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Sensing properties of solid electrolyte SO_2 sensor using metal-sulfide electrode

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Solid-state electrochemical sensor devices combined with a sodium ion conductor ($Na_5DySi_4O_{12}$) disc and metal-sulfide sensing electrodes synthesized via solution routes have been investigated for the detection of SO_2 in the range 20–200 ppm at 150–400°C. Among the various sulfide sensing electrodes tested, the metal-mono sulfide-based electrodes (NiS, CdS, SnS and PbS) gave good SO_2 sensitivity at 300–400°C. The CdS-based solid electrolyte sensor element showed the best sensing characteristics, i.e., the EMF response was almost linear with the logarithm of SO_2 concentration in the range between 20 and 200 ppm, with a 90% response time to 100 ppm SO_2 of about 2–4 min at 400°C.

1. Introduction

Sulfur oxides (SO_2 and SO_3; often referred to as SO_x) emitting from gasoline- or diesel-engines, power stations, and other industrial plants are one of the major sources of acid rain or smog, and harmful for human health. Thus, there is a need for solid-state sulfur oxides sensors, which are reliable, inexpensive, and compact. So far, many kinds of compact SO_x sensors using various materials such as solid electrolyte [1–8], oxide semiconductors [9], solid polymer electrolyte [10] and piezoelectric crystal [11] have been investigated. Among them, the solid electrolyte-type SO_x sensors are of particular interest from the viewpoints of low cost, high sensitivity, good selectivity and simple device structure.

Many solid electrolyte-type SO_x sensors have been reported in literature. These are: solid electrolyte type II [12–14] sensor devices based on the alkali sulfate-based electrolytes [1–8], the solid electrolyte type III [12–14] sensor devices using β-alumina/Na_2SO_4 [15], CaF_2/$CaSO_4$ [16], Ca-β''-alumina/$CaSO_4$ [17], CaO-ZrO_2 (CSZ)/K_2SO_4 [3], Y_2O_3-ZrO_2 (YSZ)/$BaSO_4$-K_2SO_4 [18], MgO-ZrO_2 (MSZ)/Li_2SO_4-$CaSO_4$ [19, 20], $Na_3Zr_2Si_2PO_{12}$ (NASICON)/Na_2SO_4 [17, 21, 22], YSZ: NASICON/Na_2SO_4 [23], and $MgZr_4(PO_4)_6$/Na_2SO_4 [24]-based couples. However, these sensors need relatively high operating temperatures and/or appear to suffer from the chemical instability of the alkali metal sulfates used as the solid electrolyte or the auxiliary phase. Metal-sulfide electrodes such as MoS_2 [25] and Ag_2S-MoS_x [26] have been investigated, instead of conventional metal sulfates for the auxiliary phases of CaF_2 or Ag-β-alumina based solid electrolyte sulfur gas sensors, respectively. These seem to exhibit better sensing performance in a wide temperature range, as well as improve chemical and/or thermal stability. More detailed studies, however, are needed about the sensing characteristics involving metal-sulfide electrodes.

In our previous study [27], it was found that $Na_5DySi_4O_{12}$ (NaDyCON)-based sodium ion conductor shows relatively higher chemical stability in an acidic condition as well as higher ionic conductivity at lower temperatures. It was also demonstrated that metal-sulfides work as sensing electrodes for the NaDyCON-based solid electrolyte SO_2 sensor. In this paper, we report results of a systematic study on the sensing properties of various metal-sulfides as sensing electrodes.

