagonal phase I, which can not be quenched at room temperature. The hexagonal phase Na₂SO₄-I (241°C - 884°C) with the lattice parameters of a = 5.38 Å and c = 7.26 Å[12] is a sodium ion conductor, and can be used as a solid electrolyte in a SOₓ sensor. However, the volume change due to
the III-I phase transition will cause micro cracks in the Na₂SO₄ material, while the poor sinterability of this material may lead to the presence of micro pores. All these microscopic defects will lead to gas permeation and hence to lowering of the EMF values. In order to avoid these problems, many dopants[8-11] such as Ln₂(SO₄)₃ (Ln = rare earth elements), Na₂WO₄ and NaVO₃, SiO₂ and Al₂O₃ were employed not only to increase the ionic conductivity of Na₂SO₄, but also to stabilize phase I down to room temperature, and to improve the sinterability. Usually, the rare earth sulfates act both as a stabilizer and as a conductivity increasing dopant. As a stabilizer, it reacts with sodium sulfate to form a solid solution, which is more stable than the pure Na₂SO₄-I phase, while as a doping element, the rare earth ion replaces the sodium ion in the lattice, under the formation of sodium ion vacancies for charge compensation, which will obviously increase the ionic conductivity. More recently, Dekker[12] has described the behaviour of a solid phase mixture, comprising Na₂SO₄ + Y₂(SO₄)₃ + PSZ. When partially stabilized zirconia (PSZ) is dispersed into the solid solution Na₂SO₄ - Y₂(SO₄)₃ the phase transition III-I is suppressed completely by a transformation toughening mechanism.

In the present work, Y₂(SO₄)₃, La₂(SO₄)₃ and Na₂WO₄ were applied to improve the phase stability, and electrical conductivity of the Na₂SO₄ based solid electrolyte.

2. EXPERIMENTAL ASPECTS

2.1 Materials

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Y$_2$(SO$_4$)$_3$ and La$_2$(SO$_4$)$_3$ were prepared from Y$_2$O$_3$ and La$_2$O$_3$ by a wet chemical method. Y$_2$O$_3$ (or La$_2$O$_3$) of 4N purity was dissolved in hot HNO$_3$ to yield a Y(NO$_3$)$_3$ (or La(NO$_3$)$_3$) solution. Y$_2$(SO$_4$)$_3$ (or La$_2$(SO$_4$)$_3$) was synthesized by adding concentrated H$_2$SO$_4$ to the rare earth nitrate solution and heating. Na$_2$SO$_4$ and Na$_2$WO$_4$·2H$_2$O (Shanghai Yuenong Chemicals Co. Ltd., AR) were dried at 200°C for 3 hr in order to eliminate any water content and to obtain pure Na$_2$SO$_4$ and Na$_2$WO$_4$. Mixtures of appropriate amounts of Na$_2$SO$_4$, Y$_2$(SO$_4$)$_3$ (or La$_2$(SO$_4$)$_3$), and Na$_2$SO$_4$, Y$_2$(SO$_4$)$_3$ (or La$_2$(SO$_4$)$_3$) and Na$_2$WO$_4$ were ground and calcined at 650°C for 3 hr. The calcined samples were reground and pelletized (100 kg/cm$^2$) and subsequently sintered at 700°C for 6 hr in air. The specimens were ground, pelletized and sintered in air 3 times in order to obtain dense pellets with a diameter of 1.3 cm and a thickness of 0.2 cm. It was observed that some high Y$_2$(SO$_4$)$_3$ or La$_2$(SO$_4$)$_3$ doped Na$_2$SO$_4$ samples partially melted during sintering, while the doping of Na$_2$WO$_4$ results in the absence of this partial melting. Furthermore, the mechanical properties of the pellets was substantially improved, the dense (relative density 95.5%) and tough pellets were obtained.

2.2 Measurements

The XRD patterns of the specimens were recorded on a D/max ra 12kW Diffractometer (Rikadenki, Japan). An X-650 SEM equipped with EDX (Hitachi, Japan) was used to observe the morphology of the polished surface of the specimens. DTA and TG were employed to investigate the phase transition and thermal stability of the sample materials using a DF-30 Thermoanalyzer (Shimadsu, Japan) and a Simultan Thermoanalyzer (Model 429). The ionic conductivity of the specimens was measured by the Impedance
Spectroscopy technique using a GenRad 1689 Precise RLC Digibridge computer system with a frequency range of 12 Hz to 100 kHz in the temperature range of 100 to 700°C. Fig. 3.1 gives a schematical outline of the system for measuring the temperature and composition dependence of the electrical conductivity of the solid solutions.

1. Solid electrolyte  2. Pt electrodes
3. Pt leads  4. 1689 GenRad Digibridge computer system
5 and 7. Thermocouple
6. Digital multimeter for temperature measurement
8. JWK-702 Precise temperature controller  9. Furnace

Fig. 3.1  Schematical outline of the system for the measurement of the electrical conductivity.
3. RESULTS AND DISCUSSION

3.1 Na$_2$SO$_4$ + x mol% Y$_2$(SO$_4$)$_3$ (x = 0, 3, 5, 6, 9, 12, 15)

After sintering the polished surface of the undoped Na$_2$SO$_4$ specimen (x=0) revealed a dense microstructure as is shown in Fig. 3.2(a). The grain size is not uniform. When Y$_2$(SO$_4$)$_3$ is added to Na$_2$SO$_4$, the surface microstructure changes substantially. Fig. 3.2(b) is an example for a specimen with x=15.

Fig. 3.3(a) presents the DTA curve for the sample of Na$_2$SO$_4$ + 12 mol% Y$_2$(SO$_4$)$_3$ before sintering and Fig. 3.3(b) presents the DTA curve for the same sample after sintering 3 times at 700°C for 6 hrs in air. Before sintering the DTA pattern of the Na$_2$SO$_4$ + 12mol% Y$_2$(SO$_4$)$_3$ mixture resembles the pattern for undoped Na$_2$SO$_4$. There are three peaks at 135°C, 240°C and 880°C, indicating the release of absorbed water vapour, the III-I phase transition and the melting point of Na$_2$SO$_4$, respectively. After sintering the Na$_2$SO$_4$-Y$_2$(SO$_4$)$_3$ solid solution is formed, and yields a different DTA curve with only one peak at 833°C, being its melting point. The III-I phase transition is absent in this Na$_2$SO$_4$-Y$_2$(SO$_4$)$_3$ solid solution. The Na$_2$SO$_4$-I phase has been fully stabilized down to room temperature, and the solid solution does not absorb water vapour anymore. Na$_2$SO$_4$ + 15 mol% Y$_2$(SO$_4$)$_3$ exhibits a DTA pattern similar to that in Fig. 3.3(b), but the melting point is 820°C. For the specimens with x<9 mol% in the Na$_2$SO$_4$ + x mol% Y$_2$(SO$_4$)$_3$ system, the III-I phase transition still exists at 240°C. However, with increasing doping amount a weaker peak results concordant to the partial stabilization of the Na$_2$SO$_4$-I phase by Y$_2$(SO$_4$)$_3$.
Fig. 3.2  Microstructure of solid solutions after sintering

(a) undoped Na$_2$SO$_4$, (b) Na$_2$SO$_4$ + 15 mol% Y$_2$(SO$_4$)$_3$. 

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Fig. 3.3  DTA curves for Na$_2$SO$_4$ + 12 mol% Y$_2$(SO$_4$)$_3$

(a) before sintering;  (b) after sintering
The XRD analysis gives results which are in agreement with the DTA results as mentioned below. The undoped Na$_2$SO$_4$ exhibits a phase III structure at room temperature. For $x \leq 9$ mol%, the XRD pattern reveals a mixture of phases I and III, the amount of phase I being larger with increasing amount of dopant. When $x \geq 12$ mol%, the XRD pattern is a pure phase-I pattern, the only difference being a larger $d$ value compared to that of an undoped Na$_2$SO$_4$-I phase, indicating the slight expansion of the unit cell for the Na$_2$SO$_4$-Y$_2$(SO$_4$)$_3$ solid solution.

![Graph showing Arrhenius plots of ionic conductivity](image)

Fig. 3.4 Arrhenius plots of the ionic conductivity of the Na$_2$SO$_4$-Y$_2$(SO$_4$)$_3$ solid solutions as a function of temperature, values for $x$ are given in the respective figure.
Figs. 3.4 shows the ionic conductivity of the Na$_2$SO$_4$ + x mol% Y$_2$(SO$_4$)$_3$ (x=0,3,5,6,12) solid solutions as a function of temperature. Table 3.1 presents the conductivity activation enthalpies as calculated from the Arrhenius curves. Fig. 3.5 gives the relation of the isothermal conductivities and the amount of Y$_2$(SO$_4$)$_3$ doping.

Table 3.1  Ionic conductivity and activation enthalpies of the Na$_2$SO$_4$ + x mol% Y$_2$(SO$_4$)$_3$ solid solutions

\[ \log(\sigma T) = A/T + B, \Delta H = -2.303A \cdot R \ (eV) \]

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<th>x</th>
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Fig. 3.5 Isothermal Conductivities of the Na₂SO₄-Y₂(SO₄)₃ solid solutions as a function of the dopant concentrations.

As can be seen from Fig. 3.4 the curves of solid solutions with $x < 12$ mol% exhibit two different slopes in the low and high temperature range, the slope at higher temperatures being smaller than that at lower temperatures. This result is due to the different ion conducting pathways because of the I-III phase transition. At higher temperatures, Na₂SO₄-I constitutes the stable phase, and this phase exhibits a high ionic conductivity, and a low activation enthalpy. However, at lower temperatures, the material comprises
a mixture of phases I and III. Both phases exhibit sodium ion conductivity via sodium ion vacancies. The ionic conductivity of phase III material is smaller than that of phase I material. Moreover the conductivity activation enthalpy of phase III is larger than that of phase I. Therefore, the conductivity activation enthalpy increases below the phase transition. For x = 12 mol% phase-I is completely stabilized down to room temperature, therefore a straight line of ln(σT) versus 1/T was observed. Doping with Y₂(SO₄)₃ increases the ionic conductivity of Na₂SO₄. The highest conductivity (at 400°C, σ = 1.76x10⁻² S·cm⁻¹) and lowest activation enthalpy (0.38 eV) are obtained with Na₂SO₄ + 5 mol% Y₂(SO₄)₃. This result can be explained if we consider that the dopant ion Y³⁺ ion will occupy a Na⁺ ion in the lattice of Na₂SO₄-I to produce two sodium ion vacancies. With increasing Y₂(SO₄)₃ doping level, the sodium ion vacancies may interact with the dopant ions to form a kind of defect cluster. Clustering of defects will block the motion of Na⁺ ions and hence decrease the ionic conductivity. The appropriate doping amount of Y₂(SO₄)₃ for which no defect-defect interactions occur is about 5 mol% as can be seen in Fig. 3.5.

A more extended discussion of the defect chemistry of doped Na₂SO₄ has been given by Dekker[12] and Schoonman[13]. The present results are fully in line with the reported defect chemistry.

3.2 Na₂SO₄ + y mol% La₂(SO₄)₃ (y = 2, 4, 6, 8)

The DTA curves and XRD patterns for these solid solutions are almost the same as those with the Y₂(SO₄)₃ dopant. Fig. 3.6 shows the relation between the ionic conductivity and the temperature for the specimens with y = 2, 4, 6, 8, respectively.
Table 3.2 presents the conductivity activation enthalpies as calculated from these Arrhenius plots. Fig. 3.7 shows the isothermal ionic conductivity as a function of the La$_2$(SO$_4$)$_3$ doping amount. It is apparent that the conductivity plots for $y < 8$ mol% also exhibit two different slopes at high and low temperatures. When $y = 8$ mol%, phase I is completely stabilized, and the conductivity plot displays a straight line. La$_2$(SO$_4$)$_3$ has the same function of increasing the conductivity of Na$_2$SO$_4$ as Y$_2$(SO$_4$)$_3$.

![Arrhenius plots of the ionic conductivity of the Na$_2$SO$_4$-La$_2$(SO$_4$)$_3$ solid solutions as a function of temperature, values for $y$ are given in the respective figure.](image)

Fig. 3.6  Arrhenius plots of the ionic conductivity of the Na$_2$SO$_4$-La$_2$(SO$_4$)$_3$ solid solutions as a function of temperature, values for $y$ are given in the respective figure.
Table 3.2 Ionic conductivity and activation enthalpies for $\text{Na}_2\text{SO}_4 + y \text{ mol}\% \text{La}_2(\text{SO}_4)_3$ solid solutions

$$
\log(\sigma T) = A/T + B, \ \Delta H = -2.303A \cdot R \ (\text{eV})
$$

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<th>$B$ (eV)</th>
<th>$\Delta H$ (eV)</th>
<th>$\sigma(400^\circ \text{C})$ (S · cm$^{-1}$)</th>
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<tr>
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<td>3.78</td>
<td>0.46</td>
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</table>
Fig. 3.7  Isothermal conductivities of the Na$_2$SO$_4$ - La$_2$(SO$_4$)$_3$

solid solutions as a function of dopant concentrations.

In Fig. 3.7, the maximum conductivity and the minimum activation enthalpy are achieved for Na$_2$SO$_4$ + 4 mol% La$_2$(SO$_4$)$_3$. At 400°C, the conductivity is as high as 2.95x10$^{-2}$ S·cm$^{-1}$, and at 290°C the ionic conductivity is 3.87x10$^{-3}$ S·cm$^{-1}$, and $\Delta H=0.37$ eV. This result is better than the reported result in the literature[8], i.e. at 290°C, $\sigma=1.08x10^{-3}$ S·cm$^{-1}$, and $\Delta H=0.50$ eV. It is noted that the highest ionic conductivity of Na$_2$SO$_4$ - Y$_2$(SO$_4$)$_3$ solid solutions is achieved with 5 mol% Y$_2$(SO$_4$)$_3$, while for Na$_2$SO$_4$ - La$_2$(SO$_4$)$_3$ solid solutions $\sigma_{\text{max}}$ appears with 4 mol% La$_2$(SO$_4$)$_3$. This could be explained by the difference in the radii of sodium, yttrium and lanthanum ions. The radius of an

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yttrium ion is smaller than that of a lanthanum ion, but larger than that of a sodium ion. Because the radius difference between Na\(^+\) and Y\(^{3+}\) ions is smaller than that between Na\(^+\) and La\(^{3+}\), higher concentrations of Y\(_2\)(SO\(_4\))\(_3\) can be dissolved in Na\(_2\)SO\(_4\) compared to La\(_2\)(SO\(_4\))\(_3\), i.e. it is easier to form defect clusters in Na\(_2\)SO\(_4\) - La\(_2\)(SO\(_4\))\(_3\) solid solutions than in Na\(_2\)SO\(_4\) - Y\(_2\)(SO\(_4\))\(_3\) solid solutions. The concentrations to form cluster in Na\(_2\)SO\(_4\) - La\(_2\)(SO\(_4\))\(_3\) and Na\(_2\)SO\(_4\) - Y\(_2\)(SO\(_4\))\(_3\) solid solutions are 4 mol\% and 5 mol\%, respectively.

3.3 Na\(_2\)SO\(_4\) + 5 mol\% Y\(_2\)(SO\(_4\))\(_3\) + m mol\% Na\(_2\)WO\(_4\) (m=0,5,10,15,20)

A literature survey\([8]\) reveals that Na\(_2\)WO\(_4\) has three phases from room temperature to its melting point 697°C. The cubic spinel type phase \(\gamma\) is stable up to 588°C, where it undergoes a phase transition. The \(\beta\)-phase is stable only over a degree or so and then a \(\beta \rightarrow \alpha\) transition occurs. The \(\beta\)-phase is the most conducting phase, the conductivity of the order of \(10^{-2} \text{ s \cdot cm}^{-1}\) at 589°C was reported. The conductivity of Na\(_2\)WO\(_4\) is less than Na\(_2\)SO\(_4\) at lower temperatures suggesting higher activation enthalpy of the formation and migration of Na\(^+\) ions in Na\(_2\)WO\(_4\) than in Na\(_2\)SO\(_4\). Na\(_2\)SO\(_4\)-Na\(_2\)WO\(_4\) composites can be solid solutions or two phase mixtures, depending on the composition of the composites.

In the present study of the properties and conductivity behaviour of the Na\(_2\)SO\(_4\) + 5 mol\% Y\(_2\)(SO\(_4\))\(_3\) + m mol\% Na\(_2\)WO\(_4\) (m=0,5,10,15,20) system, XRD analysis yields similar diffraction pattern for the different amounts of Na\(_2\)WO\(_4\). The d values of the strong peaks reveal a small change compared to those of Na\(_2\)SO\(_4\) + 5 mol\% Y\(_2\)(SO\(_4\))\(_3\). This XRD pattern refers to a solid solution with Na\(_2\)SO\(_4\)-I structure, indicating that as few as 5 mol\% Na\(_2\)WO\(_4\) together with 5 mol\% Y\(_2\)(SO\(_4\))\(_3\) can stabilize Na\(_2\)SO\(_4\)-I.
However, there are one or two additional peaks which are not part of I pattern, but related to Na$_2$WO$_4$ pattern although surprisingly not the strongest peaks of Na$_2$WO$_4$. These additional peaks suggest the presence of the minor second phase Na$_2$WO$_4$ in addition to the solid solution. However, DTA did not indicate any phase transition or melting peaks from the second phase, for instance, DTA demonstrates that the specimen with 5 mol% Na$_2$WO$_4$ is stable in the temperature range of 20°C to 875°C at which it melts. In addition, no inhomogeneous distribution of elements was observed by EDX, indicating very small size of the second phase particles. Fig. 3.8 (a) and (b) show the surface microstructure of the m=10 specimen after calcining and after three times of sintering, respectively. It can be seen from Fig. 3.8 (a) that solid state reaction takes place during calcining. After sintering the further solid state reaction undergoes, and the specimen has a dense surface structure.
Fig. 3.8  Microstructure of the Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ + 10 mol% Na$_2$WO$_4$ specimen after calcining and after sintering.
Fig. 3.9 presents the Arrhenius plots of the temperature dependence of the ionic conductivity of these specimens. Table 3.3 lists the $\Delta H$ values as calculated from Fig. 3.9, and Fig. 3.10 gives the ionic conductivity isotherms.

