CHEMISTRY LETTERS, pp. 1753-1756, 1994.

Potentiometric Sensor Using Stabilized Zirconia and Tungsten Oxide for Hydrogen Sulfide

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A solid-state electrochemical device based on Y_2O_3-stabilized zirconia was found to respond well to 0.6-12 ppm H_2S in air at 400 °C, when its surface exposed to H_2S was coated with a layer of WO_3. EMF decreased with an increase in H_2S concentration at a rate of -40 mV/decade. It is proposed that in this device WO_3 acts as a semiconductor electrode, its mixed potential being determined by the electrode reactions taking place at the zirconia/WO_3 interface.

As a gaseous component with strong toxicity and offensive smell, hydrogen sulfide (H_2S) has become a target of rather extensive researches to develop sensors for in recent years. So far solid-state H_2S sensors have been fabricated with semiconducting oxides or solid electrolytes. Some of the semiconductor-type sensors using $SnO_2$1-7) and $WO_3$8) have been shown to exhibit fairly good sensing properties to H_2S in air, but still these do not seem to be free from problems in sensitivity, rate of response, stability, or interference by coexistent gases, especially when dilute H_2S of around 1 ppm or less in air is concerned. On the other hand, the solid electrolyte sensors using $K_2SO_4$9) and stabilized zirconia coupled with CaO10) reportedly can only detect either H_2S in air at high temperature (820 °C)9) or H_2S in H_2 atmosphere,10) and hence lack ability to detect H_2S under more usual conditions. We have been exploring new types of stabilized zirconia-based gas sensors, and have so far demonstrated such sensors for SO_2, CO_2 and NO_x. In continued exploration, we have found a possibility of new potentiometric sensor for H_2S in which stabilized zirconia and WO_3 are combined together. This paper deals with the H_2S sensing characteristics of this device and the sensing mechanism involved.

The H_2S sensing device was fabricated by using a half open, Y_2O_3-fully stabilized zirconia tube (YSZ, 8 mol% Y_2O_3; NKT Co. Ltd) with 5 and 8 mm inner and outer diameter, respectively, as shown in Fig. 1. For the reference and sensing electrodes, Pt paste was applied on the inner and outer surfaces of the tube at the closed bottom, respectively, and connected to Pt mesh and Pt lead, followed by annealing at 1200 °C for 30 min. The outer Pt electrode (sensing) was coated with a layer of WO_3. The powder of WO_3 was prepared by pyrolyzing ammonium paratungstate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$) at 600 °C for 5 h in air, followed by milling the product in

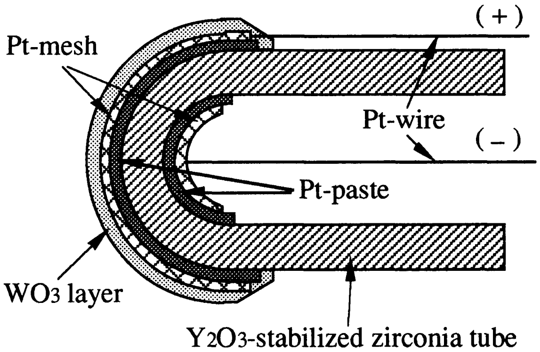

Fig. 1. Cross-sectional view of potentiometric H_2S sensor using YSZ and WO_3.

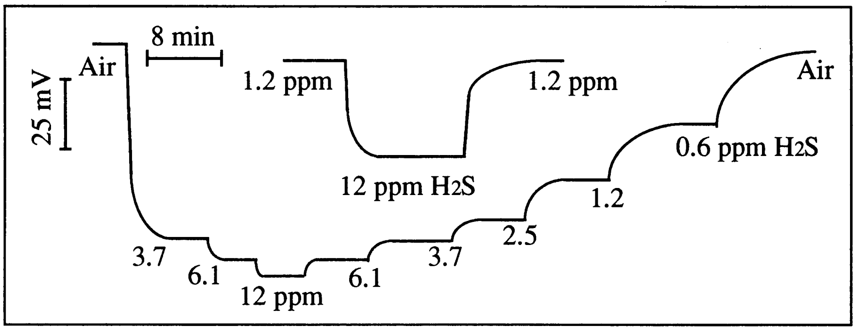

Fig. 2. H_2S response transients of the device attached with a WO_3 layer at 400 °C.

a zirconia-ball mill for 24 h. It was mixed with water and the resulting paste was applied thick (about 0.5 mm) on the Pt mesh, followed by drying at room temperature and calcining at 600 °C for 4 h.

H_2S sensing experiments were carried out in a conventional gas flow apparatus equipped with a heating facility. Sample gases containing various concentrations of H_2S under a constant oxygen concentration of 21 vol% were prepared by diluting a parent gas (42 ppm H_2S in air) with dry synthetic air. On changing the gas flow (100 cm^3/min) between air and the sample gas over the sensing electrode, while keeping the reference electrode always exposed to atmospheric air, electromotive force (EMF) of the device was monitored with a digital electrometer (Advantest, TR8652).