2. Experimental

2.1. Preparation of sensor materials

Most of the metal-sulfides used as the sensing electrode materials were prepared by the wet-chemical methods using aqueous solutions. Metal-mono sulfides (MS: M = Ni, Cu, Zn, Cd, Pb) and Ag_2S were prepared by a homogeneous precipitation method [28]. Aqueous solutions of metal-chlorides were mixed with urea at room temperature, and then thioacetoamide was added to the solution at 70°C to form a precipitate, which was boiled at 100°C for 1 h, filtered and washed with distilled water, and then heat-treated at 120–300°C in Ar. Metal di-sulfides ($M'S_2$; M' = Ni, Ru) and Bi_2S_3 were prepared by the ammonium sulfide method [29]. Ammonium sulfide aqueous solution was slowly added to the aqueous solution of metal-chlorides at room temperature, which was stirred for 1 h and then adjusted to pH < 7 with HCl to get precipitates. The obtained precipitates were filtered, washed, dried at 120°C in Ar and finally calcined at 300°C in Ar for 2 h. Thiospinels (Ni_3S_4, etc.) were prepared by a pH-controlled precipitation method [30]. Thioacetoamide solution was added

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to the aqueous solution of metal chlorides, ammonia, and ammonium chloride at 70°C under a fixed pH at 9.9. After refluxing at 70°C for 12 h, the precipitates were filtered, washed and dried at 120°C in Ar for 12 h. Commercial metal-sulfides (GeS, MoS_2: Kishida Chemical Co., Ltd.; SnS, WS_2: Kojundo Chemical Laboratory Co., Ltd.) were also used as the sensing electrode materials.

Solid electrolyte discs of $Na_5DySi_4PO_{12}$ (NaDyCON) were prepared by a solution sol-gel method [31]. Aqueous solutions of $Si(OC_2H_5)_4$, $Na_2SiO_3 \cdot 9H_2O$, and $Dy(NO_3)_2 \cdot 6H_2O$ were mixed together to form a sol. The sol was evaporated at 75°C and dried at 120°C to form a fine dry xerogel powder, which was then ground and calcined at 720–750°C for 3 h. The calcined material was ground again and pressed into discs and sintered at 1000–1050°C for 6 h in air.

The prepared materials were characterized by X-ray diffraction analysis (XRD: JDX-3500K, JEOL Ltd.) using Cu $K_{\alpha 1}$ radiation, and scanning electron microscopy (SEM: JSM-6320F, JEOL Ltd.) for phase content and microstructural features.

2.2. Sensor devices

Fig. 1 shows a schematic diagram of the SO_2 sensor device using the NaDyCON disc and metal-sulfide electrodes with a Au-mesh current collector at the outside surface (Type A) or a Au-mesh sandwiched in between the sulfide and the solid electrolyte disc (Type B). A paste prepared with the sulfide and turpentine oil was painted onto the surface of the NaDyCON disc, and dried and heat treated at 500°C for 1 h to form a layer of sulfide as the sensing electrode. A reference Pt electrode attached on the inside surface of the NaDyCON disc was always exposed to a static atmospheric air.

Sensing experiments were carried out in a conventional flow apparatus equipped with a heating source providing temperature in the range of 150–400°C. Sample gases containing SO_2 were prepared from a parent gas, i.e., SO_2 diluted with nitrogen, by mixing with nitrogen or a dry synthetic air ($N_2 + O_2$ gas mixture).

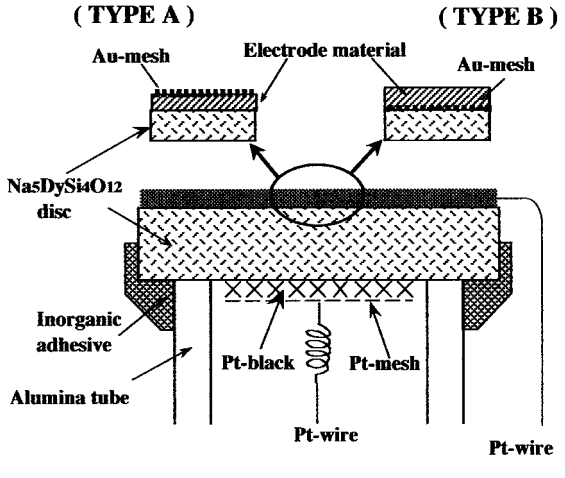

Figure 1 Schematic diagram of a solid electrolyte SO_2 sensor device using sulfide sensing electrodes with different types of Au current collectors (Type A or B).

The sensor response, EMF, was measured with a digital electrometer (Advantest, R8240) at a total flow rate of 100 cm^3/min.