Fig. 3.9   Temperature dependence of the ionic conductivity of the 

$\text{Na}_2\text{SO}_4 + 5\text{ mol}\%\ \text{Y}_2(\text{SO}_4)_3 + m\ \text{mol}\%\ \text{Na}_2\text{WO}_4$ specimens.
Table 3.3  Ionic conductivity and activation enthalpies of the

\[ \text{Na}_2\text{SO}_4 + 5 \text{ mol}\% \ Y_2(\text{SO}_4)_3 + m \text{ mol}\% \ Na_2\text{WO}_4 \text{ specimens} \]

\[ \log(\sigma T) = A/T + B, \ \Delta H = -2.303A \cdot R \ (\text{eV}) \]

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<th>m</th>
<th>Temp. range (°C)</th>
<th>A</th>
<th>B</th>
<th>(\Delta H) (eV)</th>
<th>(\sigma(400^\circ\text{C})) (S·cm(^{-1}))</th>
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<td>0.60</td>
<td>3.90\times10(^{-4})</td>
</tr>
<tr>
<td>10</td>
<td>100-700</td>
<td>-3303</td>
<td>4.63</td>
<td>0.66</td>
<td>7.89\times10(^{-4})</td>
</tr>
<tr>
<td>15</td>
<td>100-700</td>
<td>-2919</td>
<td>3.93</td>
<td>0.58</td>
<td>5.88\times10(^{-4})</td>
</tr>
<tr>
<td>20</td>
<td>100-700</td>
<td>-2902</td>
<td>3.67</td>
<td>0.57</td>
<td>2.19\times10(^{-4})</td>
</tr>
</tbody>
</table>
Fig. 3.10  Ionic conductivity isotherms of the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ - Na₂WO₄ specimens as a function of Na₂WO₄ concentrations.

It can be seen that doping with Na₂WO₄ decreases the ionic conductivity of the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ material. However, the conductivity decrease is not very sensitive to the Na₂WO₄ concentration. If we assume the presence of Na₂WO₄ as a second phase in addition to the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ - Na₂WO₄ solid solutions, and consider that the sodium ion conductivity of Na₂WO₄ is lower than that of Na₂SO₄, the conductivity decrease with Na₂WO₄ doping is reasonable. However, its conductivity is still higher than that of the undoped Na₂SO₄ (compare Tables 3.1 and 3.3). From a point
is still higher than that of the undoped Na$_2$SO$_4$ (compare Tables 3.1 and 3.3). From a
point of view of practical application as a SO$_2$ sensor material, this Na$_2$SO$_4$ + 5 mol% 
Y$_2$(SO$_4$)$_3$ + Na$_2$WO$_4$ system is better than undoped Na$_2$SO$_4$ material because of the
higher conductivity and better mechanical properties.

4. CONCLUSIONS

(1). Y$_2$(SO$_4$)$_3$ and La$_2$(SO$_4$)$_3$ were prepared by wet chemical method and used as
doping materials in Na$_2$SO$_4$ solid electrolyte. In the Na$_2$SO$_4$-Y$_2$(SO$_4$)$_3$ system,
12 mol% Y$_2$(SO$_4$)$_3$ can stabilize Na$_2$SO$_4$-I phase down to room temperature,
Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ solid solution exhibits the highest ionic
conductivity (at 400°C, $\sigma=1.76\times10^{-2}$ S·cm$^{-1}$) and lowest activation enthalpy (0.38
eV).

(2). In the Na$_2$SO$_4$-La$_2$(SO$_4$)$_3$ solid solutions, 8 mol% La$_2$(SO$_4$)$_3$ can stabilize phase
I down to room temperature, Na$_2$SO$_4$ + 4 mol% La$_2$(SO$_4$)$_3$ solid solution has the
highest ionic conductivity (at 400°C, $\sigma=2.95\times10^{-2}$ S·cm$^{-1}$) and lowest activation
enthalpy (0.37 eV).

(3). 5 to 20 mol% Na$_2$WO$_4$ with 5 mol% Y$_2$(SO$_4$)$_3$ can stabilize Na$_2$SO$_4$-I phase down
to room temperature by forming a solid solution with a Na$_2$SO$_4$-I structure which
is stable at room temperature, accompanied by a minor second phase of Na$_2$SO$_4$.  

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Na$_2$WO$_4$ decreases the ionic conductivity of Na$_2$SO$_4$·Y$_2$(SO$_4$)$_3$ solid solutions, but the ionic conductivities of the Na$_2$SO$_4$·Y$_2$(SO$_4$)$_3$·Na$_2$WO$_4$ systems are still higher than that of undoped Na$_2$SO$_4$. The Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ + Na$_2$WO$_4$ specimens are more suitable for practical applications than undoped Na$_2$SO$_4$ material because of their higher conductivity and better mechanical properties.

ACKNOWLEDGEMENTS

The author would like to thank Ms. Chen Jihong, Mr. Shi Jiaming and Mr. Zhang Zhenjung for their assistance in experimental work, and special thanks to Mr. Palle Jensen, Mr. Cliver Klitholm and Mr. Helmer Nilsson of the Metallurgy Department, Risø National Laboratory for their kind help in SEM and DTA analysis.

REFERENCES


CHAPTER 4

EVALUATION OF AN ELECTROCHEMICAL SO$_x$ ($x=2,3$) SENSOR WITH A TUBULAR NASICON SOLID ELECTROLYTE

ABSTRACT

Solid electrolyte SO$_x$ gas sensors with a tubular Nasicon solid electrolyte were assembled and tested. A large temperature difference of 50°C existed between the two electrodes of the sensors. The temperature dependence of the sensor EMF response deviates substantially from the theoretical values in the lower temperature range, while at temperatures higher than 750°C, the sensors exhibit EMF responses to SO$_2$ partial pressures which are consistent with theoretical responses derived for sensors under non-isothermal conditions. SEM, EDX and XRD analyses on the sensor after testing all indicated that the formation of Na$_2$SO$_4$ at the interface of the electrodes and the Nasicon solid electrolyte under different conditions can be the explanation for the temperature dependence of the EMF of the sensors.
1. INTRODUCTION

Since the 1970s many attempts have been made to utilize alkali sulfates Na₂SO₄[1-3], K₂SO₄[4,5], Li₂SO₄[6,7] as solid electrolytes for concentration cell-type SOₓ sensors, such as

\[
\text{Pt, (SO}_2, \text{ SO}_3, \text{ O}_2)^{\text{I}} \mid \text{A}_2\text{SO}_4 (\text{A} = \text{Li}, \text{Na,K}) \mid (\text{SO}_2, \text{ SO}_3, \text{ O}_2)^{\text{II}}, \text{Pt}
\]

(1)

The electromotive force (EMF) values of these cells were essentially consistent with those theoretically calculated from the Nernst equation in a certain SO₂ partial pressure range, indicating their reliability as gas sensors. However, these sulfates have some common shortcomings as they exhibit phase transitions on heating, resulting in the degradation of the solid electrolyte. Furthermore they can hardly be densified by sintering[5]. In recent years, several new Na⁺ ion conductors, such as Nasicon[8,9], β-alumina and β'-alumina[10,11], have been examined in order to circumvent such problems.

Nasicon (Na₃Zr₂Si₂PO₁₂) is a three dimensional sodium ion conductor, it exhibits an ionic conductivity which is two orders of magnitude higher than that of Na₂SO₄ at 1000K. In addition, Nasicon can easily be sintered to acceptable densities, and it shows no phase transition with a volume change up to 1200K. Therefore, Nasicon has advantages over alkali sulfates as a solid electrolyte in SOₓ sensors. Saito et al.[9] demonstrated that the SO₂-O₂-SO₃ concentration cell using Nasicon gave essentially the same electromotive force as the cell using Na₂SO₄ electrolyte because of the existence of a thin layer of
Na$_2$SO$_4$ formed at the interface of the Nasicon solid electrolyte and the electrodes. They also found that the sensor exhibited good response and excellent selectivity against CO$_2$ and NO$_2$. However, to date there is no report about a commercial SO$_x$ sensor using Nasicon as solid electrolyte. It is expected that the availability of this material in tubular form[12] will lead to sensors of practical interest. As gas-tight tubes of Nasicon have become available recently, it is of great interest to test the reliability of these tubes as the solid electrolyte in SO$_x$ sensors. In the present paper, we will describe the results obtained with a tubular SO$_x$ sensor with a Nasicon solid electrolyte. A discussion on unusual response behaviour of the sensors will be presented.

2. EXPERIMENTAL ASPECTS

2.1 Sensor fabrication

Nasicon tubes of 7 cm in length and 1.2 cm in diameter used in this work were fabricated by the Institute of Mineral Industry at the Technical University of Denmark. SO$_x$ gas sensors were prepared by PBI-Dansensor A/S, Pt painting was applied on the surface of the two sides of the tube and subsequently the tube was heated at 800°C for 2 hr to obtain porous Pt electrodes. Sensor SN2 has a painted thin layer of Na$_2$SO$_4$ on the surface of working electrode (the inner surface of Nasicon tube), sensor SN3 was painted with Na$_2$SO$_4$ on the surface of both working and reference electrode, while sensor SN4 has no Na$_2$SO$_4$ painted on either surface of electrodes. A schematical presentation of the tubular sensor is presented in Fig. 4.1.
2.2 Testing procedure of sensor EMF response

To test the EMF response of the sensors at a certain temperature, two gas mixtures of air and SO$_2$ in pure nitrogen were introduced into the two compartments. Mass flow controllers were employed to fix the SO$_2$ partial pressure and the gas flow rate in both the reference and the working electrode compartments. The testing system is shown in Fig. 4.2. An HP 85B PC was used to collect the measured EMF and temperature data. The relations of EMF with operating time, gas flow rate, SO$_2$ partial pressure and temperature were separately tested.

2.3 Characterization of the sensor material

The sensor SN2 (with Na$_2$SO$_4$ painted on the inner surface of the Nasicon tube) after a long term of testing was cut into four parts as indicated in Fig. 4.1 and denoted as SN2 o n and SN2 i n, respectively. Here o refers to the outside surface, i the inside surface, and n the number of the cut part. The phases and surface morphology of these specimens were investigated with XRD, SEM and EDX.
Fig. 4.1 Schematic presentation of $\text{SO}_x$ sensor based on a Nasicon tube.

Fig. 4.2 System for testing of the Nasicon based $\text{SO}_x$ sensor.
3. RESULTS AND DISCUSSION

3.1 Temperature distribution along the sensor tube

In its practical form, the sensor will be mounted in a small furnace. With the two gas streams flowing on both sides of the Nasicon tube, the temperature distribution of the sensor poses a problem. From Fig. 4.3 it can be seen that the temperature inside the tube (working temperature) is 50°C lower than outside (reference temperature) when the furnace temperature is in the range of 650°C to 850°C. This temperature difference is constant in this temperature range.

![Graph showing temperature distribution](image)

**Fig. 4.3** Temperature of the furnace set point (+), the working electrode (▲) and the reference electrode (△).
3.2 Effect of gas flow rate on sensor response

It was found that the EMF output of the sensors was seriously affected by the gas flow rate in both electrode compartments. Curve A in Fig. 4.4 presents the relation between the EMF value and the gas flow rate at working electrode when the gas flow rate at reference electrode is fixed at 100 ml/min, the temperature of working electrode is 501°C, and p(SO₂) at working and reference electrode are 70 ppm and 11.2 ppm, respectively. This behaviour is rather similar to that of a diffusion-controlled process where the process rate is proportional to the square root of the gas flow rate when a laminar boundary layer is formed on a solid surface at which the reaction takes place[13], i.e.

\[ v = A_1 \cdot t^{1/2} \]  \hspace{1cm} (2)

and

\[ dc = A_2 \cdot c \cdot dv \]  \hspace{1cm} (3)

hence

\[ \ln c = A_3 \cdot t^{1/2} \]  \hspace{1cm} (4)

Here \( f \) denotes the gas flow rate, \( v \) the process rate, \( c \) the concentration of the diffusing species, \( A_1, A_2 \) and \( A_3 \) are the temperature-dependent coefficients. Curve B in Fig. 4.4 was plotted as

\[ \text{EMF} = E_0 \cdot (f/f_0)^{1/2} \]  \hspace{1cm} (5)
where $E_0$ is the EMF value under a flow rate of $f_0$ (which here is taken as 50 ml/min), appears to fit the experimental data well at the lower flow rate range, while the less dependence of EMF on flow rate for the higher flow rate range might be explained that the boundary layer is thin enough so that the surface reaction rather than the diffusion becomes the rate limiting step.

![Graph](image)

**Fig. 4.4**  EMF response of the sensor SN2 as a function of the gas flow rate. Experimental data (△), theoretical modelling (▼).
3.3 Theoretical expression of the EMF

From the data in section 3.1 it is apparent that non-isothermal conditions occur in this tubular Nasicon based SO$_2$ sensor, For non-isothermal Nernst-type sensors, the following expression for the EMF was derived recently[14],

$$\text{EMF} = -10^3 \left[ \frac{RT}{2F} T_1 \ln \frac{K_2 p^{II}(SO_x)p^{II}(O_2)}{1 + K_2 p^{II}(O_2)} - \frac{RT}{2F} T_2 \ln \frac{K_1 p^{I}(SO_x)p^{I}(O_2)}{1 + K_1 p^{I}(O_2)} \right] + 0.5472(T_1 - T_2) \text{ (mV)} \tag{6}$$

Here $T_1$ and $T_2$ refer to the temperature of the reference electrode denoted as (I) and the working electrode denoted as (II), $K$ the equilibrium constant of the SO$_2$ oxidation reaction, $p$(SO$_x$) and $p$(O$_2$) the introduced SO$_x$ ($x=2,3$) and oxygen partial pressure, respectively. Under isothermal conditions, i.e. $T_1 = T_2$, eq.(6) can be simplified to the usual Nernst equation,

$$\text{EMF} = -\frac{RT}{2F} \ln \frac{p^{II}(SO_x)}{p^{I}(SO_x)} \tag{7}$$

which is commonly employed in the literature[5] under the assumption that Na$_2$SO$_4$ is formed and has the same chemical activity at both electrodes. Eq.(6) and Eq.(7) can be used to calculate the theoretical EMF response values using the experimental data for temperature and SO$_2$ partial pressure.
3.4 Temperature dependence of the EMF

In Figs. 4.5, 4.6 and 4.7 we present the EMF response of sensors SN2, SN3 and SN4 as a function of the operating temperature in the range from 450°C to 850°C, respectively. To obtain the theoretical values Eq.(6) was used in all cases.

![Graph showing EMF of SN2 as a function of operating temperature.](image)

**Fig. 4.5** EMF of SN2 as a function of operating temperature.

$p_{\text{ref.}(\text{SO}_2)} = 70$ ppm, $p_{\text{work.}(\text{SO}_2)} = 500$ ppm,

Experimental data (•), theoretical data (v).
Fig. 4.6  EMF of SN3 as a function of operating temperature.

\[ p_{\text{ref}}(\text{SO}_2) = 70 \text{ ppm}, p_{\text{work}}(\text{SO}_2) = 100 \text{ ppm}, \]

Experimental data (▲), theoretical data (▼).

Sensors SN2, SN3 and SN4 show different response behaviour, and the plots clearly reveal a discrepancy between experimental and theoretical results. According to theoretical prediction, the EMF should increase with temperature when the SO\textsubscript{x} partial pressure of the sample gas is higher than that of the reference gas. However, here the contrast result is observed. The experimental data in Fig. 4.5 obtained with sensor SN2 with Na\textsubscript{2}SO\textsubscript{4} painted at the working electrode shows an EMF decrease with temperature,
although the SO$_2$ partial pressure at the working electrode is higher than that of the reference gas. The plots in Fig. 4.6 obtained with sensor SN3 with the sodium sulfate painted on both inner and outer surface of the Nasicon tube are close to expectation. It is seen that the EMF value increases with temperature when the sample gas contains a higher SO$_x$ concentration than the reference gas. However, experimental data reveal a larger slope than the theoretical curve. The plots shown in Fig. 4.7 for sensor SN4 without Na$_2$SO$_4$ painted demonstrated a much lower experimental EMF than the theoretical predicted data, especially at lower temperatures.

