Potential-Type Sulfur Dioxide Planar Gas Sensor for High Temperature Application

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ABSTRACT

For high temperature applications, planar SO_2 gas sensors using Nasicon as an electrolyte and $V_2O_5/WO_3/TiO_2$ + Au as sensing electrode were fabricated and investigated. The sensors show a promising response at 600 °C with a sensitivity of 80-83 mV/decade in the SO_2 range from 20 to 200 ppm. The sensors show a good selectivity. Future work has to deal with an offset drift as it has been observed in repeated measurements.

INTRODUCTION

Today, coal is a very important fuel. Besides renewable energies, it will continue to play an important role through the 21st century [1]. 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. 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 [1]. Coal, however, faces significant environmental challenges, since exhaust gas from coal combustion contains limited emissions such as SO_2, NO_x, etc. [1]. 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 [2].

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. Such SO_2 sensors have to be made of a very stable material. For that reason, we focused on sensors based on $V_2O_5/WO_3/TiO_2$ (abbreviated VWT), because VWT is a well-known material for ammonia selective NOx catalytic reduction catalysts (NH_3-SCR) [3-5] applied for instance for NO_x removal in coal power plants or DeNO$_x$ processes in diesel exhausts. VWT shows a good stability in sulfur oxide-rich combustion exhausts [5]. It has already been suggested as a sensor material for ammonia sensing purposes in exhausts [6-8].

To the best of our knowledge, there are only a few papers reporting on SO_2 sensors utilizing V_2O_5 /TiO_2 (without WO_3) [9, 10] and there is no paper that involves VWT as an SO_2 sensitive material in potential-type gas sensors, although there are many papers about SO_2 oxidation of VWT in SCR catalysts [11-16]. Liang et al. reported on bulk-type potential or electromotive force-type (EMF) sensor using V_2O_5-TiO_2 with Au electrodes and a Nasicon sodium ion conductor [9]. In contrast, in our study, we realized a planar setup for our EMF type sensors and utilized VWT with a V_2O_5 concentration of 1.5 wt% and 3.0 wt%. We also varied the electrode materials between Pt or Au and measured the EMF changes when exposed to SO_2 and/or other gases. Unexpectedly, it was found out that for the SO_2 response the electrode materials play a more crucial role.

EXPERIMENTAL

VWT powders were supplied by a commercial catalyst supplier. The V_2O_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_2O_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. Nasicon powder was also added into an organic binder to prepare screen-printable pastes.

First, a solid electrolyte layer (Nasicon) was screen-printed. Then, two porous gold electrodes were screen-printed. Afterwards, one electrode was covered by an additional porous catalytically active film (VWT) which included 1.5 or 3.0wt%V_2O_5. The schematic setup of the sensor is given in Fig. 1. The cell can be described by:

(-) gas, Au / NASICON / Au+1.5 or 3.0%VWT, gas (+)

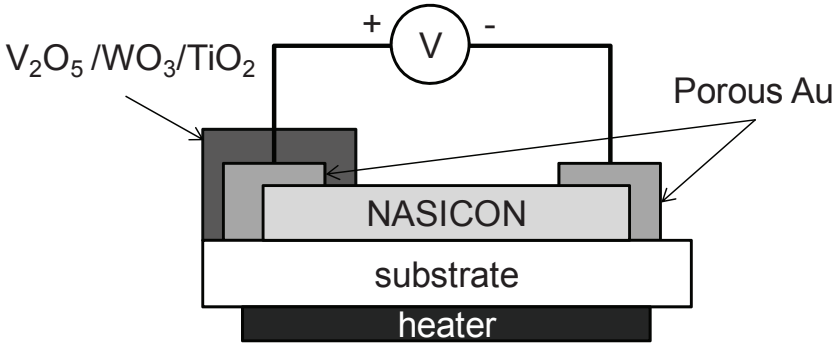

Figure 1. Schematic setup of the sensor.

To investigate its sensing properties, the sensor devices were placed into a test chamber with an angle of incidence parallel to the gas flow. The total gas flow amounted to either 1 or 5 L/min. The 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 SO_2, while a gas mixture of 20 % O_2 and 80 % N_2 was used in the case of the response measurement towards other gases like CO, CO_2, C_3H_8, H_2O, H_2, NO, and NH_3.

RESULTS AND DISCUSSION

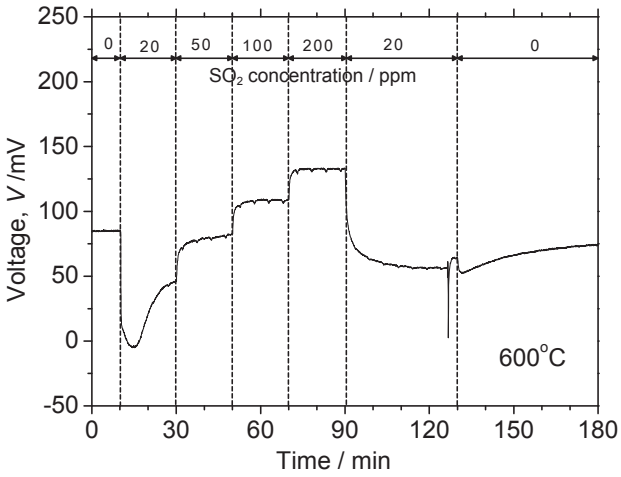

Figure 2. Response curve of the sensor using 3.0wt%V_2O_5 at 600°C

In the low temperature range (300 °C to 400 °C), the sensor shows a non-reproducible behavior, both in base gas and under SO_2 exposition. At temperatures of 500 °C or more, the voltage is stable and the

voltage increased with increasing SO_2 concentration in the SO_2 range from 20 to 200 ppm (Fig.2). The effect directly after admixing 20 ppm SO_2 to the base gas has not been understood at the moment.