3. Results and discussion

3.1. Sensor materials and elements

Fig. 2 shows XRD patterns of CdS and NiS_2 synthesized by the wet-chemical preparation processes. Although, a low-intensity peak of an impurity phase was observed for CdS, the well-crystallized and almost single-phase CdS and NiS_2 were observed. The XRD analysis also revealed that the other metal mono- and di-sulfides including the thiospinels prepared by the wet chemical methods showed well-crystallized and almost single-phase sulfides.

Fig. 3 shows XRD pattern of the prepared NaDyCON disc sintered at 1000°C. Well-crystallized and almost single phase $Na_5DySi_4O_{12}$ was determined by XRD. The densities of the discs calculated from their mass and dimensions were 3.0–3.1 g·cm^{-3}, which are about 93–95% of the theoretical density [32]. The ionic conductivity of a NaDyCON disc measured by an AC impedance method with Au electrodes was about 1.0×10^{-1} S·cm^{-1} at 300°C, which is comparable to that of the $Na_3Zr_2Si_2PO_{12}$ (NASICON) discs.

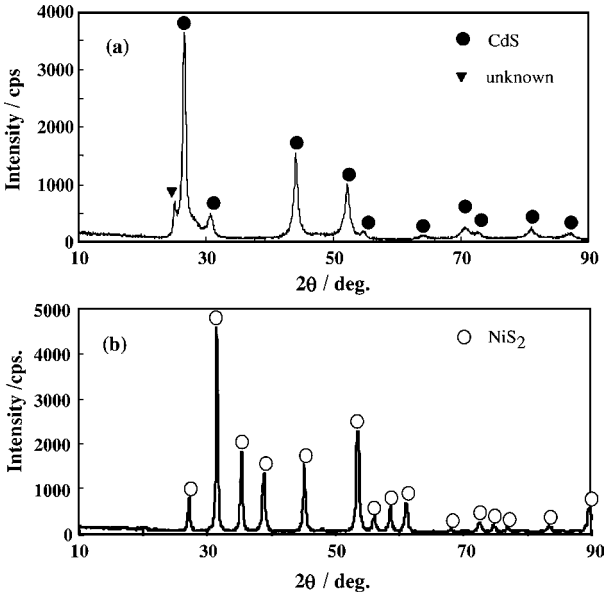

Figure 2 XRD pattern of a mono-sulfide (CdS) synthesized by the homogeneous precipitation method (a), and a di-sulfide (NiS_2) synthesized by the ammonium sulfide method (b).

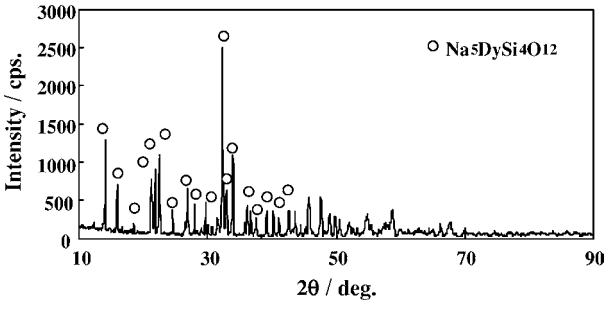

Figure 3 XRD pattern of a $Na_5DySi_4O_{12}$ electrolyte disc sintered at 1000°C for 6 h.