![Graph](image)

**Fig. 4.7** EMF response of SN4 as a function of operating temperature.

$p_{\text{ref}}(\text{SO}_2) = 70$ ppm, $p_{\text{work}}(\text{SO}_2) = 500$ ppm,

Experimental data (△), theoretical data (▼).
To understand the above results, we need to consider the theoretical derivation of the EMF expression. In the theoretical derivation[14] we used the assumption that Na₂SO₄ was formed on both sides of the Nasicon tube, hence the concentration cell would have the same EMF as that of a sensor based on a Na₂SO₄ solid electrolyte. Because in most experiments the sample gas has the higher SOₓ partial pressure the following cathodic reaction should take place,

\[
\text{SO}_3 + \frac{1}{2} \text{O}_2 + 2e^- + 2 \text{Na}^+ = \text{Na}_2\text{SO}_4
\] (8)

At the other electrode the reverse reaction occurs to provide Na⁺ ions. However, the formation of Na₂SO₄ on a Nasicon surface can take place directly during all the testing experiments as the sodium activity in Nasicon is much higher than that in Na₂SO₄. The sodium ions to form Na₂SO₄ are the mobile Na⁺ ions in the conduction pathways of Nasicon. This shall lead to a sodium deficient non-stoichiometric Nasicon according to reaction

\[
\text{SO}_3 + \frac{1}{2}\text{O}_2 + 2\text{Na-Nasicon(stoichiometric)} = \text{Na}_2\text{SO}_4 + \text{Nasicon(non-stoichiometric)}
\] (9)

Thus the open circuit potential of the cell cannot be considered to be equivalent to the EMF of a cell with Na₂SO₄ as solid electrolyte, and the above discussion will be used to describe the temperature dependence of the EMF of the different sensors. As sensor SN2 was painted with Na₂SO₄ inside the Nasicon tube, the formation of Na₂SO₄ and the consumption of SO₃ at the reference side, where no Na₂SO₄ existed previously, would
govern the EMF value. Therefore, the EMF values will decrease when the temperature increases (see Fig. 4.5). The effect will be contrary to that for sensor SN4 without Na\textsubscript{2}SO\textsubscript{4} painted on either side, as is illustrated in Fig. 4.7, since a lower temperature at the inside of the tube and a higher SO\textsubscript{2} partial pressure will favour reaction (8). Then the formation of the sodium sulfate and the consumption of SO\textsubscript{3} at working electrode will govern the EMF value. However, for sensor SN3 with Na\textsubscript{2}SO\textsubscript{4} painted on both sides, the temperature dependence of the EMF was fairly consistent with theoretical prediction as is shown in Fig. 4.6. According to the present discussion, we may conclude that it is difficult to obtain reasonable and stable EMF data before the formation of Na\textsubscript{2}SO\textsubscript{4} at the interface electrode-Nasicon surface is complete.

Two possible routes can now be considered for the fabrication of SO\textsubscript{x} sensors:

a) painting of the entire Nasicon surface with Na\textsubscript{2}SO\textsubscript{4} followed by a proper heat treatment in an atmosphere containing SO\textsubscript{x};

b) reaction of Nasicon with SO\textsubscript{x} gas to form a dense surface layer of Na\textsubscript{2}SO\textsubscript{4}.

The second route can result in an uniform and dense thin layer, but may also lead to sodium deficiency of Nasicon, its effect on sensor performance yet being unclear.

In addition, as mentioned above, the temperature difference between the electrodes leads to a much higher EMF output as compared to that predicted by the Nernst equation. While in general a temperature gradient over the sensor should be avoided as much as possible, a new kind of sensor based on a temperature difference has been shown to be feasible[14].

It should be noted, however, that the experimental EMF data at temperatures exceeding 750°C are concordant to the theoretical values (viz. Figs. 4.5-4.7). This demonstrates the
validity of the theoretical EMF expression which is based on complete conversion of the Nasicon surface layers to Na₂SO₄, and indicates the need of high operating temperatures for such sensors.

3.5 EMF response to the partial pressure of SOₓ

The curves in Figs. 4.8 and 4.9 reveal the EMF outputs of sensor SN3 as a function of the SO₂ partial pressure in the testing gas stream at two constant temperatures.

![Graph showing EMF vs. SO₂ partial pressure](image)

**Fig. 4.8** EMF of SN3 vs. SO₂ partial pressure of the sample gas at 830°C.

\[ p_{\text{ref.}}(\text{SO}_2) = 70 \text{ ppm}, \quad p_{\text{work.}}(\text{O}_2) = p_{\text{ref.}}(\text{O}_2) = 0.21 \text{ atm.} \]

theoretical values (\(\triangledown\)), experimental data (\(\blacksquare\)).
Fig. 4.9  EMF of SN3 vs. SO$_2$ partial pressure of the sample gas at 727°C.

$p_{\text{ref.}}$(SO$_2$) = 70 ppm, $p_{\text{work.}}$(O$_2$) = $p_{\text{ref.}}$(O$_2$) = 0.21 atm.

Theoretical values (△), experimental data (▲).

As expected, the EMF values increase essentially linearly with log$p$(SO$_2$), except for a deviation occurs at higher $p$(SO$_2$) in Fig. 4.9. However, the data are about 15 mV lower than the theoretical EMF values as predicted by Eq.(6).
Fig. 4.10  SEM pictures of different parts of the outer surface of sensor SN2.
(A) SN2 i 2

(B) SN2 i 4

Fig. 4.11 SEM pictures of the different part of SN2 inner surface.
Fig. 4.12  Morphology of a fracture surface of Nasicon tube.
Table 4.1 Phase identification of the specimens from sensor SN2

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Element Analysis by EDX</th>
<th>Phases indicated by XRD</th>
</tr>
</thead>
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<tr>
<td></td>
<td>wt%</td>
<td>at%</td>
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<td>SN2 o 1</td>
<td>Na</td>
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<tr>
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<tr>
<td></td>
<td>O</td>
<td>35.33</td>
</tr>
</tbody>
</table>
3.6 Phase identification of both electrode surfaces

From XRD analysis and SEM pictures (Figs. 4.10-4.12) information about the phases present in the surface layers of the sensors is obtained. EDX data obtained from a spot of the corresponding area and gathered in Table 4.1 provide some further information for phase identification especially for sensor SN2, which was tested for 200 hr at temperatures from 400°C to 850°C in an ambient containing 50 to 2000 ppm SO$_2$, 0.21 atm O$_2$ with a reference containing 70 ppm SO$_2$ and 0.21 atm O$_2$.

It is evident that the phase Na$_2$SO$_4$-I was formed during testing on the surface of the Nasicon tube at higher temperatures (viz. SN2 o 2, SN2 i 2 and SN2 o 3). For the specimen SN2 o 2 crystalline Na$_2$SO$_4$-I was formed on the surface of Nasicon not covered by the porous platinum electrode and developed to overlap part of the platinum electrode (Fig. 4.10 A); Na$_2$SO$_4$-III was formed as isolated grains on the surface of SN2 o 3 because of the lower temperature (Fig. 4.10 B). The temperatures of SN2 i 4 and SN2 o 4 are too low (about 200°C) to form the sodium sulfate and the specimen behaved as the free surface of the Nasicon tube, as shown in Fig. 4.11 B which is just like the Nasicon fracture surface (Fig. 4.12). Fig. 4.11 A is a SEM picture of an area of the inner surface SN2 i 2. It shows well developed hexagonal grains as large as 30 μm in size, which are identified as pure Na$_2$SO$_4$-I by EDX (Table 4.1). This morphology indicates the grains not to be the sodium sulfate applied before operating the sensor. Instead they have been formed by sintering or re-crystallization during the testing under a rather high SO$_2$ partial pressure. The SEM pictures and phase analysis by EDX and XRD obtained with sensor SN2 clearly support the presented explanation for the temperature
dependence of the EMF of the sensors, which is based on the formation of Na$_2$SO$_4$ at
the interface of the electrodes and the Nasicon tubes under different conditions.

4. SUMMARY AND FURTHER REMARKS

Electrochemical SO$_x$ gas sensors have been fabricated with a tubular Nasicon solid
electrolyte and platinum electrodes. A comprehensive testing of the EMF response of
the sensors under different operating conditions has been performed. The results reveal
that Na$_2$SO$_4$ has to be present at both working and reference electrode in order to yield
experimental values which are concordant with theoretical predictions. For a sensor
comprising the Nasicon solid electrolyte without Na$_2$SO$_4$ painted or with Na$_2$SO$_4$ painted
at only one side, Na$_2$SO$_4$ has to be formed during the initial operation of the sensor, and
hence the operating temperature has to be higher than 750°C in order for the
experimental data to be close to the values predicted by the EMF expression Eq.(6) for
the non-isothermal case. However, for the sensor comprising a Nasicon with Na$_2$SO$_4$
painted at both sides, the experimental data fit the theoretical EMF values as calculated
from Eq.(6) in the wide temperature range of 500 to 800°C as shown in Fig. 4.6. This
proves the validity of the theoretical expression.

Based on the above results the development of Nasicon based SO$_x$ gas sensors will
require,
A. the formation of a Na$_2$SO$_4$ layer on both sides of the Nasicon tube prior to the manufacture and measurements of the sensors in order to avoid Na$_2$SO$_4$ formation during sensor operating, which may lead to sodium deficiency in the Nasicon and may yield unstable and unpredictable EMF values.

B. A special furnace design for the sensor should be used in order to avoid a temperature difference between the two electrodes. Otherwise, a more complicated equation must be used for the calculation of the unknown SO$_x$ partial pressure of the testing gas.

C. modified electrodes. In order for the chemical equilibrium of the SO$_2$ oxidation reaction to be reached rapidly and for the sensor to have a fast response, the electrodes should be further improved with a catalyst, which activates this reaction.

D. the replacement of the gaseous reference electrode by a solid state reference electrode, and this has been a major task in the development of SO$_x$ sensors [6,10,11,15,16].

REFERENCES


CHAPTER 5

A NOVEL TEMPERATURE-GRADIENT Na\textsuperscript{+}-\textbeta"-ALUMINA SOLID ELECTROLYTE BASED SO\textsubscript{x} GAS SENSOR WITHOUT GASEOUS REFERENCE ELECTRODE

ABSTRACT

An electrochemical SO\textsubscript{x} gas sensor with a tubular Na\textsuperscript{+}-\textbeta"-alumina solid electrolyte has been fabricated and tested under non-isothermal conditions:

\[
\text{Pt}, (\text{SO}_2\text{SO}_3\text{O}_2)^{\text{I}} / \text{Na}^{+}-\text{\textbeta"-alumina} / (\text{SO}_2\text{SO}_3\text{O}_2)^{\text{II}}, \text{Pt} \\
T_1-\delta T-\cdots-T_2
\]  

(1)

The temperature difference between the reference and working electrode of the sensor cell is about 100\degree C, which causes a serious deviation of the experimental EMF response from the value as calculated using the Nernst equation for an isothermal system. The experimental results are consistent with the theoretical prediction for a non-isothermal system. The response time is usually less than 10 min. SEM and EDX have been employed to investigate the sensor material before and after use, confirming the
formation of a glassy phase of Na$_2$SO$_4$ by an electrochemical reaction at the interface of the Pt electrodes and Na$^+$-β''-alumina. According to this new theoretical derivation, the sensor design could be simplified by applying the same SO$_2$ gas at the two electrodes. The EMF of this so-called TGNB (Temperature Gradient Na$^+$-β''-alumina) SO$_x$ sensor is in good agreement with the theoretical prediction. The consistence of the experimental results with the theoretical values and the simple construction of this type of SO$_x$ sensor indicate its potential applicability.
1. INTRODUCTION

In the past decade many studies have dealt with the use of alkali sulfates, including K$_2$SO$_4$[1-3], Na$_2$SO$_4$[4,5], Li$_2$SO$_4$[6,7] as solid electrolyte for electrochemical SO$_x$ sensor cells of the Nernst-type, i.e.

$$\text{Pt, } (\text{SO}_2\text{SO}_3\text{O}_2^I) / A_2\text{SO}_4(A=\text{Li}, \text{Na}, \text{K}) / (\text{SO}_2\text{SO}_3\text{O}_2^II), \text{Pt}$$  \hspace{1cm} (2)

The electromotive force (EMF) values of these cells were essentially consistent with those theoretically calculated in a certain SO$_2$ partial pressure range from the Nernst equation, indicating their reliability as gas sensors. However, these sulfates have some common shortcomings as they undergo phase transitions with volume changes on heating which leads to the formation of micro cracks and pores. In addition, they have rather poor sinterability[5]. In recent years, several new Na$^+$ ion conductors such as Nasicon[8,9], β- and β"-alumina[10-14], have been examined in order to avoid these problems. Nasicon is a three dimensional sodium ion conductor, β- and β"-alumina are two dimensional sodium ion conductors. They exhibit much higher ionic conductivity than Na$_2$SO$_4$, they can be easily sintered to acceptable densities, and they show no phase transition with volume change in the wide temperature range of room temperature to 1200K. Therefore, Nasicon and β-, β"-alumina have advantages over alkali sulfates as solid electrolytes in SO$_2$ sensors. Saito et al.[9] demonstrated that the SO$_2$-O$_2$-SO$_3$ concentration cell using Nasicon electrolyte gave essentially the same EMF as the cell using a Na$_2$SO$_4$-based electrolyte, because a thin layer of Na$_2$SO$_4$ is formed on the
electrodes, as has been confirmed by XRD analysis. Itoh et al.[10-13] have reported several sensor systems based on β- or β"-alumina. They proved by EPMA that β- and β"-alumina could react with SO₂ and O₂ gases to form Na₂SO₄ on the surface, and that β-alumina was more stable than β"-alumina in SOₓ atmospheres at high temperature. However, β"-alumina was more suitable as the solid electrolyte than β-alumina because it turned out to be possible to detect lower SO₂ partial pressure at high temperatures. They also demonstrated that the SOₓ sensor using β- or β"-alumina solid electrolyte exhibited a good selectivity to SOₓ gas in an SOₓ-CO₂-NOₓ atmosphere.

However, to date all these results were reported under the assumption of an isothermal system, i.e. both the working and reference electrode had the same temperature. This assumption is reasonable when the sensor has the form of thin disk and is placed in a furnace with adequately wide isothermal region. But in practice, it is more convenient to have a small and simple sensing system, based on a tubular sensor with a small furnace. In this case, a temperature difference will exist between the two electrodes and this difference needs to be taken into account. In our previous work (see Chapter 4) on electrochemical SO₂ sensors based on a tubular Nasicon concentration cell in a small furnace, we found that a temperature difference of about 50°C existed between the working and reference electrode, which made the EMF response of the sensor to deviate seriously from the value calculated from the Nernst equation. In order to understand the experimental results, a new EMF expression[15] for non-isothermal SOₓ sensors was derived on the basis of electrochemical concepts. This new equation differs from the simple Nernst equation usually applied and can be used to predict theoretical EMF values. Theoretical data have been shown to fit the experimental data obtained for the
Nasicon based SO$_x$ sensors. In the present work, a non-isothermal Na$^+$$\beta^-$-alumina SO$_x$ sensor with a temperature difference of about 100°C between the two electrodes was assembled and tested. A novel temperature gradient Na$^+$$\beta^-$-alumina (TGNB) SO$_x$ sensor with the same SO$_2$ sample gas at the two electrodes was also examined and discussed.

2. EXPERIMENTAL ASPECTS

2.1 Sensor fabrication and testing system

The Na$^+$$\beta^-$-alumina tubes of 4 cm in length and 1.1 cm in diameter used in this work were obtained from the Shanghai Institute of Ceramics of the Acadamia Sinica. SO$_2$ gas sensors were fabricated by the Danish company PBI-Dansensor A/S by applying Pt porous electrodes as shown in Fig. 5.1. The sensor was placed in a small commercial furnace of 8 cm in length and 3 cm in diameter and the testing was performed in the system shown in Fig. 5.2. To measure the EMF response of the sensor, two gas mixtures of air and SO$_2$ in pure N$_2$ were introduced into the two electrode compartments at a fixed temperature. As is seen, four mass flow meters were employed to control the gas flow rate and the partial pressures of SO$_2$ gas at the working and reference electrode. An HP 85B PC was used to collect the measured data. The data were transfered to an Olivetti computer and analyzed. The relations of the EMF with operating time, gas flow rate, SO$_2$ partial pressure and temperature were tested, respectively.
For the TGNB SO$_x$ sensor, a gas mixture of SO$_2$ in pure N$_2$ and air was introduced into both the working and reference electrode and controlled by two mass flow meters.

2.2 Characterization of the sensor material

In order to obtain insight into the structure of the phases present in the surface layer and the surface morphology of the sensor material, and information about the mechanism of the electrochemical interface reaction, the sensor materials were investigated by SEM, EDX and XRD after several weeks of operation. DTA, TGA and SEM were used to investigate the thermal and chemical stability of the sensor material before and after testing.

Fig. 5.1  Na$^+$-β-alumina SO$_x$ sensor tube and the electrodes
3. RESULTS AND DISCUSSION

3.1 Characterization of the Na⁺-β"-alumina solid electrolyte

The Na⁺-β"-alumina solid electrolyte employed in this work is a Li₂O-stabilized Na⁺-β"-alumina with a composition detected by Atomic Absorption Analysis as Na₂O 9.28 wt%, Li₂O 0.68 wt% and Al₂O₃ 89.98 wt%.

Fig. 5.3 shows the DTA and TGA curve of Na⁺-β"-alumina in dry air. From the DTA data in Fig. 5.3 neither endothermic nor exothermic peaks are observed. The TGA data
do not reveal a weight change from room temperature up to 700°C, showing the good thermal stability of Na⁺-β"-alumina in dry air. However, when Na⁺-β"-alumina is exposed to air with CO₂ gas and H₂O vapour, the following reactions may take place:

\[ \text{CO}_2 + 3 \text{H}_2\text{O} + 2 \text{Na}^+ - \beta"-\text{Al}_2\text{O}_3 = \text{Na}_2\text{CO}_3 + 2 \text{H}_3\text{O}^+ - \beta"-\text{Al}_2\text{O}_3 \]  \hspace{1cm} (3)

and

\[ \text{CO}_2 + 2 \text{H}_2\text{O} + \text{Na}^+ - \beta"-\text{Al}_2\text{O}_3 = \text{NaHCO}_3 + \text{H}_3\text{O}^+ - \beta"-\text{Al}_2\text{O}_3 \]  \hspace{1cm} (4)

The chemisorption of H₂O by Na⁺-β"-alumina leads to the partial ion exchange of Na⁺ by H₃O⁺. In that case, H₃O⁺ ions can enter the conducting plane of the β"-alumina structure, while the exchanged Na⁺ ions will react with CO₂ and H₂O to form NaHCO₃ and Na₂CO₃.

![Graph showing TGA and DTA curves for Na⁺-β"-alumina in dry air.](image)

**Fig. 5.3** DTA and TGA curve of Na⁺-β"-alumina in dry air.
Fig. 5.4  DTA and TGA curve of Na$^+$-$\beta''$-alumina material exposed to moist air.