Figure 2 shows the response transients of the fabricated device to H_2S at 400 °C. EMF decreased rather sharply on turning-on a few ppm H_2S in air with a 90% response time of 2-3 min, and recovered the initial value on turning-off H_2S in about 20 min. EMF was completely reproducible and reversible on increasing or decreasing the concentration of H_2S stepwise as indicated. Figure 3 shows the steady EMF responses as a function of H_2S concentration at 400 °C, together with the EMF to synthetic air (air level). The EMF values were well correlated logarithmically with the H_2S concentration in the examined range of 0.6-12 ppm, with a slope of linearity of -40 mV/decade. It was confirmed that the slope of linearity was fairly reproducible, falling within -40 ~-46 mV/decade for the different sensor devices fabricated. It is noteworthy that the EMF to 0.6 ppm H_2S is still about 30 mV below the air level, assuring that the lower detection limit is well below this concentration. As a preliminary test for cross sensitivity, the device was exposed to 20 ppm SO_2 and 1000 ppm CO_2, each in air, at 400 °C. The resulting EMF values were about -15 and -20 mV relative.to the air level, respectively, suggesting considerable resistance of the device to these interfering gases.

On the basis of these results the present device appears to be a rather excellent sensor for dilute H_2S in air at a moderate temperature of 400 °C. Such H_2S sensing capability is obviously provided with the WO_3 coating layer attached to the device. When the coating layer was eliminated from the sensing electrode, the device showed totally different behavior, as indicated by the response transients in Fig. 4. Now EMF tended to increase very sluggishly on increasing H_2S concentration stepwise. It could not reach a steady state even in 90 min, and the EMF values could not be

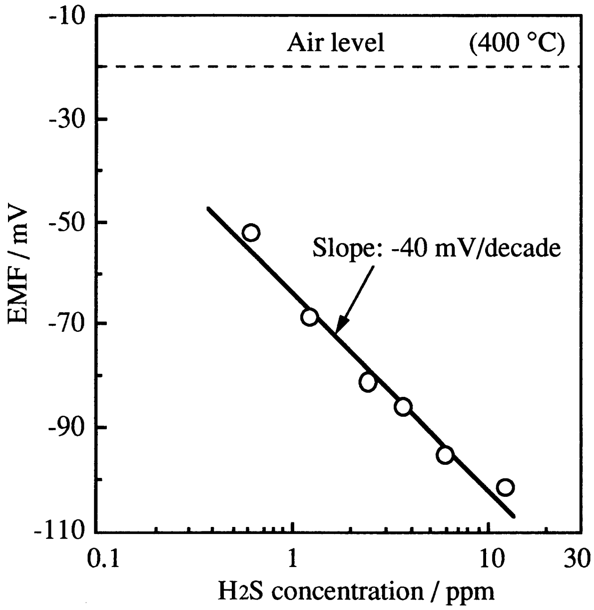

Fig. 3. Dependence of EMF on H_2S concentration for the device attached with WO_3 at 400 °C.

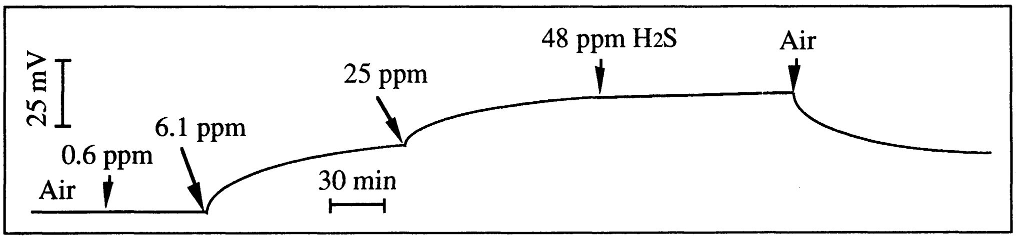

Fig. 4. H_2S response transients of the device unattached with a WO_3 layer at 400 °C.

well correlated with H_2S concentrations. These characteristics were hardly acceptable for a gas sensor. Notably the positive EMF changes on exposure to H_2S was just opposite to what was observed with the WO_3-coated device. The positive change suggests that H_2S or its oxidation products (S, SO_2 or SO_3) undergo a cathodic reaction at the YSZ/Pt interface.

