Planar potentiometric SO$_2$ gas sensor for high temperatures using NASICON electrolyte combined with V$_2$O$_5$/WO$_3$/TiO$_2$ + Au or Pt electrode

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For high temperature application, a planar SO$_2$ sensor using NASICON as an electrolyte and V$_2$O$_5$/WO$_3$/TiO$_2$ + Au or Pt as a sensing electrode was fabricated and investigated. In the case of Pt electrodes, the sensor showed a strange response in temperature range from 300–600°C. In the case of Au electrodes, the sensor showed a strange behavior at 300 and 400°C, while at 600°C the sensor showed good response to SO$_2$. The highest sensitivity with temperature range from 300°C to 400°C at 200 ppm was observed at 600°C, although offset shifting was observed in repeated measurements. The sensors showed the potential for good selectivity at 600°C in the case of Au electrodes. The fact that the electric potential difference of the sensor is strongly affected by the electrode materials may intend that the mechanism of the sensor is a mixed potential type.

Key-words : Gas sensor, Sulfur dioxide, Sodium ion conductor, VWT, Mixed potential, Electrode

1. Introduction

Coal is a very important fuel in addition to renewable energies nowadays because the identified coal reserves are expected to last for 150 years, in contrast to oil and natural gas reserves which may last for only 41 and 65 years, respectively. Additionally, the cost of coal is about 1/6 that of oil and natural gas. Therefore, it is predicted that coal consumption will increase by 2.5% per year in the range of 2003 to 2030, and it will continue to play an important role through the 21st century.1)

Coal, however, faces significant environmental challenges, since exhaust gas from coal combustion contains limited emissions such as SO$_2$, NOx, etc.2) For example, the exhaust gas from coal-fired kilns includes 300–500 ppm of SO$_2$, or flue gases and stack gas include 500–4000 ppm and 5–10% of SO$_2$, respectively.3) Thus, SO$_2$ sensors featuring a good durability in high SO$_2$ concentrations and at high temperatures are needed for SO$_2$ monitoring and control.

To meet the above-mentioned conditions, SO$_2$ sensors have to be made of very stable materials. For that reason, we focused on sensors based on V$_2$O$_5$/WO$_3$/TiO$_2$ (abbreviated VWT), because VWT is a well-known material for ammonia selective NO$_x$ catalytic reduction catalysts (NH$_3$-SCR)5,6 applied for instance for NOx removal in coal power plants or DeNOx processes in diesel exhaust pipes. VWT shows a good stability in sulfur oxiderich combustion exhausts.7) It has already been suggested as a sensor material for ammonia sensing purposes in exhausts.5,8)

To the best of our knowledge, there are only a few papers reporting on SO$_2$ sensors utilizing V$_2$O$_5$/TiO$_2$ (without WO$_3$).9,10) Recently Izu et al. have reported resistive type SO$_2$ sensor utilizing VWT11) because it is expected that VWT has a good stability. Until the report of Izu et al., there was no paper that involves VWT as an SO$_2$-sensitive material, although there are many papers about SO$_2$ oxidation of VWT in SCR catalysts.12–18) Liang et al. reported on bulky potential type sensor using V$_2$O$_5$–TiO$_2$ with Au electrodes.19) Very recently, Izu et al. have briefly reported planar potential type sensors utilizing VWT + Au electrode.19)

In this study, we varied the vanadium oxide concentration between 1.5 and 3.0 wt% and the electrode materials between Pt and Au and measured the potential changes when exposed to SO$_2$ and/or other gases in detail. As a result, it was found out that for the SO$_2$ response the electrode materials play a more crucial role. The sensing mechanism was also discussed.

2. Experimental

2.1 Fabrication of sensors

To obtain NASICON powder with a composition of Na$_3$Zr$_2$P$_2$Si$_2$O$_{12}$, Na$_2$CO$_3$ (Merk), NH$_4$H$_2$PO$_4$ (VWR), SiO$_2$ (VWR), and ZrO$_2$ (Alfa Aesar) were mixed in stoichiometric amounts in a ball mill and calcined at 1050°C for 12 h. The NASICON powder was added into an organic binder to prepare screen-printable pastes.

VWT powders were supplied by Argillon GmbH. The V$_2$O$_5$ concentration was 1.5 or 3.0 wt% and the WO$_3$ concentration was ca. 8–10 wt%. In this study, x%VWT is an abbreviation that stands for the composition x wt% V$_2$O$_5$/8–10 wt% WO$_3$/TiO$_2$, in which x is 1.5 or 3.0. The VWT powders were added into an organic binder to prepare screen-printable pastes.