Fig. 5.4 shows the DTA and TGA curve for Na$^+$-$\beta''$-alumina exposed to moist air for a week. The endothermic peak in the DTA and the weight loss in the TGA curve at 74°C indicate the loss of physisorbed water vapour at the Na$^+$-$\beta''$-alumina surface, while the endothermic peak in DTA and the slight weight loss in the TGA curve at 238°C imply the decomposition of NaHCO$_3$ and H$_3$O$^+$-$\beta''$-alumina with the loss of CO$_2$ and H$_2$O.
Figs. 5.5 and 5.6 compare the SEM pictures of the microstructure of the Na$^+$-$\beta^\prime$-alumina surface before and after a week of exposition to moist air. It can be seen that before exposing to moist air, pure Na$^+$-$\beta^\prime$-alumina has a typical polycrystalline structure (Fig. 5.5), but after exposure to moist air, three different structures coexist on the Na$^+$-$\beta^\prime$-alumina surface (Fig. 5.6). Comparing with Fig. 5.5, we can see that the polycrystalline particles in Fig. 5.6 are the Na$^+$-$\beta^\prime$-alumina base material. EDX revealed the fibers in Fig. 5.6 to have a Na content much higher than that in Na$^+$-$\beta^\prime$-alumina, indicating the existence of Na$_2$CO$_3$ or NaHCO$_3$. The laminar structure has a high content of Al but no Na, showing the possible presence of H$_3$O$^+$-$\beta^\prime$-alumina.

Fig. 5.5  SEM picture of the surface of untreated polycrystalline Na$^+$-$\beta^\prime$-alumina

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Fig. 5.6 SEM picture of the surface morphology of Na\(^+\)-\(\beta\)'-alumina after exposure to moist air.

When Na\(^+\)-\(\beta\)'-alumina is seriously attacked by CO\(_2\) and H\(_2\)O, many NaHCO\(_3\)/Na\(_2\)CO\(_3\) particles with a flower-like shape will grow on the surface of the Na\(^+\)-\(\beta\)'-alumina material as is shown in Fig. 5.7. For a reliable operation in a SO\(_x\) sensor, Na\(^+\)-\(\beta\)'-alumina should be used in dry air in order to avoid reaction with H\(_2\)O and CO\(_2\).
3.2 Effect of gas flow rate on sensor EMF response

It was found that the EMF output of the sensor is affected by the SO$_2$ gas flow rate, $f$, at the electrodes. The curve in Fig. 5.8 shows the EMF response as a function of gas flow rate at a fixed temperature, when SO$_2$-air gas mixture is flowing over the electrodes. The flow rate on the reference side has been kept constant at 100 ml/min, while that at the working electrode was varied.
Fig. 5.8  Effect of the gas flow rate on the sensor response.

$p_{\text{ref}} = 67$ ppm, $p_{\text{work}} = 90$ ppm, $T_{\text{work}} = 560^\circ$C.

It can be seen that when the flow rate is below 100 ml/min, the EMF increases with flow rate, but when the flow rate is between 100 and 150 ml/min, hardly any influence on the sensor response is observed. An explanation was given in Chapter 4 for the similar flow rate effect. In the undermentioned experiments, we have kept a constant gas flow rate of 100 ml/min at both electrodes.
3.3 Temperature gradient between the sensor electrodes

Since a practical sensor will in general be operated with a small furnace having a rather short isothermal region, and because there are two gas streams flowing over both sides of the Na$^+$-$\beta^\prime$-alumina tube, the temperature distribution of the sensor can be a problem and should be taken into account. Fig. 5.9 shows the temperature of the furnace, the reference and the working electrode of the studied Na$^+$-$\beta^\prime$-alumina sensor cell. The temperature inside the tube (working electrode) is 100°C lower than outside the tube (reference electrode) for a furnace temperature in the range of 550°C to 850°C.

![Temperature graph](image)

\( T_{\text{furnace}} \) (°C)

Fig. 5.9 Temperature of the furnace (○), sample electrode (+) and reference electrode (×) as a function of the furnace temperature.
This large temperature difference between the two electrodes causes the EMF response of this sensor to deviate from that of the isothermal system, since the thermoelectric power and the equilibrium constant $K(T)$ for the $SO_2$ oxidation reaction at the two electrodes will be quite different.

3.4 Theoretical expression of the EMF

For this non-isothermal system, the following EMF theoretical expression[15] for the EMF has been derived recently,

$$\text{EMF} = 10^3 \left[ \frac{RT_2}{2F} \ln \left( \frac{K_2 p^I(SO_2)p^I(O_2)}{1+K_2[p^I(SO_2)]} \right) - \frac{RT_1}{2F} \ln \left( \frac{K_1 p^I(SO_2)p^I(O_2)}{1+K_1[p^I(O_2)]} \right) \right] + 0.5472(T_1 - T_2)(mV)$$  \hspace{1cm} (5)

Here $T_1$ and $T_2$ refer to the temperature of the reference electrode (I) and working electrode (II), respectively. Eq.(5) can be used to calculate the theoretical values of the EMF for non-isothermal systems. From Eq.(5) it is seen that with the same $SO_2$ partial pressure at both the working and reference electrode an EMF response can be obtained, which depends on temperature and $SO_2$ partial pressure. In this case, a separate and gas-tight reference gas system with a constant $SO_2$ partial pressure at the reference electrode is no longer required as in the usual gas sensing concentration cells. Hence, the sensor device can be simplified substantially. When the same $SO_2$-air gas mixture is introduced into the two electrodes of the sensor, Eq.(5) becomes
\[ EMF = 10^3 \left[ \frac{RT_2}{2F} \ln \frac{K_2 p(SO_2)p(O_2)}{1+K_2\sqrt{p(O_2)}} - \frac{RT_1}{2F} \ln \frac{K_1 p(SO_2)p(O_2)}{1+K_1\sqrt{p(O_2)}} \right] + 0.5472(T_1-T_2)(mV) \] (6)

where \( K_1 \) and \( K_2 \) refer to the equilibrium constant of \( SO_2 \) oxidation reaction at the reference and working temperature, respectively. Eq.(6) yields the theoretical values for the EMF of this novel TGNB \( SO_x \) sensor.

3.5 Temperature dependence of the EMF

![Graph showing time dependence of sensor EMF response](image)

**Fig. 5.10** Time dependence of the sensor EMF response.

\[ p_{\text{ref.}}(SO_2) = 140 \text{ ppm}, \quad p_{\text{work.}}(SO_2) = 50 \text{ ppm}, \]

working temperatures (°C) are given in the figure.
The curve in Fig. 5.10 shows the EMF response to the temperature changes under the condition of \( p_{\text{work}}(\text{SO}_2) = 50 \text{ ppm} \), and \( p_{\text{ref}}(\text{SO}_2) = 140 \text{ ppm} \). Here, \( p_{\text{work}}(\text{SO}_2) \) and \( p_{\text{ref}}(\text{SO}_2) \) refer to the introduced \( \text{SO}_2 \) partial pressure at the working and reference electrode, respectively. It is seen that it usually takes less than 10 min for the EMF response to adjust to a change in temperature. The temperature increases to a new value within 1 min. Generally, the higher the temperature, the shorter is the response time of the sensor. This is related to an increased rate of the electrochemical reaction at higher temperature.

Fig. 5.11 gives an example of the experimental EMF values measured at different temperatures when \( p_{\text{work}}(\text{SO}_2) = 70 \text{ ppm} \), and \( p_{\text{ref}}(\text{SO}_2) = 600 \text{ ppm} \).

![Graph showing EMF dependence on temperature](image)

**Fig. 5.11** Temperature dependence of the EMF for \( p_{\text{ref}}(\text{SO}_2) = 600 \text{ ppm} \), \( p_{\text{work}}(\text{SO}_2) = 70 \text{ ppm} \). (x) theoretical data, (o) experimental data.
It is evident that the experimental EMF values at different temperatures are in good agreement with the theoretical ones calculated from Eq.(5). Similar results have also been obtained in other measurements with different SO$_2$ partial pressures. These results prove the validity of the theoretical equation for the EMF.

3.6 Sensor response to SO$_2$ partial pressure

Fig. 5.12 is a typical EMF response of the sensor to SO$_2$ partial pressure changes at a constant operating temperature of 468°C. The response time of the sensor is about 10 min.

![Graph showing EMF response to SO$_2$ partial pressure](image)

Fig. 5.12 A typical EMF response to the SO$_2$ partial pressure at $T_{\text{work.}} = 468^\circ$C. $p_{\text{ref.}}(\text{SO}_2) = 600$ ppm, $p_{\text{work.}}(\text{SO}_2)$ in ppm are given in the figure.
Fig. 5.13  EMF as a function of SO$_2$ concentration for $p_{\text{ref.}}$(SO$_2$)=100 ppm, $T_{\text{work.}}$=558°C. (×) theoretical data, (α) experimental data.

Fig. 5.13 gives the EMF response to the SO$_2$ partial pressure on the working electrode when $p_{\text{ref.}}$(SO$_2$)=100 ppm and the operating temperature is 558°C. As can be seen, the experimental EMF data fit the theoretical values very well. Such consistence of experimental and theoretical values was also observed at different temperatures and reference SO$_2$ partial pressures.
3.7 Phases present on the solid electrolyte surface

Fig. 5.14 presents a SEM picture of the cross section of the sensor tube. We can see that the porous Pt electrode layer has a thickness of about 20 μm. This thick Pt layer might be the cause of the rather long response times of the sensors. At the interface of the Pt electrode and Na$^+$-$\beta''$-alumina solid electrolyte, there is a particle with the appearance of a glassy phase. EDX indicated that this apparent glassy particle consists of Na$_2$SO$_4$. Besides the Na$_2$SO$_4$ glassy phase, there is a laminar structure on the surface of the solid electrolyte. EDX indicated a lower sodium content in this laminar structure, suggesting that it is the sodium ion deficient Na$^+$-$\beta''$-alumina produced from the direct reaction of Na$^+$-$\beta''$-alumina with SO$_3$ and O$_2$.

$$\text{SO}_3 + \frac{1}{2}\text{O}_2 + 2\text{Na}^+ - \beta''\text{-alumina} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{Na}_2\text{O}\text{-deficient Na}^+ - \beta''\text{-alumina}$$ (7)

Fig. 5.14  SEM picture of the cross section of the Na$^+$-$\beta''$-alumina/Pt interface showing an apparent glassy particle of Na$_2$SO$_4$.  

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3.8 Temperature dependence of the EMF of the TGNB SO\textsubscript{x} sensor

Fig. 5.15 shows an example of the EMF response curve of the TGNB SO\textsubscript{x} sensor when the working temperature changes, and for \( p_{\text{work}}(\text{SO}_2) = p_{\text{ref}}(\text{SO}_2) = 200 \text{ ppm} \). The response time for this TGNB sensor is also about 10 min. Fig. 5.16 gives a typical temperature dependence of the TGNB sensor response. Here we also obtain the expected results, for the experimental EMF values fit the theoretical data well. Similar results have been obtained for other SO\textsubscript{2} concentrations.

![Response time of the TGNB SO\textsubscript{x} sensor.](image)

**Fig. 5.15** Response time of the TGNB SO\textsubscript{x} sensor.

\( p_{\text{work}} = p_{\text{ref}} = 200 \text{ ppm} \), \( T_{\text{ref}} = T_{\text{work}} + 100^\circ \text{C} \),

\( T_{\text{work}} \) (in °C) are indicated in the plot.
Fig. 5.16 EMF of TGNB sensor as a function of the working temperature.

$P_{\text{work.}} = P_{\text{ref.}} = 200$ ppm, $T_{\text{ref.}} = T_{\text{work.}} + 100^\circ$C.

(♦) theoretical data, (σ) experimental data.

3.9 EMF of TGNB SO$_x$ sensor as a function of SO$_2$ partial pressure

Fig. 5.17 is an example of the variation of the EMF response to the SO$_2$ partial pressure at a working temperature of 476°C. The experimental EMF data are quite consistent with the theoretical values as calculated from Eq.(6). At other working temperatures the
sensor EMF response also fits the theoretical data well. These results strongly indicate the possibility to develop this novel TGNB SO₂ sensor further for practical applications.

Fig. 5.17  EMF response of the TGNB sensor as a function of the SO₂ partial pressure. $p_{\text{ref.}} = p_{\text{work.}}$, $T_{\text{work.}} = 476^\circ\text{C}$, $T_{\text{ref.}} = T_{\text{work.}} + 100^\circ\text{C}$.

(*) theoretical values, (o) experimental data.
4. CONCLUSIONS

(1). Tubular Na⁺-β"-alumina based SOₓ sensors have been constructed and tested. A temperature difference of 100°C exists between the two electrodes, which caused the EMF of the sensor to deviate from the theoretical value calculated from the Nernst equation for isothermal conditions. However, the EMF can be modelled very well with the theoretical EMF equation for a non-isothermal system in the SO₂ concentration range of 10 to 1000 ppm, and in the temperature range of 450°C to 650°C. The response time is usually less than 10 min.

(2). Na⁺-β"-alumina has very good thermal stability in dry air, but it can easily react with CO₂ and H₂O to form Na₂CO₃/NaHCO₃ and hydronium-β"-alumina. Na⁺-β"-alumina based SO₂ sensors should therefore be used in dry air to avoid corrosion by carbon dioxide and water vapour.

(3). A novel temperature gradient Na⁺-β"-alumina (TGNB) SOₓ sensor having the same SO₂ concentration at both electrodes was also tested. In the temperature range of 400 to 650°C and for SO₂ partial pressure in the range of 10 to 1000 ppm, the EMF response is concordant with theoretical prediction. The response time is also about 10 min.

(4). Amorphous particles of Na₂SO₄ are observed by SEM and EDX at the interface of the Pt electrodes and Na⁺-β"-alumina solid electrolyte. The Na₂SO₄-I
hexagonal structure could not be detected with XRD. A laminar structure of sodium ion deficient Na$^+$-β"-alumina formed by the direct reaction of Na$^+$-β"-alumina with SO$_3$ and O$_2$ is also found on the Na$^+$-β"-alumina surface by SEM.

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REFERENCES


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CHAPTER 6

Ag$^+\text{-}\beta^\text{''}$-ALUMINA SOLID ELECTROLYTE BASED SO$_x$ SENSORS
WITH SILVER METAL AS SOLID REFERENCE ELECTRODE

I. Planar Sensor

ABSTRACT

Ag$^+\text{-}\beta^\text{''}$-alumina was prepared from Na$^+\text{-}\beta^\text{''}$-alumina by ion exchange, and characterized by XRD, XPS, SEM and EPMA methods. The ionic conductivity of Ag$^+\text{-}\beta^\text{''}$-alumina was measured using ac Impedance Spectroscopy. The solid state SO$_x$ sensor comprising Ag$^+\text{-}\beta^\text{''}$-alumina as the solid electrolyte, metal Ag as the solid reference electrode and porous Pt as the working electrode was constructed, i.e.

$$\text{Pt, Ag / Ag}^+\text{-}\beta^\text{''}\text{-Al}_2\text{O}_3 / \text{Ag}_2\text{SO}_4 / (\text{SO}_2, \text{SO}_3, \text{O}_2) \text{ Pt}$$

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The EMF of the cell as a function of the $SO_2$ partial pressure is fairly consistent with the expected theoretical values in the temperature range of 450 to 700°C and for $SO_2$ partial pressures in the range of 10 to $10^4$ ppm. The response time is usually 3 min when a $V_2O_5$ catalyst is used next to the working electrode to promote the $SO_2$ oxidation equilibrium. The formation of a $Ag_2SO_4$ layer at the interface of the solid electrolyte and the porous Pt working electrode is indicated by an XPS analysis.
I-1. INTRODUCTION

Since the first SO\textsubscript{x} sensor with a solid electrolyte was reported by Gauthier et al.[1,2], many attempts have been made to use alkali sulfates, including K\textsubscript{2}SO\textsubscript{4}[1,2], Na\textsubscript{2}SO\textsubscript{4}[3] and two phases mixtures Li\textsubscript{2}SO\textsubscript{4}-Ag\textsubscript{2}SO\textsubscript{4}[4] as solid electrolytes for SO\textsubscript{x} sensors. However, these alkali metal sulfates undergo phase transitions which are accompanied by volume changes on heating. In addition their sinterability is poor. In recent years, several Na\textsuperscript{+} ion conductors such as Nasicon[5], β- and β\textsuperscript{"} -alumina[6] were studied in order to circumvent the above problems because no structural phase transition takes place during heating from room temperature up to the melting point of these materials. Besides, densification up to 100% has been achieved. A gas reference electrode with a known SO\textsubscript{2} partial pressure has been utilized in combination with these solid electrolytes.

In this paper, the use of a Ag reference electrode is described. The choice of this reference electrode is based on the ion exchange properties of Na\textsuperscript{+}-β\textsuperscript{"} -alumina. The sodium ions in this structure can be easily exchanged by silver ions. Ag\textsuperscript{+}-β\textsuperscript{"} -alumina has been prepared by ion exchange and with the Ag reference electrode a solid state sensor has been fabricated and studied. During the course of our research Itoh et al.[7] reported on a similar type of solid state sensor. The present results will be discussed in light of the reported results.

I-2. EXPERIMENTAL ASPECTS
Na\textsuperscript{+}-\textbeta\textsuperscript{n}-alumina pellets with a diameter of 15 mm and a thickness of about 2 mm used in this work were supplied by the Shanghai Institute of Ceramics of the Academia Sinica. To obtain Ag\textsuperscript{+}-\textbeta\textsuperscript{n}-alumina, Na\textsuperscript{+}-\textbeta\textsuperscript{n}-alumina pellets were dipped into molten AgNO\textsubscript{3} at 300°C for 30 hr. The extent of the ion exchange reaction was examined through the weight increase of the pellets, while the Na\textsuperscript{+} content was detected with XPS (ESCA MKII, VG3 Co.VK) and EPMA.