The WO_3-coated device is described as

air, Pt | YSZ | Pt, WO_3, H_2S in air (1)
(reference electrode) (O^{2-} conductor) (sensing electrode)

As just mentioned, the presence of WO_3 is essential for the H_2S sensing capability. WO_3 is known to be an n-type semiconductor and thus can act as a semiconductor electrode when contacted to the stabilized zirconia solid electrolyte. In fact such contact was possible in the present device because the Pt electrode was porous. We consider that the device can be reduced as consisting of the following two electrochemical cells.

air, Pt | YSZ | Pt, H_2S in air (2)
air, Pt | YSZ | WO_3 (Pt), H_2S in air (3)

In the later cell, it is assumed that H_2S sensing reactions take place at the YSZ/WO_3 (Pt) interface while the Pt present there simply acts as a reservoir of electrons kept in equilibrium with the WO_3. With the same Pt terminal shared by the two cells, actual EMF of the device would be determined by one which is more influential. We have seen that the former cell exhibits EMF behavior just opposite to that of the WO_3-coated device, suggesting the domination of the YSZ/WO_3 (Pt) interface under the present conditions. On the basis of these considerations, we tentatively propose an H_2S sensing mechanism as schematically illustrated in Fig. 5 (a). The reference electrode potential is determined by the following electrode reaction taking place at the Pt/YSZ interface and it is fixed under the constant O_2 concentration.

$$O_2 + 4e^- \rightleftharpoons 2O^{2-} \quad (4)$$

At the YSZ/WO_3 (Pt) interface, on the other hand, cathodic and anodic reactions involving O^{2-} ions can proceed simultaneously, for example as follows.

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (5)$$

$$H_2S + 3O^{2-} \rightarrow H_2O + SO_2 + 6e^- \quad (6)$$

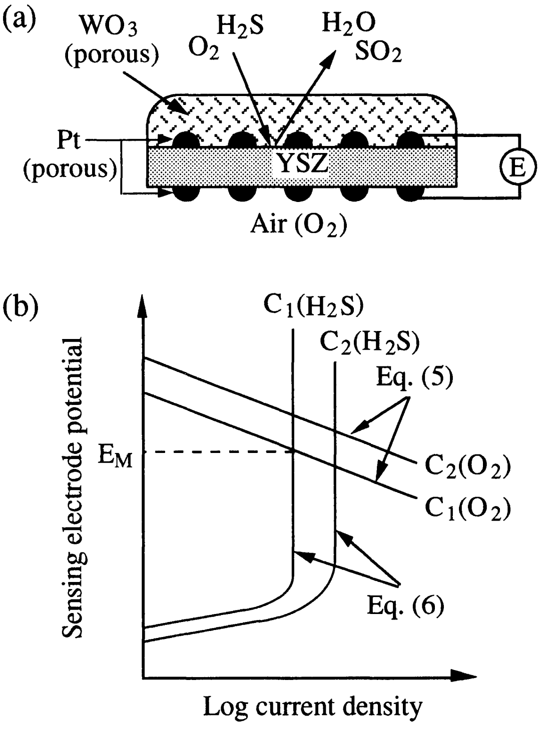

Fig. 5. H_2S sensing model (a) and schematic polarization curves of reactions (5) and (6).

These reactions conform a local cell, causing the sensing electrode potential to be fixed at a mixed potential at which the two reactions proceed at an equal current density. We have to consider that H_2S is very dilute (ppm levels) compared to O_2 (21 vol%). In such a situation, the polarization curve of reaction (6) will show a limiting current density I(6), while the other reaction follows a Tafel equation,

$$E(5) = a \log I(5) + b \tag{7}$$

as schematically depicted, respectively, in Fig. 5 (b). Here E(5) and I(5) stand for the electrode potential and current density for reaction (5). The mixed potential, E_M, is given by the intersection of the two polarization curves, and EMF of the device is given by the difference between this potential and the reference electrode potential. It should be pointed out that the limiting current density I(6) is usually proportional to the concentration of H_2S, $C(H_2S)$, that is, the polarization curve will shift as $C(H_2S)$ changes as shown in Fig. 5 (b) where $C_1(H_2S)<C_2(H_2S)$. This implies that the slope of the EMF vs. H_2S concentration correlation in Fig. 3 will present the Tafel slope of equation (5). When O_2 concentration ($C(O_2)$) changes, on the other hand, the polarization curve of equation (5) shifts as depicted in Fig. 5 (b), where $C_1(O_2)<C_2(O_2)$. Accordingly EMF of the device to a fixed H_2S concentration will shift upward as $C(O_2)$ increases, and this was in fact confirmed experimentally: EMF increased at a slope of 50 mV/decade on increasing O_2 concentration. Similar discussion involving mixed potential has been made for proton conductor-based sensors for H_2 in air.[11,12)]

In conclusion, the WO_3-coated YSZ device exhibits rather excellent sensing properties to dilute H_2S in air. Its working mechanism can be explained consistently on assuming that the gas sensing reaction proceeds at the interface between YSZ and WO_3. This assumption as well as the others should be verified by further investigations.

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 03453090) from Ministry of Education, Science and Culture of Japan.

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(Received July 1, 1994)