First, a solid electrolyte layer (NASICON) was screen-printed and fired at 1050°C. Then, two porous gold or platinum electrodes were screen-printed and fired at 850 and 1000°C, respectively. Afterwards one electrode was covered by an additional porous catalytically active film (VWT) which included 1.5 or 3.0 wt% V$_2$O$_5$ by screen-printing. The screen-printed VWT layer was fired at 700°C. The obtained powder or layer was characterized by scanning electron microscopy (SEM, Leo1450VP) with energy dispersive X-ray spectroscopy (EDX,
Oxford EDX-System INCA Energy 300), and powder X-ray diffraction (PANalytical X’Pert Pro, Cu Kα radiation). The schematic drawing of the sensor is described in Fig. 1 and the cell equation is as follows:

\[ (-) \text{gas, Au or Pt/NASICON/Au} \]
\[ \text{or Pt} + 1.5 \text{ or } 3.0\% \text{VWT, gas (+)} \]

2.2 Measurement

In order to investigate its sensing properties, the sensor devices were placed into a test chamber. They were placed to be parallel with the gas flow. The total gas flow amounted to either 1 or 5 L/min. The experiment was carried out with a total gas flow of 5 L/min, except that 1 L/min was used for 5000 ppm SO₂. It was confirmed that the electric potential difference was independent of the total gas flow rate in base gas and 200 ppm SO₂. The electric potential difference (voltage) between two gold or platinum electrodes was measured as an output of the sensor with a digital multimeter (Keithley 2700 series). As a base gas, compressed air was used to measure the response to SO₂, while a gas mixture of 20% O₂ and N₂ was used in the case of the response measurement towards other gases like CO, CO₂, C₃H₈, H₂O, H₂, NO, and NH₃.

3. Results and discussion

3.1 Sensors using Au electrodes

In the low temperature range (300–400°C), the sensors show unstable responses to SO₂. At temperatures of 500°C or more, the voltage is stable and increases with increasing SO₂ concentration in the range from 20 to 200 ppm (Fig. 2). An unexpected response is observed at 600°C when the gas changes from air without SO₂ to air with 20 ppm SO₂ (at 10 min in Fig. 2). The effect after changing between 20 ppm SO₂ and base gas has not been understood at the moment. Figure 3 shows the relationship between the voltage and the logarithm of the SO₂ concentration at 500°C or more. The slope of the line in a semilogarithmic plot increases with increasing temperature in the range from 20 to 200 ppm. The sensitivity of the sensors with 1.5 and 3.0% VWT was 75–85 mV/decade at 600°C. This

![Fig. 1. (a) Optical microscope image and (b) schematic drawing of cross section of the sensor element.](image)

![Fig. 2. Typical response curve of the sensor with 3.0% VWT and Au electrodes to SO₂ at 500 and 600°C.](image)

![Fig. 3. Relationship between potential difference of the sensor with Au electrodes and logarithm of SO₂ concentration.](image)
sensitivity would be suitable for high temperature applications. The results are different to the bulky sample reported in Ref. 10. In Ref. 10, no information about the sensor response over 300°C was given, and a stable response was observed at 300°C, although the unstable signal is observed in our sensors at that temperature. When we repeated our measurements, an offset shift was observed but the slope remains almost the same. This problem may be related to the strange response when SO2 concentration changes between 0 and 20 ppm (at 10 and 130 min in Fig. 2). The signal behavior in high SO2 concentrations was also investigated. In high SO2 concentrations (1000−5000 ppm), a decreasing slope was observed (Fig. 4). This means that a kind of saturation of the signal occurs at high SO2 concentrations.

Figure 5 shows the results of cross sensitivity tests. The sensors with 1.5 and 3.0 wt % V2O5 shows little or no response to CO2, CO, H2O, C3H8 and NO, while H2 and NH3 lead to marked effects. It seems that the sensors are selective enough for in-situ exhaust gas monitoring for coal combustion, because in the exhaust gas there is only few H2 and NH3. The oxygen concentration dependency of potential difference was also investigated. The results are shown in Fig. 6. The potential difference increases with increasing oxygen concentration in the range of 0.5 to 50%. The sensors with 1.5 and 3.0% VWT show 24 mV/decade of O2 concentration. This is smaller than the sensitivity to SO2, which is about 80 mV/decade.

### 3.2 Sensors using Pt electrodes

The sensing properties for sensors using Pt electrodes were investigated as well. Figure 7 shows the potential difference change at 600°C. When the gas including SO2 is introduced in the test chamber, the potential difference decreases dramatically but then increases gradually. However, the potential difference remains constant, when the SO2 concentration changes, although the spike-like change of the potential difference is observed soon after the SO2 concentration is varied. This signal independence towards SO2 concentration variations over 20 ppm is also observed at 300, 400, 500, and 550°C.

Figure 8 shows the oxygen concentration dependency of the potential difference. As soon as the oxygen concentration is changed, the potential difference responds strongly, but returns gradually to its initial value. Therefore, in the case of Pt
electrodes, the potential difference does not depend on oxygen. This response behavior to oxygen concentration variations is similar to that to the SO2 response. At the moment, this strange response behavior to SO2 and O2 concentration changes has not been clarified yet.