The XRD patterns of the specimens were taken on a D/max-ra 12 kW Diffractometer (Rikadenki, Japan) in the 2θ range from 20° to 70°. An X-650 SEM (Hitachi, Japan) was used to observe the surface morphology of the sensor material. DTA and TGA were employed to investigate the thermal stability of the materials by a DF-30 Thermoanalyzer (Shimadzu, Japan). X-ray fluorescence spectroscopy (Shimadzu, VF-320, Japan) and XPS were employed to examine their composition. The ionic conductivity of the Ag\textsuperscript{+}-\textbeta\textsuperscript{n}-alumina samples was measured with ac Impedance Spectroscopy using a GenRad 1689 Precise Digibridge computer system in the frequency range of 12 Hz to 100 kHz and in the temperature range from 100°C to 800°C.

Using Ag\textsuperscript{+}-\textbeta\textsuperscript{n}-alumina pellet as the solid electrolyte, Ag metal as the solid reference electrode and porous Pt as the working electrode, planar type SO\textsubscript{x} sensors were constructed and tested in the system as shown schematically in Fig. 6-I.1. The sample gas compositions with different SO\textsubscript{2} partial pressures were made by mixing air with pure SO\textsubscript{2}. The Nernst response of the sensor was examined in a gas flow system with fixed SO\textsubscript{2} concentrations. The electromotive force (EMF) of the sensor cells was measured with an HP 3466 digital multimeter in the SO\textsubscript{2} partial pressure range of 10 to 10\textsuperscript{4} ppm, and the temperature range of 400°C to 800°C.
Fig. 6-I.1  The schematics of the SO$_x$ sensor with Ag$^{+}$-$\beta''$-alumina as solid electrolyte and experimental set up.
I-3. RESULTS AND DISCUSSION

I-3.1 Preparation and characterization of Ag⁺-β"-alumina

The study of the kinetics of the Na⁺-Ag⁺ ion exchange in β"-alumina reveals that in a AgNO₃ melt at 300°C the ion exchange process is completed. XPS, EPMA and X-ray fluorescence analysis all indicate that no Na⁺ was present in the sample after 30 hr of ion exchange. The Ag distribution in the β"-alumina structure as measured by EPMA shows that the distribution is homogeneous. SEM pictures indicate no cracks on the surface of the sample after ion exchange. XRD pattern indicates that Ag⁺-β"-alumina has the same crystal structure as Na⁺-β"-alumina. The lattice parameters calculated from the XRD data are a = 5.59 Å, c = 33.92 Å for Na⁺-β"-alumina and a = 5.59 Å, c = 33.63 Å for Ag⁺-β"-alumina, respectively. The slight compression in c-axis for Ag⁺-β"-alumina might be attributed to the polarizability of Ag⁺.

Ag⁺-β"-alumina exhibits good thermal stability and does not undergo structural phase transitions from room temperature to 1200°C. It becomes dark on heating at higher temperatures. XRD, DTA, TGA and XPS did not indicate that changes in either the structure or the composition had occurred. This darkening phenomenon is considered to be due to the partial thermal and photochemical decomposition of Ag₂O. While Na⁺-β"-alumina is easily corroded by CO₂ and/or H₂O to form Na₂CO₃ and NaHCO₃, Ag⁺-β"-alumina is fairly inert to H₂O and CO₂. After storage of the Ag⁺-β"-alumina samples in water for 10 hr, their structure and electrical properties had not been changed.
XPS analysis revealed that after prolonged use sulfur is present at the sensing electrode, indicating the formation of Ag$_2$SO$_4$. However, no Ag$_2$SO$_4$ diffraction pattern could be detected by XRD.

I-3.2 Ionic conductivity measurements

Fig. 6-1.2 shows the temperature dependence of the ionic conductivity of a Na$^+$-β'-alumina and two Ag$^+$-β'-alumina pellets, one being the normal white sample, and the other a black pellet obtained after 72 hr of heating at 900°C.

![Graph showing Arrhenius plot](image)

**Fig. 6-1.2** Arrhenius plot of the temperature dependence of the ionic conductivity of Na$^+$-β'-alumina(1), white Ag$^+$-β'-alumina(2), and black Ag$^+$-β'-alumina(3).
In general, the conductivity plots are concordant with the literature data[9]. The change of the conductivity activation enthalpy of Na\(^+\)-\(\beta\)-alumina at about 320°C is attributed to the order-disorder transition in the conduction plane. As expected the conductivity activation enthalpy for Ag\(^+\)-\(\beta\)-alumina is larger than that of Na\(^+\)-\(\beta\)-alumina, while the ionic conductivity of the silver compound is lower. After thermal treatment the ionic conductivity has decreased by a factor of 2, while the activation enthalpies are almost the same (0.23 eV and 0.24 eV for white and black Ag\(^+\)-\(\beta\)-alumina, respectively). This effect has also been reported in reference[8]. It is assumed that upon thermal and/or photochemical decomposition metallic silver clusters cause the darkening, and reduce the number of the Ag\(^+\) ions available for the ionic conduction. The magnitude of the conductivity of this solid electrolyte is still adequate for it to be used in a SO\(_x\) sensor.

I-3.3 Theoretical EMF expression for isothermal conditions

The theoretical EMF values can be calculated from the following equations derived in Chapter 2 II,

\[
EMF = \frac{RT}{2F} \ln \frac{K_p(O_2)}{1 + K_p(O_2)} - \frac{\Delta G^o}{2F} + \frac{RT}{2F} \ln p(SO_2)
\]  

(1)

\(\Delta G^o(600-703K) = 227.36T-312148\) J/mol  

(2)

\(\Delta G^o(703-933K) = 196.10T-290016\) J/mol  

(3)

\(\Delta G^o(933-1100K) = 165.52T-261600\) J/mol  

(4)

\(K = \exp(-11.15 + 11783/T)\) (600-1100K)  

(5)
Here $\Delta G^\circ$ is the standard free energy change for the reaction:

$$\text{SO}_3 + \frac{1}{2} \text{O}_2 + 2 \text{Ag} = \text{Ag}_2\text{SO}_4 \quad (6)$$

$K$ is the equilibrium constant for $\text{SO}_2$ oxidation, $p(\text{SO}_2)$ and $p(\text{O}_2)$ are the introduced $\text{SO}_2$ and oxygen partial pressure, respectively.

Fig. 6-I.3 and 6-I.4 show the theoretical EMF as a function of $\text{SO}_2$ concentration and temperature, respectively. While the EMF increases with $\text{SO}_2$ partial pressure, it decreases with temperature.

![Graph](image)

**Fig. 6-I.3** Theoretical EMF as a function of $\text{SO}_2$ concentration.

$p(\text{O}_2) = 0.21 \text{ atm}$, $T_{\text{work}}$, values in °C are given in the plot.
Fig. 6-I.4  Theoretical temperature dependence of the EMF response.

SO₂ concentrations in ppm are given in the plot.

I-3.4 Effect of gas flow rate on sensor response

It is generally observed that the EMF response values are affected by the rate of the SO₂ sample gas flowing over the working electrode. Table 6-I.1 is an example showing the relation between the EMF value and the gas flow rate when the operating temperature is 545°C and the SO₂ sample gas contains 120 ppm of SO₂. The theoretical value of the EMF under these conditions is calculated to be 313.1 mV.
It can be seen that when the gas flow rate is equal to about 24 ml/min, the EMF reaches its highest value, lower and higher flow rates both lead to a decrease of the EMF value. It seems that for this type of sensor, operated at a fixed temperature and SO$_2$ partial pressure, there is an optimum gas flow rate at which the maximum EMF response value which is close to the theoretical value of the EMF can be obtained. This optimal flow rate is influenced by electrocatalytic effects at the sensing electrode, the operating temperature and the sample gas concentration, but the quantitative relation between them has not been revealed. This effect of gas flow rate was also observed in reference[7].

Table 6-I.1  Effect of gas flow rate on EMF response

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
<th>1.5</th>
<th>3.0</th>
<th>12</th>
<th>24</th>
<th>32</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMF (mV)</td>
<td>226.2</td>
<td>255.2</td>
<td>301.9</td>
<td>307.2</td>
<td>305.5</td>
<td>296.5</td>
</tr>
</tbody>
</table>

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I-3.5 Experimental EMF as a function of SO$_2$ partial pressure

Fig. 6-I.5 shows the EMF response of the planar SO$_x$ sensor as a function of SO$_2$ partial pressure at different temperatures. It can be seen that the EMF values are essentially consistent with the theoretical prediction in the p(SO$_2$) range of 10 to 10$^4$ ppm and in the temperature range from 500°C to 700°C. As the temperature decreases, the experimental data gradually deviate from the calculated values. This negative deviation is attributed to an incomplete SO$_2$/SO$_3$ conversion reaction due to insufficient catalytic activity of the Pt sensing electrode at low temperatures. A p(SO$_2$) value lower than the equilibrium one leads to a lower EMF response of the sensor.

Fig. 6-I.5 The EMF of the planar sensor as a function of the SO$_2$ partial pressure. T$_{work}$ values in °C are given in the plot.
I-3.6 Temperature dependence and influence of $V_2O_5$ catalyst

The curve shown in Fig. 6-I.6 was obtained from a planar sensor in a gas flowing system with and without $V_2O_5$ catalyst for comparison. The sample gas has a $SO_2$ partial pressure of 42.7 ppm.

Fig. 6-I.6 Comparison of the temperature dependence of the sensor with and without $V_2O_5$ catalyst. $p(SO_2)=42.7$ ppm. (•) with $V_2O_5$, (○) without $V_2O_5$, (—) calculated.
It is apparent that at the lower temperatures the EMF of the sensor without catalyst deviates from the calculated values. However, when the V$_2$O$_5$ catalyst is put upstream into the gas system, the EMF values are in good agreement with the theoretical values in the temperature range from 450 to 700°C. This result demonstrates the necessity of the presence of a catalyst at the working electrode in order to establish the SO$_2$ oxidation. At high temperatures and low SO$_2$ partial pressures, the theoretical EMF values become negative. In this case, the Ag$_2$SO$_4$ layer formed by the electrochemical reaction at the working electrode will decompose

$$\text{Ag}_2\text{SO}_4 = 2\text{Ag} + \text{SO}_3 + 1/2\text{O}_2$$  \hspace{1cm} (7)

while at the reference electrode no chemical reaction will happen. Ag$^{+}$-$\beta$"-alumina can coexist with silver metal. When the theoretical EMF becomes zero as shown in Fig. 6-1.6, the electrochemical reactions at the interface of this Ag$^{+}$-$\beta$"-alumina based SO$_2$ sensor will stop instead of going in the reversed direction. Then the sensor will no longer operate and the EMF of the sensor will be equal to zero.

The plots in Fig. 6-1.7 show the temperature dependence of the EMF response for this planar SO$_2$ sensor with a V$_2$O$_5$ catalyst at different SO$_2$ partial pressures. In the temperature range of 450 to 700°C and p(SO$_2$) range of 10 to $10^4$ ppm the EMF values agree with the theoretical EMF values.
Fig. 6-1.7 Temperature dependence of a planar Ag⁺-β⁺-alumina SOₓ sensor with the V₂O₅ catalyst. a 10900 ppm, b 4200 ppm, c 950 ppm, d 580 ppm, e 117 ppm and f 12 ppm.

The solid lines represent calculated EMF values.

Fig. 6-1.8 shows a series of EMF response curves of the planar sensor with V₂O₅ catalyst to a sudden change of the sample gas with different p(SO₂). The data clearly reveal that the response time is usually less than 3 min. This response time is adequate for the continuous detection of SOₓ (x=2,3) in many cases, including air pollution monitoring.
Fig. 6-I.8  The dynamic response to a sudden change of the SO$_2$ partial pressure, given in ppm, at different temperatures, 500°C (1), 550°C (2), 600°C (3), 650°C (4).

Itoh et al.[7] reported two types of SO$_x$ sensor comprising Ag$^+$-ß-alumina as the solid electrolyte: for type I a gaseous reference electrode was used, while for type II silver metal was employed as the reference electrode. The measured EMF for type I was approximately equal to the calculated value. For type II a large difference between the experimental and calculated EMF was observed, for instance, in the temperature range
of 440 to 840°C, the measured EMF values were about 150 mV higher than the calculated values. This deviation was explained to be due to the formation of a compound from the \( \text{Ag}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \) system by the reaction of \( \text{Ag}^+ \)-\( \beta \)-alumina with \( \text{SO}_x \) gas in the reaction layer which was confirmed by EPMA. In our work, such a large deviation of the experimental EMF values from the calculated values is absent, a good agreement between the measured and theoretical EMF values is observed in Fig. 6-I.5, 6-I.6 and 6-I.7 with the presence of a catalyst of \( \text{V}_2\text{O}_5 \). This agreement indicates the formation of a pure \( \text{Ag}_2\text{SO}_4 \) layer at the interface of the \( \text{Ag}^+ \)-\( \beta \)-alumina solid electrolyte and the Pt working electrode. The difference between the reaction of \( \text{SO}_x \) gas with \( \text{Ag}^+ \)-\( \beta \)-alumina and \( \text{Ag}^+ \)-\( \beta \prime \)-alumina is due to the different chemical activity of \( \text{Ag}_2\text{O} \) in the two materials. From the above comparison it turns out that \( \text{Ag}^+ \)-\( \beta \prime \)-alumina is a more suitable solid electrolyte for the solid state \( \text{SO}_x \) sensor than \( \text{Ag}^+ \)-\( \beta \)-alumina.

I-4. CONCLUSIONS

1. \( \text{Ag}^+ \)-\( \beta \prime \)-alumina with a homogeneous \( \text{Ag}^+ \) distribution was prepared from \( \text{Na}^+ \)-\( \beta \prime \)-alumina by ion exchange at 300°C in molten \( \text{AgNO}_3 \).

2. \( \text{Ag}^+ \)-\( \beta \prime \)-alumina has the same crystal structure as \( \text{Na}^+ \)-\( \beta \prime \)-alumina. Its ionic conductivity obeys the Arrhenius law in the temperature range of 100 to 800 °C. In addition, it exhibits better chemical stability than \( \text{Na}^+ \)-\( \beta \prime \)-alumina.
All solid state planar SO\textsubscript{x} sensors using Ag\textsuperscript{+}-β\textsuperscript{-}-alumina as solid electrolyte and metal Ag as solid reference have been constructed. When the temperature is higher than 500\textdegree C, the EMF of the sensor exhibits a Nernst response consistent with the theoretical EMF data. The use of a catalyst like V\textsubscript{2}O\textsubscript{5} is required. It also shortens the sensor response time by accelerating the SO\textsubscript{2} oxidation reaction at the working electrode. The response time of this planar SO\textsubscript{x} sensor is usually less than 3 min.
II. Tubular Sensor

ABSTRACT

Polycrystalline Ag\(^+\)-β'-alumina tubes were prepared from Na\(^+\)-β'-alumina tubes by ion exchange and characterized by XRD, DTA, TGA, SEM and EDX analysis. With tubular Ag\(^+\)-β'-alumina as solid electrolyte, Ag metal as solid reference electrode and porous Pt as working electrode solid state galvanic cells were constructed as SO\(_2\) electrochemical sensors

Pt, Ag / Ag\(^+\)-β'-alumina / (SO\(_2\), SO\(_3\), O\(_2\)), Pt

The sensors are measured in a small commercial testing system. The EMF response of the sensor to the SO\(_2\) partial pressure is fairly consistent with theoretical prediction in the working temperature range of 500 to 700°C and the p(SO\(_2\)) range of 10 to 1000 ppm. The response time is usually about 5 to 10 min.
II-1. INTRODUCTION

In addition to the planar $SO_x$ sensor

$$\text{Pt, Ag} / \text{Ag}^+ - \beta''\text{-alumina} / (\text{SO}_2, \text{SO}_3, \text{O}_2), \text{Pt}$$ (8)

a tubular sensor has been developed. In this case a tube of Na$^+ - \beta''\text{-alumina}$ has been used to form Ag$^+ - \beta''\text{-alumina}$ by ion exchange. It has been shown that metallic silver can be employed as a reference electrode against Ag$^+ - \beta''\text{-alumina}$.

In this part of Chapter 6 we present the results obtained with the tubular $SO_x$ sensor.

II-2. EXPERIMENTAL ASPECTS

Polycrystalline Na$^+ - \beta''\text{-alumina}$ tubes with a diameter of 11 mm, wall thickness of 1.5 mm, and a length of 40 mm used in this work were supplied by the Shanghai Institute of Ceramics of the Academia Sinica. To obtain Ag$^+ - \beta''\text{-alumina}$, the tubes were dipped into a AgNO$_3$ melt at 300°C for the ion exchange reaction. The duration of the ion exchange reaction was set at 30 hr. The equipment for analysis of the ion exchanged tubes has been described in part I of this Chapter. Prototype sensors were fabricated by the Danish company PBI-Development Dansensor A/S. Fig. 6-II.1 shows the sensor tube with the electrodes. The sensor was tested in a system shown in Fig. 6-II.2. This system
was described in Chapter 4 and 5. The EMF response of the sensor was measured as a function of operating time, SO\textsubscript{2} partial pressure, and working temperature, respectively.

Fig. 6-II.1  Tubular Ag\textsuperscript{+}-β'-alumina SO\textsubscript{x} sensor.

Fig. 6-II.2  System for the testing of tubular Ag\textsuperscript{+}-β'-alumina SO\textsubscript{x} sensor.
II-3. RESULTS AND DISCUSSION

II-3.1 Preparation and characterization of Ag⁺-β"-alumina

Measurement of the weight increase of the Na⁺-β"-alumina tubes after ion exchange revealed that at 300°C in AgNO₃ melt complete ion exchange of Na⁺ by Ag⁺ in β"-alumina is achieved in 30 hr. This result is concordant with the ion exchange results obtained with flat discs. With XPS, EPMA and X-ray fluorescence analysis no Na⁺ ions can be detected in the sample after 30 hr of ion exchange.

