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Solid-State Sensor for Sulfur Oxides Based on Stabilized Zirconia and Metal Sulphate

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Electrochemical cells using MgO-stabilized zirconia tube coated with metal sulphates were found to exhibit fairly good sensing properties to 20-200 ppm SO_2 in air at 650-800 °C. With various sulphates such as Li_2SO_4 and Na_2SO_4, EMF responses to SO_2 followed Nernst's equations for a 2-electron reduction of SO_2. With Li_2SO_4-$CaSO_4$ (6:4 in molar ratio), 90% response- and 90% recovery-times were 12 s and 2.5 min, respectively, for 130 ppm SO_2 at 800 °C.

Sulphur oxides (SO_2 and SO_3, hereafter referred to as SOx) are typical hazardous components which cause air pollution and acid rain. Their monitoring is urgently needed for air pollution control as well as for industrial applications. Conventionally SOx has been measured with analytical or optical instruments, which are rather expensive and large in size, and are not always suitable for continuous on-site monitoring. There has been an increasing need for all-solid-state compact SOx sensors which are free from these drawbacks. A great deals of effort has been exerted for developing solid electrolyte SOx sensors using various metal sulphates, e.g., K_2SO_4,[1] Na_2SO_4,[2,3] Li_2SO_4,[4,5] and Ag_2SO_4.[6,7] The EMF responses of these sensors, however, were often unstable or drifting with time, possibly because of the leakage of gases through the poorly sintered sulphate electrolytes or the formation of pyrosulphate at the interfaces. Recently attempts were made to utilize cation-conducting solid electrolytes such as Na-β-alumina[8] and NASICON[9,10] together with metal sulphates. These sensors still appear to suffer from the chemical instability of the solid electrolytes in SOx-containing atmospheres, in addition to providing rather sluggish responses. Under such a circumstance, we have found that stabilized zirconia, a typical oxide ion conductor, can be used for SOx sensors, if it is combined with a coating layer of metal sulphates. The stabilized zirconia is quite tough chemically and mechanically and it has been utilized extensively for the oxygen sensors equipped to automobiles. Just like these oxygen sensors, the present SOx sensor has been fabricated on a stabilized zirconia tube, being free from the gas leakage as well as the chemical stability problem. Previously Gauthier et al.[11] briefly tested the use of a disc of stabilized zirconia as one of solid electrolyte reference for K_2SO_4-based SO_2 sensors, but little was disclosed about the actual sensing data of the obtained device. This paper deals with the SO_2 sensing characteristics of the stabilized zirconia tube-based devices.

The assembly of the SO_2 sensor device is shown in Fig. 1. MgO-stabilized zirconia tube with a closed end (ZR-15M, NKT Co. Ltd), 5 and 8 mm in inner- and outer-diameter, respectively, was attached with the reference Pt electrode at the inside bottom by applying Pt black, followed by annealing it at about 900 °C. The reference electrode was connected to a Pt lead through a mechanically pressed Pt mesh, and was always exposed to the at-

mospheric air. The coating of a metal sulphate (Li_2SO_4, Na_2SO_4, or Li_2SO_4-MSO_4 (M=Ca, Ba)) on the outside bottom of the tube was prepared by dipping that part of the tube in the molten sulphate, followed by cooling it in air. Then it was covered with a Pt mesh (sensing electrode) connected to a Pt lead. Gas sensing experiments were carried out in a conventional gas flow apparatus equipped with a heating facility. The sample gases containing SO_2 varying levels under a constant oxygen concentration of 21 vol% were prepared by diluting a parent gas (197 ppm SO_2 in air) with dry synthetic air. On changing the gas flow (100 cm^3/min) between air and the sample gas, the electromotive force (EMF) of the sensor device was monitored with a digital electrometer (Advantest, TR8652).

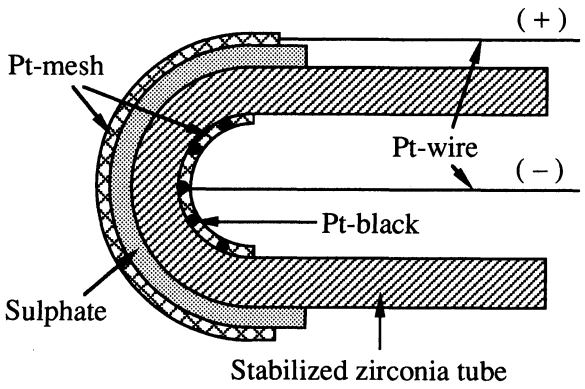

Fig. 1. Assembly of SO_2 sensor device using a zirconia tube.