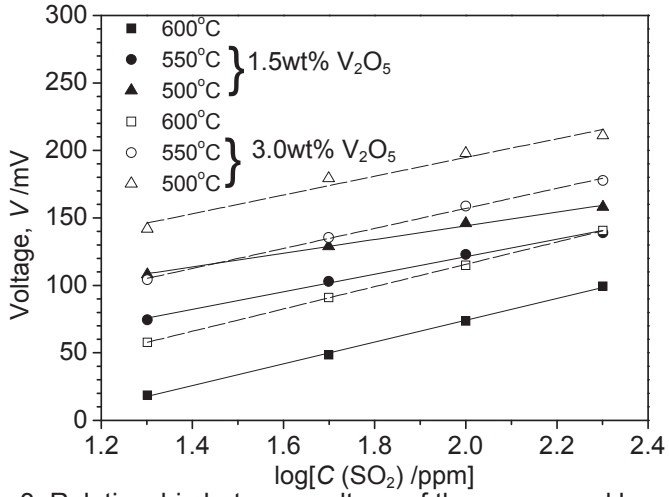

Figure 3. Relationship between voltage of the sensor and log of SO_2 concentration ($C(SO_2)$).

Figure 3 shows the relationship between the obtained sensor voltage and the logarithm of the SO_2 concentration. The slope of the line in a semi-logarithmic plot increases with increasing temperature in the range from 20 to 200 ppm. The sensitivity of the sensor with 1.5, 3.0 wt%V_2O_5 is 80 - 83 mV/decade at 600 °C. The slope of the sensors with 3.0 wt% V_2O_5 is higher than that of the sensors with 3.0 wt% V_2O_5 at each temperature. This sensitivity would be suitable for high temperature application.

The results are different to the bulk-type sample as reported in Ref. [9]. There, no information about the sensor response over 300 °C was given, and a stable response was observed at 300 °C. When we repeated our measurements, an offset shift is observed but the slope remains almost the same. This problem may be related to the strange response when SO_2 concentration changes from 0 ppm to 20 ppm. In high SO_2 concentrations (200 ppm - 5000 ppm), a decrease of the slope is observed. This means that a kind of saturation of the signal occurs at high SO_2 concentrations.

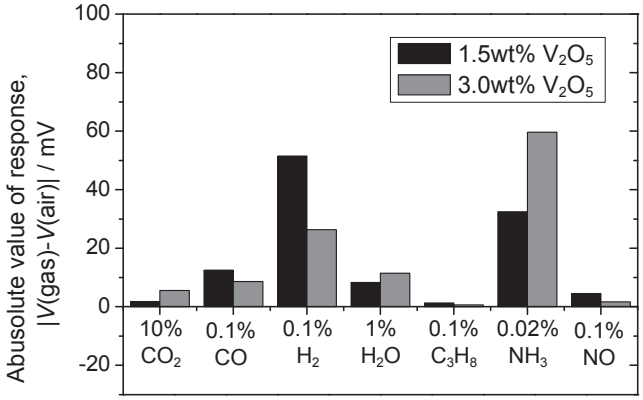

Figure 4. Response to various gases.

Figure 4 shows the results of the cross sensitivity tests. The sensors with 1.5 wt% and 3.0 wt% V_2O_5 show only little or no response to CO_2, CO, H_2O, C_3H_8 and NO, and only H_2 and NH_3 lead to marked effects. 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.

Conclusions

In this study, we manufactured a planar type sensor with Nasicon as an electrolyte and Au and Au/VWT as electrodes. We investigated the response properties towards SO_2 and towards many interfering gases. The results and conclusions obtained in this study are as follows:

1) In the low temperature range (300 °C - 400 °C), the sensor showed a non-reproducible response to SO_2. At temperatures of 500 °C or more, the voltage is stable and the sensor output increases with increasing SO_2 concentration in the SO_2 range from 20 to 200 ppm.
2) The slope in a semi-logarithmic plot (voltage vs. log of SO_2 concentration) increases with increasing temperature in the range from 20 to 200 ppm. The sensitivity of the sensor with 1.5, 3.0 wt%V_2O_5 is 80 - 83 mV/decade SO_2 at 600 °C.
3) In high SO_2 concentrations (200 ppm - 5000 ppm), a saturation of the sensor signal in high SO_2 concentrations is observed.
4) The sensors with 1.5wt% and 3.0wt% V_2O_5 showed little or no response to CO_2, CO, H_2O, C_3H_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.

These investigations are a part of a series that studies how VWT can be used for SO_2 sensing. Whereas at the moment the long-term stability of the potential-type sensors requires further improvements, conductometric sensors using VWT as the sensitive film perform better. They can be operated at 400 °C. The resistance of VWT decreases with an increasing SO_2 concentration in the range from 20 ppm to 5000 ppm. The sensor response is linear in a logarithmic scale, but no saturation effect occurs. The long-term stability is promising and the cross-sensitivity is similar to the one as found out in this work. Further details can be found in [17].

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