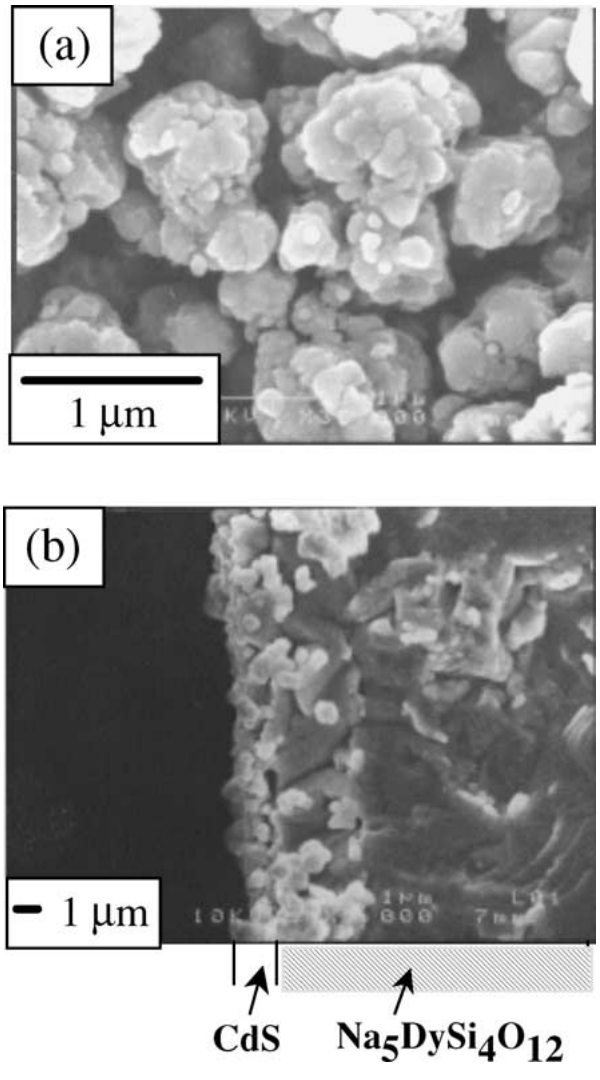

Figure 4 SEM images of the sensor device using $Na_5DySi_4O_{12}$ electrolyte and CdS electrode: (a) electrode surface and (b) cross-section of the device.

SEM images of the sensor device using the NaDyCON disc and the CdS sensing electrode are shown in Fig. 4. The CdS powder consists of primary particles of 50–100 nm and they are aggregated into secondary particles of about 0.5–1 μm to form the porous structure. The sulfide sensing electrode appears well bonded to the surface of the NaDyCON disc and the thickness of the CdS layer is about 1 μm. It also reveals that the NaDyCON disc is relatively dense without much evidence of any large pores.

3.2. SO_x sensing characteristics

As it is well known that the properties of metal-sulfides are largely dependent on the type of metal cation, the effects of metal cation in the metal mono-sulfides (MS; M = Ni, Zn, Cd, Cu, Ge, Sn, Pb) on SO_2 sensing properties were first investigated.

Most of the devices showed no response to SO_2 at temperatures between 150 and 250°C. Only the NiS-based device showed SO_2 response with a slope of −58 mV/decade, while the response time was as long as 15 min. At the temperature of 300°C, the devices based on NiS-, CdS-, SnS-, PbS-based electrodes showed SO_2 responses with different values of the slope and the response time. At the same temperature CuS-, GeS-based sensors showed no SO_2 response, and ZnS-based sensor showed high resistance and poor response characteristics.

Fig. 5 shows the SO_2 sensing properties of the elements using metal mono-sulfide systems, which showed SO_2 responses at 300 and 400°C. At 300°C, the NiS-based element showed the highest sensitivity (slope) but slow response rate. On the other hand, CdS- and SnS-based sensors showed rather large slope and relatively good response time at 400°C. Fig. 6 shows SO_2 sensing properties of the device with the SnS electrode at 400°C. The device showed good and reversible EMF responses to SO_2 at 400°C. The EMF response was linear with the logarithm of SO_2 concentration (log P_{SO_2}) between 20 and 200 ppm with a slope of −49 mV/decade at 400°C. The 90% response time (T_{90}) to 198 ppm SO_2 was about 7 min at 400°C. Table I summarizes the SO_2 sensing performance for the sensor devices with metal mono-sulfides, which were stable even in 2N H_2SO_4 solution at room temperature. Among