Figure 2 shows the response transients of the device coated with Li_2SO_4 to 23, 71, and 197 ppm SO_2 at 800 °C. The responses to switching-on SO_2 were quick with 90% response times of 0.25-1.5 min. However, the recovery responses to switching-off SO_2 were quite slow. Each recovery transient went through two steps, i.e., an initial step for the sharp decrease of EMF down to an intermediate level and a succeeding one for the very slow decrease to the stationary level in air. Because of the second step, complete recovery took fairly long time of more than 30 min even at 800 °C, and far longer at lower temperatures. Despite such slow recovery, the stationary EMF responses to SO_2 were quite stable. As shown in Fig. 3, the EMF values were linearly correlated with the logarithm of SO_2 concentration at both 700 °C and 800 °C, following Nernst's equations for the 2-electron

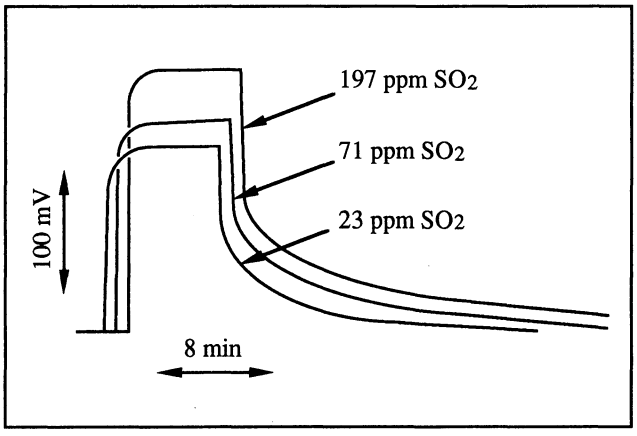

Fig. 2. Response transients of the SO_2 sensor coated with Li_2SO_4 at 800 °C.

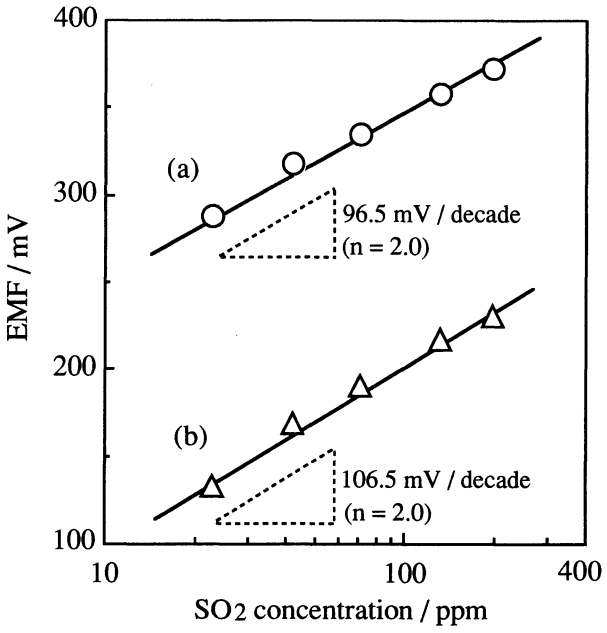

Fig. 3. Correlations between EMF and SO_2 concentration for the Li_2SO_4-coated sensor at 700 °C (a) and 800 °C (b).

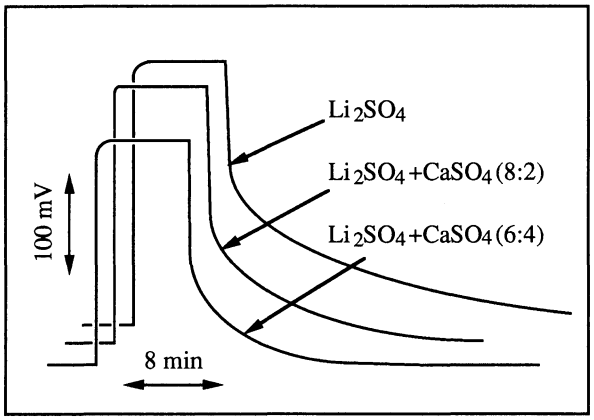

Fig. 4. Response transients of the SO_2 sensors coated with various Li_2SO_4-$CaSO_4$ mixtures to 130 ppm SO_2 at 700 °C.

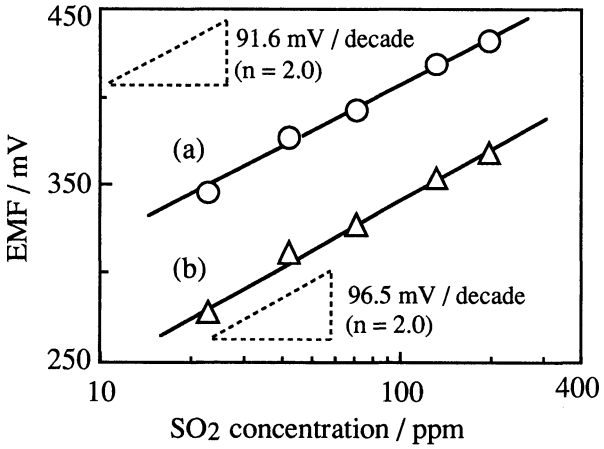

Fig. 5. Correlations between EMF and SO_2 concentration for the sensor with Li_2SO_4-$CaSO_4$ (8:2) at 650 °C (a) and 700 °C (b).

reduction of SO_2. Because of the slow recovery, however, this device could not work so stably at temperatures below 700 °C. This difficulty was found to be mitigated by the use of binary metal sulphates as described below.