Fig. 6-II.3 presents a SEM picture showing the microstructure of polycrystalline Ag⁺-β"-alumina. The thermal, chemical, and mechanical stability of the ion exchanged tubes compares well with the stability of the ion exchanged flat discs.

Fig. 6-II.3  SEM picture showing a typical microstructure of Ag⁺-β"-alumina
II-3.2 EMF response to SO$_2$ partial pressure

Fig. 6-II.4 (a) shows the sensor EMF response to the variation in the SO$_2$ partial pressure from 30 to 140 ppm at the working temperature of 615°C. The response curve reveals a response time of about 5 to 10 min. At low SO$_2$ partial pressure the response time increases substantially. For concentrations below about 70 ppm, equilibrium EMF values are only attained for impractically long response times.

![Graph showing EMF response over time and SO$_2$ partial pressures.](image)

Fig. 6-II.4 (a)  Time dependence of the sensor EMF response. T$_{\text{work}}$ = 615°C.

SO$_2$ partial pressures in ppm are given in the plot.
Fig. 6-II.4 (b) EMF as a function of the SO$_2$ concentration at $T_{\text{work}} = 615^\circ$C.

(o) theoretical values, (x) experimental data.

Fig. 6-II.4 (b) presents the EMF response as a function of SO$_2$ partial pressures as calculated from Fig. 6-II.4 (a). The experimental EMF values are essentially consistent with the theoretical EMF values obtained with Eq.(1) in part I of this Chapter. The small negative deviation of the experimental results from the theoretical values can be attributed to a lack of catalytic activity of the Pt electrode for SO$_2$ oxidation reaction. SO$_3$ partial pressures smaller than the equilibrium value would result, and hence a lower EMF value.
Fig. 6-II.5 (a) presents the EMF response curve for the SO$_2$ partial pressure range of 100 to 550 ppm at the working temperature of 615°C. A sharp increase of the EMF response is observed when the SO$_2$ concentration increases. However, when the SO$_2$ concentration changes to a smaller value, the EMF response is much slower. This delayed response is ascribed to slow desorption of SO$_3$ from the porous working electrode structure.

Fig. 6-II.5 (a)  Time dependence of the sensor EMF response at $T_{\text{work.}} = 615^\circ$C.
Fig. 6-II.5 (b) EMF as a function of the SO$_2$ partial pressure at $T_{\text{work}} = 615^\circ$C.

(o) theoretical values, (x) experimental data.

Fig. 6-II.5 (b) shows the SO$_2$ dependence of the EMF calculated from the data in Fig. 6-II.5 (a). Again the experimental EMF data are in good agreement with the theoretical values.
Fig. 6-II.6 presents the EMF response as a function of the SO\textsubscript{2} partial pressure at the working temperature of 565°C. The experimental EMF values fit the theoretical values quite well in the low SO\textsubscript{2} concentration range.

Fig. 6-II.6  EMF as a function of the SO\textsubscript{2} partial pressure at T\textsubscript{work.} = 565°C.  
(□) theoretical data, (×) experimental data.
II-3.3 Temperature dependence of the EMF

The curves shown in Fig. 6-II.7 and 6-II.8 represent the theoretical and experimental temperature dependence of the sensor EMF response for $p(\text{SO}_2) = 10$ ppm and 100 ppm, respectively. Similar results have been obtained in the $\text{SO}_2$ partial pressure range upto 1000 ppm. Obviously, from 570 to 620°C the experimental EMF values are in excellent agreement with the theoretical ones, while in the low temperature range a negative deviation of the EMF output is observed. It is assumed that the catalytic activity of the porous Pt electrode is not sufficient for the $\text{SO}_2$ oxidation to reach the equilibrium values. If $\text{V}_2\text{O}_5$ is used as a catalyst upstream in the gas system, the low temperature sensor response can be improved.

Fig. 6-II.7  EMF as a function of the operating temperature for $p(\text{SO}_2)=10$ ppm.

(*) theoretical data, (+) experimental values.
Fig. 6-II.8  Temperature dependence of the sensor response for $p(\text{SO}_2) = 100$ ppm.

(□) theoretical values, (+) experimental values.

II-4. CONCLUSIONS

(1) Polycrystalline $\text{Ag}^+\text{-}\beta^\prime$-alumina polycrystalline tubes were obtained by ion exchange from $\text{Na}^+\text{-}\beta^\prime$-alumina tubes at 300°C in a $\text{AgNO}_3$ melt. Its thermal and chemical stability is better than that of $\text{Na}^+\text{-}\beta^\prime$-alumina.
(2) All-solid state SO$_x$ sensors with tubular Ag$^+\text{-}\beta$-alumina as solid electrolyte, silver metal as solid reference electrode and porous Pt as working electrode have been fabricated. If the temperature is higher than 500°C and the SO$_2$ concentration is in the partial pressure range of 10 to 1000 ppm, the EMF of the sensor exhibits a good Nernst response consistent with theoretical prediction. The response time is about 5 to 10 min. The experimental results indicate the potential of this SO$_2$ sensor for practical applications, and the necessity to improve the catalytic conversion of SO$_2$ to SO$_3$ at the working electrode.

ACKNOWLEDGEMENTS

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REFERENCES

[2]. M. Gauthier, A. Chamberland, A. Belanger and M. Poirier, ibid, 124, (1977) 1584
[3]. K.T. Jacob and D.R. Rao, ibid, 126, (1979) 1842
CHAPTER 7

NERNST TYPE NO\textsubscript{x} SENSORS BASED ON Ag\textsuperscript{+}-\textbeta"-ALUMINA

ABSTRACT

A new Nernst-type NO\textsubscript{x} (x=1,2) sensor was designed with Ag\textsuperscript{+}-\textbeta"-alumina as the solid electrolyte, porous platinum together with AgNO\textsubscript{3} as the gas-sensing working electrode, and silver metal as the solid reference electrode. Both planar and tubular Ag\textsuperscript{+}-\textbeta"-alumina based NO\textsubscript{x} sensors have been prepared and tested in a simple configuration which allows these sensors to be commercially developed.

The planar NO\textsubscript{x} sensors with a thin sputtered Pt electrode are sensitive to a variation in the NO concentration at a fixed temperature around 200\textdegree 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 Pt electrode revealed experimental EMF values close to the theoretical values in the NO concentration range of 10\textsuperscript{3} to 10\textsuperscript{4} 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 Pt 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 Pt 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.
1. INTRODUCTION

In recent years, many efforts have been focussed on the development of technologies to detect the NO\textsubscript{x} content in industrial exhaust gases, such as chemoluminescence methods\cite{1}, ion selective electrodes\cite{2,3}, biochemical sensors\cite{4,5}, semiconductor sensors\cite{6} and solid electrolyte sensors\cite{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\textsubscript{2} poses also a problem.

**Biochemical sensors**
using a gas-permeable membrane with immobilized nitrite oxidizing bacteria can detect NO\textsubscript{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. They 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.

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 \( \text{NO}_x \) 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\(^+\)-\(\beta^\prime\)-alumina solid electrolyte and NaNO\(_3\) as the gas-sensing layer. Na\(^+\)-\(\beta^\prime\)-alumina is one of the best sodium ion 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\(^+\)-\(\beta^\prime\)-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\(^+\)-\(\beta^\prime\)-alumina has been selected as the solid electrolyte. It can be easily prepared from Na\(^+\)-\(\beta^\prime\)-alumina by ion exchange. Then, silver metal can be applied as solid reference electrode as has been described in Chapter 6. Ag\(^+\)-\(\beta^\prime\)-alumina is a pure silver ion conductor with a high conductivity comparable to Na\(^+\)-\(\beta^\prime\)-alumina. Its thermal and chemical stability are also satisfactory.

The solid electrolyte Ag\(^+\)-\(\beta^\prime\)-alumina based \( \text{NO}_x \) sensor

\[ \text{Pt, Ag} / \text{Ag}^+\text{-\(\beta^\prime\)-alumina} / \text{AgNO}_3 / (\text{NO, O}_2, \text{NO}_2), \text{Pt} \]

where AgNO\(_3\) is formed by the reaction between Ag\(^+\)-\(\beta^\prime\)-alumina and the NO-O\(_2\)-NO\(_2\) ambient at the Pt working electrode has been studied for the detection of NO\(_2\) in the
range of $10^2$ to $10^4$ ppm from industrial exhaust gases in the 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 Chapter 2 III.

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 Chapter 6. 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 Pt structure. The latter has a high catalytic activity for the NO/NO$_2$ conversion. For planar sensors, both Pt and Ag paste, or sputtered Pt and Ag thin layers can be use as electrodes. The silver reference electrode has to be protected from the NO$_x$ containing ambient.
1. Ag-β"-alumina solid electrolyte
2. Porous Pt working electrode
3. Pt lead of Ag reference electrode
4. Pt lead of working electrode

1. Pt lead of reference electrode
2. Pt lead of working electrode
3. Cement
4. Metal Ag reference electrode
5. Alumina tube
6. Ag-β"-alumina electrolyte
7. Porous Pt working electrode
8. Pt mesh

(a) Tubular sensor (b) Planar sensor

Fig. 7.1 Schematic configuration of Ag⁺-β"-alumina based NOₓ sensors.
Fig. 7.2  Alternative construction of a planar sensor.

(a) Top view  (b) Side view

1. Porous Pt working electrode
2. Cement
3. Glass support
4. Ag-β'-alumina electrolyte
5. Metal Ag reference electrode
6. Pt lead of working electrode
7. Pt lead of reference electrode

Fig. 7.1 shows the schematics of the tubular and planar NOx sensors. Fig. 7.2 presents an alternative configuration of the planar sensor. The sensors are tested in a system shown in Fig. 7.3. The sample gas mixtures with different NO and O2 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 of the sensor was obtained as a function of operating time, NO and O2 partial pressure as well as the working temperature.
Fig. 7.3  Schematics of the sensor testing system.
3. RESULTS AND DISCUSSION

3.1 Effect of gas flow rate on sensor response

Here it is generally observed that the EMF response is influenced by the gas flow rate. Fig. 7.4 gives a typical example of the gas flow effect for tubular sensor AgBNSt1 with a construction as indicated in Fig. 7.1 (a). It is seen that at 200 ml/min, the sensor response reaches its highest value. Therefore, in the following measurements with both planar and tubular sensors the total gas flow rate has been fixed at 200 ml/min.

![Graph showing the effect of gas flow rate on sensor response.](image)

**Fig. 7.4** Effect of gas flow rate on sensor response at 190°C for tubular sensor AgBNSt1. $p(\text{NO}) = 2241$ ppm, $p(\text{O}_2) = 0.016$ atm.
3.2 EMF response to variations in the NO partial pressure

Fig. 7.5 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. 7.1 (b).

Fig. 7.5 EMF response of a planar sensor as a function of the NO concentration at $T_{\text{work.}} = 200^\circ\text{C}$ and $p(O_2) = 0.011$ atm.

(+) theoretical values, (△) experimental values.
Fig. 7.6 Conversion efficiency of NO to NO₂ in a planar sensor as calculated from the data in Fig. 7.5 at T_{work} = 200°C and p(O₂) = 0.011 atm.

There is a substantial difference between the theoretical and experimental EMF values. Considering the use of a thin layer of sputtered Pt 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 Pt sensing electrode, which will result in NO₂ concentrations which are lower than the equilibrium values. Fig. 7.6 shows the percentage of NO in...
equilibrium with NO\textsubscript{2} in the total gas flux as a function of the NO concentration. The data were calculated from Fig. 7.5. With increasing NO concentration the efficiency of NO conversion to NO\textsubscript{2} is decreasing. For a NO concentration of 4500 ppm, only 50\% of NO is in equilibrium with NO\textsubscript{2}. Improved results as presented in Figs. 7.7 and 7.8 were obtained with a tubular sensor AgBNSt1.

Fig. 7.7  EMF response of a tubular sensor to NO concentration at $T_{\text{work.}} = 197^\circ$C and $p(O_2) = 0.016$ atm. ($+$) theoretical data, ($\Delta$) experimental data.
Fig. 7.8 Conversion efficiency of NO to NO₂ in a tubular sensor as calculated from the data in Fig. 7.7 at $T_{\text{work.}}=197^\circ\text{C}$ and $p(O_2)=0.016$ atm.

From Figs. 7.7 and 7.8 it is seen that at the fixed temperature of $197^\circ\text{C}$ and an $O_2$ 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 a tubular sensor the use of Pt paste leads to a thicker porous electrode structure.
Fig. 7.9  EMF response as a function of NO partial pressure for a tubular sensor at 198°C and p(O₂)=0.016 atm. (+) theoretical data, (Δ) experimental data.

Fig. 7.10  Conversion efficiency of NO to NO₂ in a tubular sensor as calculated from the data in Fig. 7.9.
Figs. 7.9 and 7.10 present EMF values at lower NO partial pressures, and conversion data, respectively, using the same tubular sensor and results similar to those presented in Fig. 7.7. and 7.8 have been obtained. If, however, the O$_2$ 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 $10^3$ to $8\times10^3$ ppm, and O$_2$ partial pressures of 0.01 to 0.05 atm was obtained with the tubular sensor AgBNSt1. The agreement between the experimental EMF values and the theoretical values can be seen in Fig. 7.11.

![Graph showing EMF response of sensor AgBNSt1](image)

**Fig. 7.11** EMF response of sensor AgBNSt1 as a function of the NO and O$_2$ partial pressures at 191°C and $p(\text{O}_2) = c \cdot p(\text{NO})$ with $p(\text{O}_2)$ in the range of 0.01 to 0.05 atm. (+) theoretical data, (△) experimental data.
The EMF response of the tubular sensors in the low NO concentration regime has also been tested using the AgBNSt1 and AgBNSt2 sensors. Fig. 7.12 presents the response of sensor AgBNSt1 to NO variation in the range of 50 to 700 ppm. The $O_2$ 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 AgBNSt2 as displayed in Figs. 7.13 and 7.14. The better response of AgBNSt2 compared with AgBNSt1 can be explained by their testing history.

![Graph showing EMF response vs NO concentration](image)

**Fig. 7.12**  EMF response of sensor AgBNSt1 as a function of NO and $O_2$ concentrations at 184°C and $p(O_2) = c \cdot p(NO)$ in the range of 0.008 to 0.1 atm. (▲) theoretical data, (△) experimental data.
Fig. 7.13 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 values.

Fig. 7.14 Conversion efficiency of NO to NO$_2$ in sensor AgBNSt2 as calculated from the data in Fig. 7.13.
Sensors AgBNSt1 and AgBNSt2 have exactly the same configuration, but AgBNSt1 had been exposed to very concentrated NO/NO₂ containing ambients and 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 Pt working electrode and solid electrolyte, and impart into the porous Pt structure. This would limit the adsorption of NO and NO₂ on the Pt surface and hence the establishment of the NO to NO₂ conversion equilibrium. However, AgBNSt2 was a newly fabricated sensor, which was first tested in this low NO concentration 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 Pt electrode. Fig. 7.15 and 7.16 are also obtained with sensor AgBNSt2 showing another example of the sensor response to low NO concentrations. In this case, the O₂ partial pressure is fixed. In Fig. 7.15, the experimental EMF response even fits the theoretical values better than in Fig. 7.13, and the conversion of NO to NO₂ as presented in Fig. 7.16 is also better than that in Fig. 7.14. However, the same results could not be obtained in the subsequent measurement runs of sensor AgBNSt2, and this is obviously due to the growth of the silver nitrate layer at the porous Pt electrode of sensor AgBNSt2.
Fig. 7.15  EMF response of sensor AgBNSt2 as a function of the NO partial pressure at 172°C and p(O₂) = 0.016 atm, (+) theoretical data, (Δ) experimental data.

Fig. 7.16  Conversion efficiency of NO to NO₂ in sensor AgBNSt2 as calculated from the data in Fig. 7.15.
3.3 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. 7.17. The experimental temperature dependence fits the theoretical values reasonably well.

![Graph showing temperature dependence of EMF response](image)

**Fig. 7.17** Temperature dependence of EMF response of sensor AgBNSt1.

\[ p(\text{NO}) = 1.12 \times 10^4 \text{ ppm and } p(\text{O}_2) = 0.016 \text{ atm}, \]

(+): theoretical values, (△): experimental data.
3.4 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. 7.18 shows the porous structure of the working electrode of a planar sensor before testing. For comparison, Fig. 7.19 presents a picture of the platinum working electrode of the same sensor after a long period of testing.

Fig. 7.18  SEM picture of the porous Pt working electrode of a planar sensor before testing.
Fig. 7.19 SEM picture of the Pt working electrode of Fig. 7.18 after testing in a NO-O$_2$-NO$_2$ ambient.

Fig. 7.19 reveals that many crystalline particles have been formed at the Pt working electrode, and these particles represent the formed electroactive layer of AgNO$_3$. 

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3.5 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, for instance, of kinetic reasons, the sensor can still be of practical use, provided that the sensor has been calibrated before use.

Fig. 7.20 shows the result of a preliminary study of the reproducibility of tubular sensor AgBNSt1. The duration of the test was 3 weeks with the sensor at 197°C and p(NO) being 1120 ppm, and p(O₂) 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.

![Graph showing EMF over time](image)

**Fig. 7.20** Reproducibility of tubular sensor AgBNSt1 at 197°C, p(NO)=1120 ppm, and p(O₂)=0.016 atm, (+) theoretical values, (△) experimental data.
This result as well as the simple configuration make the Ag⁺-β"-alumina based NOₓ sensor to be a promising candidate sensor for development for commercial application.

