

Solid-State SO₂ Sensor Using Sodium-Ionic Conductor and Metal-Sulfide Electrode

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Abstract All solid-state SO_x sensor devices combined with a sodium ionic conductor (Na₅DySi₄O₁₂) disc and metal-sulfide sensing electrodes synthesized via solution routes have been systematically investigated for the detection of SO₂ in the range 20 – 200 ppm at 150 - 400°C. Among the various sulfide sensing electrodes tested, the metal-mono sulfide-based electrodes gave good SO₂ sensitivity at 400°C. The Pb_{1-x}Cd_xS (x = 0.1, 0.2) -based solid electrolyte sensor element showed the best sensing characteristics, i.e., the EMF response of was almost linear to the logarithm of SO₂ concentration in the range between 40 and 400 ppm, with a 90 % response time to 100 ppm SO₂ of about 3 - 15 min, and also showed high selectivity to SO₂ at 400°C.

Keywords: Metal-sulfide electrode, SO₂ sensor, NASICON, NaDyCON, Na₅DySi₄O₁₂, Solid electrolyte, Gas sensor

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1. Introduction

Sulfur oxides (SO_2 and SO_3) as the emissions from gasoline- or diesel- engines, power stations, and other industrial plants, and so on are the typical air pollutants as well as one of the major sources of acid rain or smog. Thus, continuous on-site monitoring of sulfur oxides has been becoming very important. So far, many kinds of compact SO_x sensors using various materials, such as solid electrolyte,¹⁻¹³ oxide semiconductors,¹⁴ solid polymer electrolyte,¹⁵ and piezoelectric crystal¹⁶ and so on have been investigated. Among them, the solid electrolyte-type SO_x sensors are of particular interest from the viewpoints of low cost, high sensitivity, high selectivity and simple element structure. So far, various kinds of solid electrolyte sensor devices based on alkali-sulfate based electrolytes^{1,4,5}; solid electrolyte sensors using Na- β -alumina/ Na_2SO_4 ,⁶ $\text{CaF}_2/\text{CaSO}_4$,¹⁰ NASICON/ Na_2SO_4 ¹¹ were demonstrated. However, these sensors still 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 auxiliary phase. Previously it was tested the use of the metal-sulfide electrodes, such as MoS_2 ¹² or $\text{Ag}_2\text{S-MoS}_x$,¹³ instead of conventional metal sulfates for the auxiliary phases of CaF_2 or Ag- β -alumina based solid electrolyte sulfur gas sensors, respectively, they seem to bring about better sensing performance at wide operation temperature as well as chemical and/or thermal stability. However, little was disclosed about the sensing characteristics of the solid electrolyte SO_x sensor combined with solid electrolyte and metal-sulfide electrode.

Recently, it was found that the $\text{Na}_5\text{DySi}_4\text{O}_{12}$ (NaDyCON)-based sodium ion conductor showed relatively higher chemical stability in an acidic condition as well as higher ionic conductivity at lower temperatures, and it was also revealed the metal-sulfides have worked as a sensing electrode for the

NaDyCON-based solid electrolyte SO₂ sensor¹⁷. In this study, the NaDyCON-based solid electrolyte electrochemical sensor has been systematically investigated by using metal-mono-, di-sulfides and thiospinels as a sensing electrode for the detection of sulfur dioxide. As a result, it was turned out that the metal-mono sulfide, especially the Pb_{1-x}Cd_xS (x = 0.1, 0.2) -based device showed good sensing properties to SO₂ at 400°C.

2. Experimental

2.1 Preparation of sensor materials

Solid electrolyte discs of Na₅DySi₄PO₁₂ (NaDyCON) were prepared by a solution sol-gel method^{17,18}: Aqueous solutions of Si(OC₂H₅)₄, Na₂SiO₃·9H₂O, and Dy(NO₃)₂·6H₂O were mixed together to form a sol, which 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 sample discs, and then finally sintered at 1000 - 1050°C for 6h in air.