Figure 4 depicts the response transients to 130 ppm SO_2 at 700 °C for these devices fitted with different mixtures of Li_2SO_4-$CaSO_4$ system. The responses to switching-on SO_2 were quick in all cases, but the rates of recovery on switching-off SO_2 depended on the sulphate composition. With pure Li_2SO_4, the 90% recovery time was 40 min, while it decreased to 12 and 7 min, with 8:2 and 6:4 mixtures (in molar ratio) of Li_2SO_4 and $CaSO_4$, respectively. Thus the best recovery response was obtained with the 6:4 mixture. With this device, the times for 90% response and 90% recovery to 130 ppm SO_2 at 800 °C were 12 s and 2.5 min, respectively. Because of such improvements in sensing characteristics, the devices using the binary sulphate system could operate at lower temperatures than that using Li_2SO_4. Figure 5 shows the EMF responses of the device using Li_2SO_4-$CaSO_4$ (8:2 in molar ratio) at 650 °C and 700 °C as a function of SO_2 concentration. Again the data fit the Nernst's correlations for the 2-electron reduction of SO_2. Another binary system, Li_2SO_4-$BaSO_4$, also gave similar sensing characteristics. The origins of preferable effects of binary sulphate systems are to be clarified in the future study.

The present sensor devices form the following electrochemical cell.

$$\underset{\text{(Sensing electrode)}}{SO_2,\ \text{air, Pt,}} \ \mid \ \underset{\text{(}Li^+ \text{ or } Na^+ \text{ conductor)}}{\text{metal sulphate}} \ \| \ \underset{\text{(}O^{2-} \text{ conductor)}}{\text{zirconia}} \ \mid \ \underset{\text{(Reference electrode)}}{\text{Pt, air}} \qquad (1)$$

The sulphate may be considered as an auxiliary sensing electrode material if one compares this cell with a conventional stabilized zirconia oxygen sensor. However, we consider that the role of the sulphate as a conductor of Li^+ or Na^+ is very important. In the present sensor the Pt mesh works as a catalyst for the oxidation of SO_2,

$$SO_2 + \tfrac{1}{2} O_2 = SO_3, \qquad (2)$$

which produces an equilibrium concentration of SO_3 over the sensing electrode. The sensing electrode reaction is assumed to be, for example,

$$2Li^+ + SO_3 + \frac{1}{2}O_2 + 2e^- = Li_2SO_4, \quad (3)$$

while the reference electrode reaction on the stabilized zirconia is

$$O^{2-} = \frac{1}{2}O_2 + 2e^-. \quad (4)$$

To achieve an electrochemical junction between the sulphate and the zirconia, one has to assume the presence of an auxiliary phase containing Li^+ and O^{2-} at the interface. We tentatively assume the formation of a small amount of Li_2ZrO_3 as such

$$2Li^+ + O^{2-} + ZrO_2 = Li_2ZrO_3. \quad (5)$$

Then the sensor device can be considered as combining two half cells in series, i.e., an SOx electrode and an O_2 electrode, both of which are referenced to Li_2ZrO_3. The EMF response of this device would then be a sum of the contributions from the two cells.

$$E = E_0 + \frac{RT}{4F}\ln\left(\frac{P^s_{O_2}}{P^c_{O_2}}\right) + \frac{RT}{2F}\ln P^s_{SO_3}, \quad (6)$$

where P_{SO_3} and P_{O_2} are the partial pressures of SO_3 and O_2, and the superscripts s and c mean sensing and counter electrodes, R, T and F have the usual meanings. From the equilibrium of Eq. 2,

$$P^s_{SO_3} = \frac{K(P^s_{O_2})^{1/2}}{1+K(P^s_{O_2})^{1/2}}(P_{SO_2})_{in}, \quad (7)$$

where K is an equilibrium constant and $(P_{SO_2})_{in}$ is the SO_2 partial pressure of the inlet gas. When both $P^s_{O_2}$ and $P^c_{O_2}$ are fixed, EMF is reduced to

$$E = E_0' + \frac{RT}{2F}\ln(P_{SO_2})_{in}, \quad (8)$$

in accordance with the experimental results.

In conclusion, the devices using a stabilized zirconia tube coated with metal sulphates provided fairly good sensing characteristics to 20-200 ppm SO_2 at 650-800 °C. The rates of responses could be improved by the use of a binary sulphate system.

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