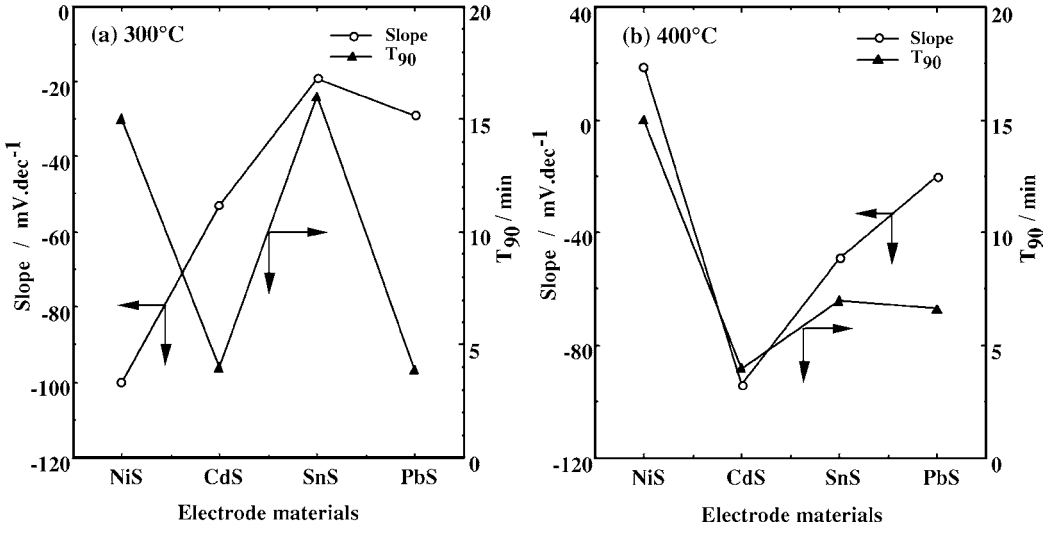

Figure 5 Sensing performance to SO_2 of the sensor devices attached with various metal mono-sulfides at (a) 300°C and (b) 400°C (Type A). Slope: slope for the line of ΔE vs. log P_{SO_2}; T_{90}: 90% response time to 100 ppm SO_2 (for SnS, PbS: 198 ppm SO_2).

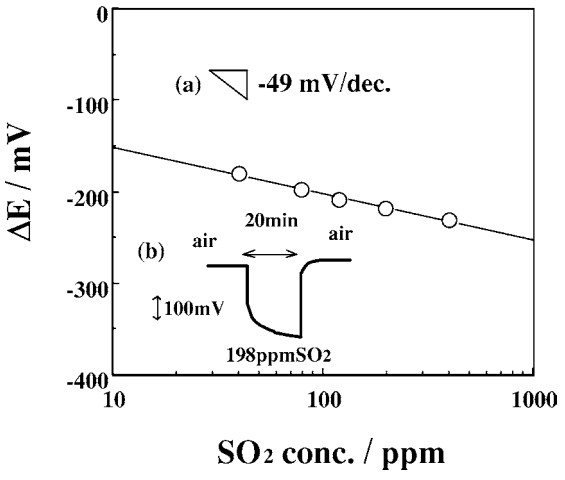

Figure 6 Sensing performance to SO_2 of the device using SnS electrode at 400°C (Type A): (a) ΔE vs. SO_2 concentration and (b) response transient to 198 ppm SO_2.

the metal mono-sulfides tested, sensor devices using the sulfides (MS; M = Ni, Cd, Sn, Pb) were found to exhibit good performance for the sensing of SO_2 at 300–400°C.

Table II summarizes SO_2 sensing performance for the sensors with metal di-sulfides, thiospinel and other metal sulfides. No response to SO_2 was obtained with the electrodes of metal di-sulfides or thiospinels, such as NiS_2 or Ni_3S_4 and Ag_2S at 300°C. Sensors based on MoS_2, WS_2, RuS_2, and Bi_2S_3 electrodes showed good sensing properties and stability to SO_2 at 400°C, although their response times were as long as 10–14 min. The reason for the dependence of the sensor response on the electrode material is not clear yet, but it may be related to the electro-catalytic activity and/or adsorption-desorption behavior of the reaction gases to the sulfide electrodes used. This aspect needs further investigation.