3.6 Selectivity of the sensor to NOₓ against CO₂

According to the theoretical analysis in Chapter 2 III, this type of NOₓ sensors should have excellent selectivity to NOₓ against CO₂. In the experimental EMF measurements, the response of 124.1 mV to 1000 ppm NO and 0.1 atm O₂ at 199°C (theoretical value is 128.6 mV) was not changed by the presence of 0.01 atm CO₂. This preliminary investigation of the selectivity of the sensor confirms that the interference of CO₂ in the NOₓ detection is not a problem for this type of NOₓ sensors.

3.7 Problem of oxygen partial pressure measurement

If in the practical use of NOₓ (and also SOₓ) 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 NOₓ sensor. However, the currently commercially available stabilized zirconia based O₂ sensor is not suited, 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 species as suggested by Michaels et al.[11]. Multiple charge-transfer processes result in mixed potentials, which fall between the thermodynamical potentials of the individual charge-transfer reactions[12]. 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 O₂/O²⁻ charge transfer reaction on the Pt electrode of the NOₓ (SOₓ) sensors. Therefore,
the measurement of an unknown $O_2$ partial pressure will remain a problem in the practical use of $NO_x$ and $SO_x$ sensors.

In addition, it is well known that a porous Pt electrode does not fulfill entirely the long term stability requirement, gauge response time and accuracy requirements for high temperature oxygen sensors[13]. To overcome these problems, the use of metal oxides and mixed metal oxides as electrode materials was proposed[14,15]. However, much research has to be done before a proper oxidic electrode material can be applied, and a smart multiple sensor system for the detection of $SO_x$, $NO_x$ and $O_2$ is commercially available.

4. CONCLUDING REMARKS

(1). A new Nernst-type $NO_x$ ($x = 1,2$) sensor was designed with surface modified $Ag^+\beta$"-alumina as the solid electrolyte, porous platinum together with $AgNO_3$ as the gas-sensing working electrode and metallic silver as the solid reference electrode. Both planar and tubular $Ag^+\beta$"-alumina based $NO_x$ 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 Pt working electrode before testing reveals a porous structure, while after testing, some crystalline particles are observed, most
probably due to the reaction of Ag⁺-β-alumina with NO₂ in the presence of oxygen to form AgNO₃.

(3). The planar NOₓ sensors with a thin sputtered Pt 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 Pt 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 10³ to 10⁴ ppm, if the O₂ 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 Pt 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 NO\textsubscript{x} sensor to NO\textsubscript{x} against CO\textsubscript{2} gas.

REFERENCES


CHAPTER 8

SEMICONDUCTOR NO\textsubscript{x} GAS SENSORS

ABSTRACT

Mixtures of Al\textsubscript{2}O\textsubscript{3}-ZnO-V\textsubscript{2}O\textsubscript{5} have been explored for use as active sensor material in Taguchi-type NO\textsubscript{x} sensors. The electrical resistance and Seebeck effect of these semiconducting oxide mixtures have been measured as a function of the oxide composition. The sensitivity and selectivity of the sensor to NO and NO\textsubscript{2} gases against CO\textsubscript{2} were studied in order to find the optimal composition of the oxides. The experimental results indicate that sensors based on mixtures of Al\textsubscript{2}O\textsubscript{3}-ZnO-V\textsubscript{2}O\textsubscript{5} exhibit sensitive and fast response to 20 to 600 ppm of NO and/or NO\textsubscript{2} in the temperature range of 200 to 400°C, the sensitivity to NO is usually larger than that to NO\textsubscript{2}, the presence of NO\textsubscript{2} and oxygen being of influence on the sensitivity. The sensors are almost insensitive to even 0.01 atm CO\textsubscript{2} gas.
1. INTRODUCTION

Since the 1960s, when the high sensitivity of the electrical conductivity of some metal oxides like SnO₂, ZnO and Fe₂O₃ to the gaseous environment was found and proposed to be utilized for the detection of inflammable gases by Taguchi[1] and Seiyama[2,3], thin film semiconductor gas sensors have been developed and marketed worldwide. To date, the Taguchi-sensor for CO has found widespread application.

Because metal oxide gas sensors are usually sensitive to a variety of gaseous species in the atmosphere, a major drawback of these Taguchi-type sensors is the almost complete lack of selectivity, which has limited their use to non-quantitative applications. Several routes to improve their selectivity have been investigated, and these include the use of different metal oxides, varying the temperature of operation[4], and the introduction of additives to the oxide surfaces[5], for which usually known oxidation catalysts like Pd and Pt are being selected. Varying degrees of success have been achieved using combinations of these methods.

Regarding metal oxide semiconductor NOₓ sensors, many investigations have been reported[6-15]. Among these, the use of mixtures of two oxides was studied in Japan[14,15]. Table 8.1 summarizes the major results of this work. From Table 8.1 it can be seen that a mixture of alumina and vanadium oxide exhibits a good selectivity to NO and NO₂ gases in a NOₓ and COₓ containing atmosphere, while the sensitivity is not high. In contrast with this mixture, a mixture of alumina and zinc oxide exhibits very high sensitivity to NOₓ, but if used as a NOₓ detector, CO will cause a rather strong noise signal. It seems that zinc oxide which is a well-known semiconducting gas-sensing
material, has a high sensitivity to various kinds of gaseous species. However, its selectivity is poor. The surface and adsorption properties of $V_2O_5$, which is a well-known catalytic material, can be greatly modified by materials such as $Al_2O_3$, $TiO_2$ and $SiO_2$. In the $V_2O_5$-$Al_2O_3$ mixture, part of the $V_2O_5$ is assumed to react with $Al_2O_3$ to form $AlVO_4$, which will give rise to new adsorption sites for $NO/NO_2$[16]. Therefore, the effect of $V_2O_5$-$Al_2O_3$ mixed oxides on the selectivity to $NO_x$ gases seems to result from the creation of these new sites.

In the present study, we have explored the use of a mixture of three oxides in order to find an optimal composition in the system $Al_2O_3$-$ZnO$-$V_2O_5$, which has both high sensitivity and good selectivity to $NO_x$ against $CO$ and $CO_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature$^a$ (°C)</th>
<th>Sensitivity$^b$</th>
<th>NO</th>
<th>NO$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al_2O_3$-$V_2O_5$</td>
<td>400</td>
<td>2.54</td>
<td>2.71</td>
<td>1.09</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>$Al_2O_3$-$ZnO$</td>
<td>400</td>
<td>5.37</td>
<td>6.39</td>
<td>7.08</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>$V_2O_5$-$ZnO$</td>
<td>400</td>
<td>2.41</td>
<td>2.61</td>
<td>2.00</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Optimum temperature for NO and NO$_2$ detection

$^b$ Sensitivity = $R_{air}/R$

NO, NO$_2$, CO and CO$_2$ concentration: 600 ppm
2. EXPERIMENTAL PROCEDURES

Semiconducting mixtures of $\text{Al}_2\text{O}_3$-$\text{ZnO}$-$\text{V}_2\text{O}_5$ with different compositions can be prepared either by a wet chemical method using co-precipitation from the corresponding nitrates or by solid state reaction of the binary oxides. In this study, solid state synthesis was employed to prepare the mixed oxide semiconductor materials.

The powders of mixed oxides were calcined at 450°C for 5 hr and then pressed into pellets which were sintered at 500°C for 3 hr. Platinum electrodes were sputtered to one of the faces of the pellets using a mask. The sensor element provided with the electrodes was finally assembled on a glass substrate as shown in Fig. 8.1.

![Schematic diagram of the semiconductor NO$_x$ sensor element.](image)

1. 2. Electrode leads
2. Pt sputtered electrodes
3. Oxide semiconductor
4. Glass substrate
5. Glass substrate

Fig. 8.1 Schematic diagram of the semiconductor NO$_x$ sensor element.
The electrical resistance of the semiconductor sensor elements was measured at room temperature in air using a dc voltage supply and a 150B Microvolt Ampere meter. The voltage drop over the sensor element was measured with a 197 Multimeter DMM. The Seebeck effect of these semiconductor materials was measured in order to determine the type of semiconductivity by applying a temperature gradient between the two electrodes and detecting the thermoelectric potential using a Nanovoltmeter TE 925.

The semiconductor sensors were exposed to different NO\textsubscript{x}-containing ambients in the sensor testing system as shown in Fig. 8.2. The sensitivity and selectivity of the sensor elements to NO and NO\textsubscript{2} gases against CO\textsubscript{2} were measured at different temperatures.

Fig. 8.2  Sensor testing system.
3. RESULTS AND DISCUSSION

3.1 Composition and Seebeck effect of the semiconductors

The composition, resistance and Seebeck effect data of the different compositions of the mixtures of Al₂O₃-ZnO-V₂O₅ are presented in Table 8.2. The sign of the Seebeck coefficient, S, provides a simple, direct test of the dominant charge carrier concentration. The semiconducting materials denoted S5, S6 and S7 have the equimolar composition of ZnO-V₂O₅, Al₂O₃-V₂O₅ and Al₂O₃-ZnO, respectively, corresponding to the specimen in Table 8.1. S1, S2 and S3 are the equimolar combinations of S6 and S7, S5 and S6, S5 and S7, respectively. S4 comprises an equimolar composition of the three oxides. It is apparent that the composition of the mixtures determines the type of the dominant charge carrier. The Seebeck coefficient is greatly affected by the defect structure of the materials, the nature and level of the doping compounds, and in case of oxidic semiconductors the oxygen partial pressure. ZnO is a well-known n-type semiconductor, but when different amounts of V₂O₅ and Al₂O₃ are added, both p-type (S4 and S5 in Table 8.2) and n-type (S1, S2, S3, S7 in Table 8.2) semiconductors are obtained. Sample S6 indicates that V₂O₅ is a p-type semiconductor. Also dispersing upto about 40 % Al₂O₃ into electrical conductors is known to enhance the ionic and electronic conductivity. At higher levels the conductivity starts to decrease. Based on these effects, the type of conductivity in these mixtures can be discussed. It is understandable that sample S4 and S5 which have relatively high V₂O₅ content and low Al₂O₃ content are p-type, whereas the others (S1, S3, S7) with relatively low V₂O₅ concentration and high Al₂O₃ concentration exhibit n-type conductivity. However, the result of sample S2 is

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difficult to explain: a higher $V_2O_5$ content (even higher than that of S4) in the three-oxide mixture still results in n-type conductivity. While it is known that grain boundary interfaces play an important role in the electrical property variation of dispersions, a quantitative interpretation depends on insights into the microstructure - particle size relations. A study of these relations was beyond the scope of this project.

Table 8.2 Composition, resistance and Seebeck effect of $Al_2O_3-ZnO-V_2O_5$ semiconductors

<table>
<thead>
<tr>
<th>Sample</th>
<th>$Al_2O_3$ (mol%)</th>
<th>ZnO (mol%)</th>
<th>$V_2O_5$ (mol%)</th>
<th>$S=dV/dT$</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td>-</td>
<td>n</td>
</tr>
<tr>
<td>S2</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
<td>-</td>
<td>n</td>
</tr>
<tr>
<td>S3</td>
<td>0.25</td>
<td>0.50</td>
<td>0.25</td>
<td>-</td>
<td>n</td>
</tr>
<tr>
<td>S4</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>+</td>
<td>p</td>
</tr>
<tr>
<td>S5</td>
<td>0</td>
<td>0.50</td>
<td>0.50</td>
<td>+</td>
<td>p</td>
</tr>
<tr>
<td>S6</td>
<td>0.50</td>
<td>0</td>
<td>0.50</td>
<td>+</td>
<td>p</td>
</tr>
<tr>
<td>S7</td>
<td>0.50</td>
<td>0.50</td>
<td>0</td>
<td>-</td>
<td>n</td>
</tr>
</tbody>
</table>

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3.2 Temperature dependence of the sensor resistance

In the sensor testing system as shown in Fig. 8.2, the voltage drop $V_0$ is measured and this parameter is used to calculate the resistance $R$ of the sensor element with

$$ R = \frac{E_0 - V_0}{V_0} R_0 $$  \hspace{1cm} (1)

Here $R_0$ denotes a standard resistance, $E_0$ the output voltage of the dc voltage supply, and $V_0$, the voltage drop over $R_0$. Fig. 8.3 presents the resistance of the 7 sensor elements as a function of temperature.

![Temperature dependence of the resistance of sensors](image)

**Fig. 8.3** Temperature dependence of the resistance of sensors based on mixtures of Al$_2$O$_3$-ZnO-V$_2$O$_5$. (+) S1, (▲) S2, (○) S3, (+) S4, (▲) S5, (●) S6 and (▼) S7.
In general, the conductance of the 7 sensors increases with temperature. It is seen that from about 90°C until 270°C, the magnitude of the conductance of the semiconductors follows the sequence S1 < S3 < S7 < S5 < S2 < S4 < S6. The differences in the temperature dependence of the sensor materials are probably due to their differences in composition and microstructure. The results seem to indicate that two effects play an important role. Firstly, the data for sample S6 which is based on a mixture of Al₂O₃ and V₂O₅, reveal that V₂O₅ exhibits a high electronic p-type conductivity. The higher conductivities are found for mixtures with the larger V₂O₅ contents. Secondly, as has been mentioned before, dispersing an inert oxide into a conducting matrix has a marked influence on the electrical properties, and usually the dependence as depicted in Fig. 8.4 is observed. The influence of this second effect is seen by comparing the data for S1 and S7.

![Diagram](image)

**Fig. 8.4** Effect of dispersed Al₂O₃ on the electrical conductivity of solid electrolyte and semiconducting materials.

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From the data for S1 and S7 it may be concluded that the Al₂O₃ content is too high, and beyond the maximum conductivity value indicated in Fig. 8.4. Indeed, the maximum in such curves occurs usually at about 30-40 % inert dispersed oxide. If this were to be correct the data for S6 could be improved by adding less Al₂O₃, and in fact the data for S4 do support this approach, where the enhancement of a moderate level of Al₂O₃ outweighs the deleterious effect of the addition of the very low conducting ZnO. This balance of opposing effects swings the other way in S3 where a very low conductivity exists.

3.3 Sensitivity as a function of NO concentration

The sensitivity of the sensor elements to NO or other gases is defined as

\[ Sensitivity = \frac{\sigma}{\sigma_{air}} \frac{R_{air}}{R} \]  

(2)

where \( \sigma \) and \( R \) are the conductivity and resistance of the sensor element on exposure to NO or other gases, respectively, while \( \sigma_{air} \) and \( R_{air} \) denote the conductivity and resistance of the sensor element in air as a reference, respectively.

The sensor sensitivity has been studied for all above mentioned sensors. The experimental results of the sensitivity testing of sensors S1, S3, S4 and S5 are given below as examples. S1 was expected to be the most promising sensor material with both high sensitivity and selectivity to NO detection, since S1 is an equimolar mixture of the highly selective mixture Al₂O₃-V₂O₅ and the highly sensitive material Al₂O₃-ZnO as indicated in Table 8.1. Fig. 8.5 gives an example of the sensitivity of this sensor as a function of
NO concentration at a fixed operating temperature of 290°C. For NO concentrations up to 350 ppm, S1 yields a linearly increasing response. However, in the NO concentration range of 350 to 1200 ppm, the sensitivity as defined by Eq.(2) first dropped to 2 and then gradually decreased. This result shows that sensor S1 can be used for NO detection as an alternative to the Ag⁺-ß'-alumina based NOₓ sensor (see Chapter 7) for higher temperatures and lower NO concentrations.

![Graph](image)

**Fig. 8.5** Sensitivity of sensor S1 as a function of NO concentration at 290°C.

Three runs of sensor S3 yielded quite different results of the sensitivity as is shown in Fig. 8.6. The first run was performed at 290°C, the second and third were carried out at 295°C. In the first run, a high sensitivity to NO concentrations in the range of 0 to 500 ppm was observed. An increasing NO concentration yields an increase of sensitivity.
However, when the NO concentration reaches 600 ppm, the sensitivity drops substantially, and then the sensor becomes insensitive. The second run gives different results as compared with the first. While the sensitivity increases with NO concentration in the region of 0 to 600 ppm NO, it levels off in the range of 600 to 1400 ppm. In the third run the sensitivity shows a result similar to that of S1. The sensor is only sensitive to NO in the range of 0 to 350 ppm. At higher concentrations, the sensitivity decreases gradually to zero sensitivity. From Fig. 8.6 it is concluded that sensor S3 can also be an alternative to the Ag⁺-β-alumina solid electrolyte based NOx sensor for NO detection at elevated temperatures and low concentrations, i.e. upto about 300 ppm. The differences in responses during the different runs is not yet understood.

![Graph showing sensitivity to NO concentration](image)

**Fig. 8.6** Sensitivity of sensor S3 to the NO concentration.

(+) 1st, 290°C, (△) 2nd, 295°C and (●) 3rd, 295°C.
The response of sensor S4 with the equimolar mixture of the three oxides also goes through a maximum. However, an important difference is noted that sensor S4 exhibits a much higher sensitivity than sensors S1 and S3 under similar testing conditions.

![Graph showing sensitivity vs. NO concentration](image)

**Fig. 8.7** Sensitivity of sensor S4 as a function of NO concentration at 284°C.

The NO concentration dependence of the sensitivity of sensor S5 was studied at 306°C and the results are presented in Fig. 8.8. The two runs of sensor S5 reveal similar results. While the sensitivity increases with NO concentration it is obvious that a broad maximum exists. Also a high sensitivity is noted for low NO concentrations, and even down to 20 ppm the sensitivity is as high as 3.37. This result is quite different from the
results reported in the literature (see Table 8.1) and may be explained by the different preparation procedure of the semiconductor materials.

Fig. 8.8  Sensitivity of sensor S5 as a function of NO concentration at $T_{\text{work}} = 306^\circ \text{C}$. (•) 1st run, (○) 2nd run.