The response to H2O is very complicated and not further illustrated here. First, the potential difference increases suddenly when the gas including H2O is introduced. Then, the potential difference decreases gradually. Next, the potential difference decreases dramatically when the gas water-free gas is applied to the sensor chamber and then the potential difference increases gradually. The response to NH3 of the sensor using Pt electrodes is larger than that of the sensor using Au electrodes.

3.3 Discussion about the reaction mechanism
The response behavior is much different between Pt and Au electrodes. This behavior indicates that the mechanism of the sensor may be of the mixed potential type, since the electrode material dependency is typical for this type of sensors. This is supported Liang et al., who also suggested a mixed potential type behavior of their SO2 sensors based on Na ion conductors.\(^{10}\) They proposed the following electrode reactions

\[
2\text{Na}^+ + \text{SO}_2 + \text{O}_2 + 2\text{e}^- \rightarrow \text{Na}_2\text{SO}_4
\]
\[
\text{Na}_2\text{O} \rightarrow 2\text{Na}^+ + (1/2)\text{O}_2 + 2\text{e}^-
\]

On the contrary, Shimizu et al. suggested the following reactions:\(^{20}\)

\[
(1/2)\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}
\]
\[
\text{SO}_2 + \text{O}^{2-} \rightarrow \text{SO}_3 + 2\text{e}^-
\]

At the moment, it is not clear to which reaction the sensors prepared in this study follow. To clarify this, half cell experiments or polarization curve experiments will be needed in future.

The different response behaviors between Pt and Au electrodes were observed also in the resistive type sensor using VWT.\(^{12}\) These results indicate that the interaction between VWT and the electrodes plays an important role for the response to SO2 gas.

3.4 Reaction between NASICON and SO2
To detect sulfur aging, the 3.0% VWT powder was annealed in 200 ppm \(\text{SO}_2\) + air at 600°C for 16 h. XRD patterns were taken. The powder after annealing was almost the same as that of the powder before annealing. The surface of the sensor after sensor measurements in \(\text{SO}_2\) was analyzed by EDX. Sulfur was detected on the NASICON part in the sensing electrode but not on the VWT layer or Au electrode. From these results, it is clear that VWT does not react with \(\text{SO}_2\); nor it forms other sulfur-containing compounds. NASICON, however, can react with \(\text{SO}_2\). This result may be related to the offset shift and strange response when SO2 concentration changes from 0 to 20 ppm. To improve the long-term stability, a sodium ion conductor that is less prone for sulfur aging needs to be found.

4. Conclusions
In this study, we fabricated a planar type sensor with NASICON as an electrolyte and noble metal/VWT as a sensing electrode. We investigated the response properties towards \(\text{SO}_2\) and towards many interfering gases. The results and conclusions obtained in this study are as follows:

- In the case of Pt electrodes, the sensor shows strange responses in temperature range from 300–600°C to \(\text{SO}_2\).
- In the case of Au electrodes, the electric potential difference is stable and the sensor output increases with increasing \(\text{SO}_2\) concentration in the \(\text{SO}_2\) range from 20 to 200 ppm at temperatures of 500°C or more, although the sensor showed a non-reproducible response to \(\text{SO}_2\) in the low temperature range (300–400°C).
- It is found that the electric potential difference of the sensor is affected strongly by the electrode materials. This result may intend that the mechanism of the sensor is a mixed potential type.
- The slope in a semi-logarithmic plot (electric potential difference vs. log of \(\text{SO}_2\) concentration) for the sensor using Au electrodes increases with increasing temperature in the range from 20 to 200 ppm. The sensitivity of the sensor with 1.5, 3.0 wt % \(\text{V}_2\text{O}_5\) is 80–83 mV/decade \(\text{SO}_2\) at 600°C.
- In high \(\text{SO}_2\) concentrations (200–5000 ppm), a saturation of the signal for the sensor using Au electrodes in high \(\text{SO}_2\) concentrations is observed.
- The sensors using Au electrodes with 1.5 and 3.0 wt % \(\text{V}_2\text{O}_5\) showed little or no response to \(\text{CO}_2\), \(\text{CO}\), \(\text{H}_2\text{O}\), \(\text{C}_3\text{H}_8\) and NO. It seems that the sensors may be selective enough for in-situ waste gas monitoring of coal combustion processes. However, the long-term signal stability needs to be further investigated.
- From XRD and EDX analysis, NASICON can react to \(\text{SO}_2\), while VWT does not react to \(\text{SO}_2\) nor form other compounds. This result may be related to the offset shift.

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References
8) D. Schönauer, I. Siechert and R. Moos, \textit{Sens. Actuators, B}, 155,