It was further observed that the Type B structure gave better sensing properties for the devices with high electrical resistance of the electrode, such as ZnS and CdS. Fig. 7 shows SO_2 sensing properties of the device with a CdS electrode in the Type B structure at 400°C. The 90% response time to 100 ppm SO_2 was as short as 2 min, and the recovery time was drastically improved by using Type B structure for CdS based element at 400°C. The EMF response was found to be linear with the logarithm of SO_2 concentration ($\log P_{SO_2}$) between 20 and 200 ppm with a slope of −44 mV/decade at

TABLE I Sensing performance to SO_2 of the devices using metal mono-sulfide electrodes

Electrode material	Temperature (°C)	ΔE[a] (mV)	Slope (mV/dec.)	90% response time (min)[b]	Element type
Nis	150–200	0	0	–	A
	250	−83	−58	15 (DR)	A
	300	−144	−100	15 (DR)	A
	400	−86	+19	15	A
ZnS	200–300	×	×	×	B
	400	−334	+6	9	B
CdS	200	×	×	×	A
	300	−308	−53	4 (DR)	A
	300	−159	+34	11	B
	400	−405	−94	4 (DR)	A
	400	−179	−44	2	B
CuS	200–400	×	×	×	B
GeS	300	0	0	–	A
	400	0	0	–	A
SnS	300	−51	−19	16[c]	A
	400	−217	−49	7[c]	A
PbS	300	−105	−29	3.9[c]	A
	400	−287	−20	6.6[c]	A

[a] $\Delta E = E_{100\,ppm} - E_{Air}$, ×; unstable, DR; drift.
[b] 90% response time to 100 ppm SO_2.
[c] 90% response time to 198 ppm SO_2.

TABLE II Sensing performance to SO_2 of the devices using various metal sulfide electrodes

Electrode material	Temperature (°C)	ΔE[a] (mV)	Slope (mV/dec.)	90% response time (min)[b]	Element type
NiS_2	150–400	0	0	0	A
Ni_3S_4	150–250	0	0	0	A
Ag_2S	150–250	0	0	0	A
MoS_2	300	0	0	0	A
	400	−300	−12	10	A
WS_2	300	0	0	0	A
	400	−176	−11	14	A
RuS_2	300	×	×	×	A
	400	−123	−48	12	A
Bi_2S_3	300	−73	+2	14	A
	400	−200	+73	11	A

[a] $\Delta E = E_{100\,ppm} - E_{Air}$, ×; unstable.
[b] 90% response time to 100 ppm SO_2.

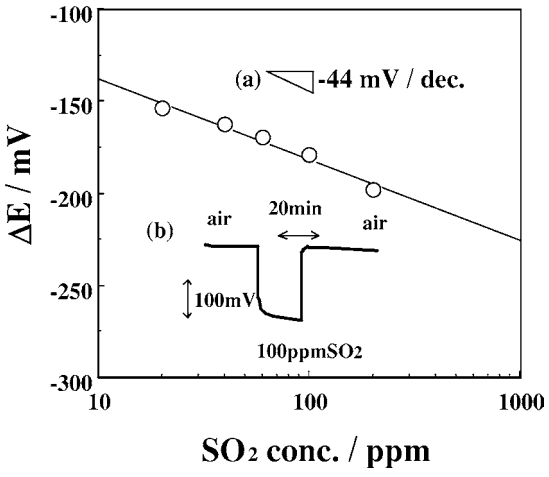

Figure 7 Sensing performance to SO_2 of the device using CdS electrode at 400°C (Type B): (a) ΔE vs. SO_2 concentration and (b) response transient to 100 ppm SO_2.

400°C. The CdS based element responded to oxygen, i.e., the EMF response was linear with the logarithm of oxygen concentration with a slope of +100 mV/dec. On the other hand, it responded poorly to NO and CO_2. Tests of cross-sensitivity and effect of humidity are yet to fully explored.

4. Conclusion

Solid electrolyte SO_x sensor devices using NaDyCON electrolyte and metal sulfide electrodes were found to exhibit good sensing performance in the temperature range of 300–400°C. The EMF responses were linear with the logarithm of SO_2 concentration between 20–200 ppm SO_2. The device using the CdS electrode with Type B structure gave the best sensing properties.

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