The tested sensors differ in several aspects. First, the active materials of sensors S1 and S3 exhibit n-type conductivity, while those of sensors S4 and S5 are p-type conductors. In addition, the conductivity of sensor S1 is smaller than that of sensor S3, while the conductivity of sensor S4 is larger than that of sensor S5. Although the testing temperatures are not the same in all experiments, the data in Fig. 8.3 indicate that the
observed sensitivity differences cannot be ascribed to a conductivity variation due to the temperature effect. The present data clearly indicate that the sensitivity is better for sensors based on p-type type conductors, and tends to increase with increasing conductivity. It should, however, be borne in mind that the sensor materials are composites, comprising inert, n-type and/or p-type conducting oxides, except for S5, which is based on n-type ZnO and p-type V$_2$O$_5$. The active sensor materials, therefore, will contain many p-n junctions at the grain boundaries. Their role in the sensing mechanism is not understood, but with regard to the data for sensor S5 cannot be ruled out.

3.4 Temperature dependence of sensitivity and response time

The temperature dependence of the sensitivity of sensor S3 to 330 ppm NO is presented in Fig. 8.9 as an example. The temperature dependence of the sensitivity of sensor S4 to 20 ppm NO is presented in Fig. 8.10. Similar results have been obtained for other sensors. The sensitivity of the sensor elements to both low and high NO concentrations can be enhanced by increasing the operating temperature. In addition, at higher temperatures, shorter response times are observed. It should, however, be mentioned that, in general, the response times of this type of sensor is much shorter than that of the Ag$^+$.β$^-$-alumina based NO$_x$ sensors.
Fig. 8.9 Temperature dependence of the sensitivity of sensor S3 at $p(\text{NO}) = 330$ ppm.

The working temperature of the sensors is limited by the thermal stability of the active materials. The present three oxide composites are stable up to 500°C. At higher temperatures the materials will melt.
3.5 Effect of gas flow rate on sensor performance

The influence of gas flow rate on the sensor performance of solid electrolyte gas sensors has been described in the previous chapters. Also for semiconductor $\text{NO}_x$ ($x=1,2$) sensors, the gas flow rate is an important factor which needs to be taken into account. For instance, the sensitivity of sensor S3 as a function of the total gas flow rate has been determined at a constant NO concentration of 410 ppm and a constant temperature of
295°C. The results are presented in Fig. 8.11. It is seen that the sensitivity of S3 decreases with increasing gas flow rate, the highest sensitivity being obtained under zero-flow conditions.

![Graph showing the effect of gas flow rate on sensor sensitivity](image)

**Fig. 8.11** Effect of gas flow rate on the performance of sensor S3 at 295°C and p(NO) = 410 ppm.

This result differs from the observations on solid electrolyte sensors, where the sensor output reveals a maximum. Instead of using a proper gas flow rate in the case of solid
electrolyte sensor testing, in the measurements with semiconductor sensors, the gas flow rate is kept as low as possible.

3.6 Selectivity to NO and NO\textsubscript{2} against CO\textsubscript{2}

The interference of CO\textsubscript{2} with the detection of NO and NO\textsubscript{2} was primarily investigated by measuring separately the sensitivity to NO, NO\textsubscript{2} and CO\textsubscript{2}. The effect of CO has not been studied because of safety reasons of the used gas sensor testing system. Table 8.3 describes the experimental results of the sensitivity to CO\textsubscript{2} in comparison with the sensitivity to NO and NO\textsubscript{2} at fixed working temperature in the range of 284 to 325\textdegree C. It appears that all the sensors are practically insensitive to CO\textsubscript{2} even if the CO\textsubscript{2} concentration is as high as 0.01 atm. Therefore, a high concentration of CO\textsubscript{2} in the gas to be analyzed will not interfere with the detection of NO and NO\textsubscript{2}. It is also noticed that the semiconductor sensors are more sensitive to NO than to NO\textsubscript{2}, which is in disagreement with the reported results in Table 8.1. This result is also quite different from the situation in the solid electrolyte based NO\textsubscript{x} sensors (Chapter 7), since for this type of NO\textsubscript{x} sensor, it is NO\textsubscript{2} rather than NO that reacts with the solid electrolyte. It therefore appears that the combined use of the semiconductor and solid electrolyte NO\textsubscript{x} sensors provides the possibility to detect NO and NO\textsubscript{2} separately.
Table 8.3 Sensitivity of the mixed oxides

<table>
<thead>
<tr>
<th>Sample</th>
<th>Operating Temperature (°C)</th>
<th>Sensitivity$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NO</td>
</tr>
<tr>
<td>S1</td>
<td>290</td>
<td>2.25</td>
</tr>
<tr>
<td>S2</td>
<td>325</td>
<td>1.74</td>
</tr>
<tr>
<td>S3</td>
<td>295</td>
<td>1.25</td>
</tr>
<tr>
<td>S4</td>
<td>284</td>
<td>3.17</td>
</tr>
<tr>
<td>S5</td>
<td>306</td>
<td>4.22</td>
</tr>
<tr>
<td>S6</td>
<td>325</td>
<td>2.80</td>
</tr>
<tr>
<td>S7</td>
<td>325</td>
<td>2.23</td>
</tr>
</tbody>
</table>

$^a$ Sensitivity = $R_{\text{air}}/R$

* NO, NO$_2$: 100 ppm, CO$_2$: 0.01 atm

3.7 Effect of oxygen on sensor output

The presence of oxygen changes the resistivity and the sensitivity of the sensor elements to NO. Generally speaking, there are several possibilities for an explanation:

(a) The sensor material is only sensitive to NO, and neither sensitive to O$_2$ nor to NO$_2$. Oxygen influences the resistivity and sensitivity of the sensor via the reaction
of NO to NO₂, and because the concentration of NO is reduced, the sensitivity to NO changes as a function of NO partial pressure.

(b) The sensor material is sensitive to NO and NO₂, but not to O₂, while the sensitivity to NO and NO₂ is different. The influence of oxygen is similar to that mentioned in (a).

(c) The sensor material is sensitive to NO and oxygen but not to NO₂. In this case the change of sensitivity comprises two parts, one being the change of NO concentration as caused by oxidation, and the other being the effect of oxygen itself.

(d) The sensor material is sensitive to the three species, and the sensitivity to NO and NO₂ is the same. The total concentration of NO and NO₂ then remains constant, and the change of sensitivity can be attributed to the effect of oxygen.

(e) The sensor material is sensitive to NO, NO₂ and oxygen, with the sensitivity to NO and NO₂ being different. In this case the situation will be complicated. The influence of oxygen, the equilibrium percentage of NO to NO₂ conversion, the individual concentrations of NO and NO₂ as well as their effect on the sensitivity have to be taken into account.

The sensor elements S1, S5 and S6 are sensitive to oxygen in the absence of NO, and an example for sensor of S1 is given in Table 8.4. These sensors are also sensitive to NO₂ as indicated in Table 8.3. Therefore, it seems that the explanation (e) is required to described the response of sensors S1, S5 and S6. From Table 8.4 it is seen that the presence of oxygen leads to decrease of the sensitivity and this decrease is attributed to
an increase of the resistance of the sensor element as indicated by Eq.(1). A possible explanation for this increase is, that when oxygen is adsorbed on the surface of the n-type semiconducting oxide mixture of sensor S1, some oxygen ions like $O_2^-$, $O^-$ and $O^{2-}$ will be produced, and hence the number of electrons in the conducting band of most probably ZnO will decrease, and hence the electronic conductivity of the material will be lowered. Because of the complexity of the sensor materials, it is virtually impossible to extract a mechanism from the present data. With regard to NO$_2$ sensitivity only sensor S7 is inactive, and this could indicate that V$_2$O$_5$ plays an important role in the NO$_2$ detection. Also the presence of p-n junctions seem to be important as sensor S5 exhibits the largest sensitivity to NO$_2$. Sensors S2, S3 and S4 are sensitive to O$_2$ in the presence of NO. This would indicate explanation (b) to hold. Explanation (b) and (e) differ only in the role of oxygen.

<table>
<thead>
<tr>
<th>$P$(O$_2$) (atm)</th>
<th>0.0</th>
<th>0.013</th>
<th>0.025</th>
<th>0.046</th>
<th>0.08</th>
<th>0.126</th>
<th>0.30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>1.65</td>
<td>1.36</td>
<td>1.26</td>
<td>1.14</td>
<td>1.10</td>
<td>1.06</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 8.4 Effect of oxygen on the sensitivity of sensor S1

Operation Temperature : 290°C.
4. CONCLUSIONS

(1) The semiconductor NO\textsubscript{x} sensor materials with different compositions of Al\textsubscript{2}O\textsubscript{3}, V\textsubscript{2}O\textsubscript{5} and ZnO were prepared. The resistivity and Seebeck coefficient of the sensors as a function of oxide composition and temperature were studied.

(2) The sensors with different compositions reveal fast and sensitive response to 20 to 600 ppm NO. At higher NO concentrations, the sensitivity is gradually decreasing. The p-type sensors with larger content of V\textsubscript{2}O\textsubscript{5} show higher sensitivity to NO. In the temperature range up to 400°C, sensitivity increases with increasing operating temperature.

(3) All the sensors containing V\textsubscript{2}O\textsubscript{5} are sensitive to NO\textsubscript{2}, and usually the sensitivity to NO\textsubscript{2} is lower than that to NO. All the sensors are essentially insensitive to CO\textsubscript{2}, suggesting that the interference of CO\textsubscript{2} in NO and NO\textsubscript{2} detection will not be a problem.

(4) The presence of oxygen influences the sensor sensitivity to NO. Several possible explanations for the effect of oxygen were given to fit the different cases, depending on the composition.

(5) This Taguchi-type NO\textsubscript{x} sensor is promising for NO and NO\textsubscript{2} detection as an alternative to the Ag\textsuperscript{+}-\textsuperscript{β}-alumina solid electrolyte based NO\textsubscript{x} sensors at higher temperatures and lower NO\textsubscript{x} concentrations, although the sensing mechanism is not yet understood from the present data.
REFERENCES

Actuators, 17, (1989) 377
Films, 186, (1990) 349
259

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Summary

SO$_x$ and NO$_x$ are air polluting gases, the monitoring of which has attracted worldwide attention in recent years. A study on solid electrolyte and semiconductor based SO$_x$ (x=2,3) and NO$_x$ (x=1,2) sensors has been carried out, with major attention to Nernst type solid electrolyte sensors. Taguchi-type semiconductor NO$_x$ sensors were developed as an alternative to Nernst type NO$_x$ sensors. Solid electrolyte and semiconductor gas sensors have several advantages over other conventional analytical methods, i.e. in situ measuring, fast response, easy to handle, and low cost. In this thesis, the preparation, and structure, as well as the thermal, chemical and electrical properties of solid electrolyte materials such as doped Na$_2$SO$_4$, Nasicon, Na$^+$-$\beta'-$-alumina, and Ag$^+$-$\beta''-$-alumina are studied. Electrochemical SO$_x$ (x=2,3) gas sensors based on these solid electrolytes have been fabricated and tested. Research of the solid electrolyte and semiconductor NO$_x$ (x=1,2) gas sensors has also been performed using Ag$^+$-$\beta''-$-alumina as the electrolyte and Al$_2$O$_3$-ZnO-V$_2$O$_5$ mixed oxide semiconductors as the gas-sensing materials, respectively.

The Na$_2$SO$_4$-based solid electrolyte was studied as a candidate material in SO$_x$ electrochemical concentration cells. The preparation, phase transitions, and electrical properties were discussed. Yttrium and lanthanum sulfate have been employed as dopants to enhance the ionic conductivity of Na$_2$SO$_4$-I and to stabilize this high-temperature and fast-ion conducting phase down to room temperature. Na$_2$WO$_4$ is also used to stabilize Na$_2$SO$_4$-I down to room temperature, and to improve the mechanical properties of Na$_2$SO$_4$-based materials. It was found that doping of Na$_2$SO$_4$ with 5 mol% Y$_2$(SO$_4$)$_3$ or 4 mol% La$_2$(SO$_4$)$_3$ yields the highest ionic conductivity and lowest activation enthalpy. 5 mol% Na$_2$WO$_4$ together with 5 mol% Y$_2$(SO$_4$)$_3$ can stabilize the Na$_2$SO$_4$-I phase down to room temperature.

After the investigation of Na$_2$SO$_4$-based solid electrolyte materials, a potentiometric SO$_x$ gas sensor based on a tubular Nasicon solid electrolyte was developed. A temperature gradient between the two electrodes of the sensor has been found to be the
reason for the deviation of the experimental EMF response from the Nernstian response. A new theoretical EMF equation which covers both isothermal and non-isothermal SO$_x$ concentration cells was derived. According to the new theoretical EMF calculation, the deviation could be eliminated to a certain degree. However, Nasicon is not a suitable sensor material for SO$_x$ detection at low temperatures.

Considering the outstanding properties of Na$^+$-$\beta^-$-alumina in a wide temperature range and the use of non-isothermal conditions, a novel Temperature Gradient Na$^+$-Beta$^-$-alumina (TGNB) SO$_x$ sensor without reference gas electrode was examined. The same gas mixture flowing over the two electrodes of the sensor acts as both sample gas and reference gas under non-isothermal conditions. The response of the TGNB SO$_x$ sensors revealed good agreement with the theoretical EMF. Because of this agreement and the simple sensor configuration the TGNB SO$_x$ sensor is promising.

In order to obtain a stable and simple solid reference electrode for Nernst-type SO$_x$ sensors, planar and tubular Ag$^+$-$\beta^-$-alumina as solid electrolyte and silver metal as solid reference electrode were assembled and tested as SO$_x$ sensor. The testing of planar sensors with V$_2$O$_5$ as catalyst reveals a Nernstian response to 10 to $10^4$ ppm SO$_2$ in the temperature region of 450°C to 700°C, the response time being 3 min. The tubular sensors exhibit an experimental response which is consistent with theoretical calculation for the SO$_2$ range of 10 to 1000 ppm at operating temperatures of 500 to 700°C. The response time is about 5 to 10 min.

With the experience of Nernst-type SO$_x$ sensors, and a theoretical derivation of the response of Nernst type NO$_x$ sensors, a planar and tubular NO$_x$ gas sensor using Ag$^+$-$\beta^-$-alumina as the solid electrolyte, Ag as the solid reference electrode, and porous Pt against a AgNO$_3$ thin layer as the working electrode were developed. The performance of the planar and tubular sensors has been examined in the temperature region of 150 to 220°C and a NO concentration in the range of 50 to 10,000 ppm. Reproducible EMF values were obtained. They were quite close to the theoretical response values calculated using the Nernst equation. However, the response time was in the order of a few hours because of the low operating temperature. The microstruc-
ture of the gas-sensing electrode was examined by SEM, in order to get insight into the mechanism of the electrochemical reactions on the interface of the electrolyte and the gas-sensing electrode. According to theoretical calculations, this type of NO$_x$ sensor should have excellent selectivity to NO/NO$_2$ against CO/CO$_2$, and this was proven by a measurement of 0.01 atm CO$_2$ with 1000 ppm NO, and 0.1 atm O$_2$ in argon at 200°C.

Finally Taguchi-type semiconductor based NO$_x$ sensors were studied at higher temperatures and lower NO concentrations as an alternative to the Nernst-type NO$_x$ sensors. Al$_2$O$_3$-ZnO-V$_2$O$_5$ oxide mixtures have been employed as the active semiconductor materials. Sensor materials with different compositions were fabricated and tested in order to find the optimal composition of the oxides for which high sensitivity and selectivity to NO$_x$ gases are achieved. The sensors exhibit sensitive and fast response to NO and NO$_2$ of 20 to 600 ppm at 200 to 400°C; while CO$_2$ will not interfere with the measurements. The experimental testing results demonstrate the possibility of using this type of sensors for NO/NO$_2$ detection under practical conditions.
List of Publications

The results of the investigations described in this thesis have been or will be published in the following papers,


10. N. Rao, O.T. Sørensen, C.M. van den Bleek and J. Schoonman, "Electrochemical SO$_2$ and NO$_x$ Gas Sensors with Tubular Ag$^+\cdot$-$\beta$"-alumina as Solid Electrolyte and Ag as Solid Reference", Proc. Int. Workshop on Beta-Aluminas and Beta Batteries, Materials Science Forum, Switzerland, (1991), in press.


13. N. Rao, O.T. Sørensen, C.M. van den Bleek and J. Schoonman, "Potentiometric NO$_x$(x = 1,2) Sensors with Ag$^+\cdot$-$\beta$"-alumina as Solid Electrolyte and Silver as Solid Reference", 8th Int. Conference on Solid State Ionics, Canada, (1991), Solid State Ionics, Submitted.
Curriculum Vitae

Ningling Rao was born on 12th May 1963 in Jiangsu, China. She entered in the University of Science and Technology of China (USTC) in 1980 with Number One position of the high school in the National University Entrance Examinations. In 1985, she graduated from USTC with BSc degree and was recommended with the best rating for the postgraduate study in the Department of Materials Science and Engineering, USTC. She obtained her MSc degree in 1988 with the highest mark of the degree courses as well as the thesis and was recommended to be a PhD student of the Department of Materials Science and Engineering, USTC.

In 1989, she was sent to the Department of Materials Research, Risø National Laboratories in Denmark to perform her PhD thesis work under the guidance of Prof. Dr. O.Toft Sørensen. From 1990, she continued the PhD study in the Faculty of Chemical Technology and Materials Science, Delft University of Technology under the supervision of the co-promotors Prof. Dr. J. Schoonman and Prof. Ir. C.M. van den Bleek. After the PhD graduation, she will continue to work in the Laboratory for Inorganic Chemistry as a research fellow for some time.

Her research interest has been mainly focussed on the application of solid electrolyte and semiconductor materials in chemical gas sensors.