Metal-mono sulfides (MS: M = Ni, Cu, Zn, Cd, Pb, Cd_{1-x}Ni_xS, Pb_{1-x}M'_xS; M' = Cd, Ni, x=0-0.1) and Ag₂S were prepared by a homogeneous precipitation method^{19,20}: 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'S₂; M' = Ni, Ru) and Bi₂S₃ were prepared by the ammonium sulfide method²⁰: Ammonium sulfide aqueous solution was slowly added to the aqueous solution of metal-chlorides at room temperature, which was stirred at room temperature for 1h 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 , Co_3S_4 , AlNi_2S_4 , FeNi_2S_4 , CoNi_2S_4) were prepared by a pH-controlled precipitation method^{21,22}:

Thioacetoamide solution was added 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 12h, the precipitates were filtered, washed and dried at 120°C in Ar for 12 h. Some 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 material.

The obtained products were characterized by X-ray diffraction analysis (XRD: JDX-3500K, JEOL Ltd.) using $\text{CuK}_{\alpha 1}$ radiation, and scanning electron microscopy (SEM: JSM-6320F, JEOL Ltd.), etc.

2.2 Sensor devices

Figure 1 shows a schematic diagram of SO_2 sensor devices using the NaDyCON disc and the metal-sulfide electrode. A paste prepared with sulfides and turpentine oil was painted onto the surface of the NaDyCON disc, and dried and sintered at 500°C for 1 h to form a layer of sulfide as a sensing electrode. A reference Pt electrode attached on the inside surface of the NaDyCON disc was always exposed to static atmospheric air.

SO_2 sensing experiments were carried out in a conventional flow apparatus equipped with a heating facility at 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 ($\text{N}_2 + \text{O}_2$ gas mixture). The

sensor response, EMF, was measured with a digital electrometer (Advantest, R8240) at a total flow rate of 100 cm³/min.

3. Results and Discussion

3. 1 Sensor materials and elements

XRD pattern of the prepared NaDyCON disc sintered at 1000°C revealed that well-crystallized and almost single phase Na₅DySi₄O₁₂ could be obtained. The densities of the discs calculated from their mass and dimensions were ca. 3.1 g cm⁻³, which are about 95 % of the theoretical density.²³ The ionic conductivity of an NaDyCON disc measured by an AC impedance method with Au electrodes was about 1.0x10⁻¹ S cm⁻¹ at 300° C, which is comparable to that of the Na₃Zr₂Si₂PO₁₂ (NASICON) discs.

Figure 2 shows XRD pattern of the three types of sulfides synthesized by the wet-chemical preparation processes. The well-crystallized and almost single-phase metal-mono-sulfide (NiS), metal-di-sulfide (NiS₂), and thiospinel (Ni₃S₄) could be observed. The other metal mono-, di- sulfides and thiospinels thus prepared showed well-crystallized and almost single-phase sulfides.

SEM image of the sensor device using the NaDyCON disc and the CdS revealed that the electrode form the porous structure and was tightly fixed on the surface of the NaDyCON disc. The thickness of the CdS layer was about 2 μm as shown in Fig. 3. It was also revealed that the NaDyCON disc was relatively dense without any large pores.

3. 2 SO_x sensing properties

As most of the metal-sulfide could be synthesized via wet-chemical routes, the effects of metal – sulfides on SO₂ sensing properties were first investigated. Most of the devices with metal-sulfide showed no response to SO₂ at the temperatures between 150 and 250°C. At the temperatures of 300 - 400°C, the devices based on metal-sulfide based elements showed SO₂ responses with different values of the slope and the response time. Table 1 shows sensing performance of the SO₂ sensors using various kinds of metal-sulfide electrodes, which were stable even in 2N H₂SO₄ solution at room temperature. For the types of the sulfides, metal-mono sulfide were found to be most promising materials for SO₂ sensor, such as CdS, SnS, PbS-based elements showed good sensing properties to SO₂, although NiS-, GeS- based elements showed poor or no SO₂ response. For example, the device attached with an SnS electrode showed good and reversible EMF responses to SO₂ at 400°C. The EMF response was linear to the logarithm of SO₂ concentration (log P_{SO2}) between 20 and 200 ppm with the slope of -49 mV / decade at 400°C. The 90 % response time to 200 ppm SO₂ was about 7 min at 400°C. Poor response to SO₂ was obtained with the elements using electrodes metal di-sulfides or thiospinels, such as NiS₂, MoS₂, WS₂, or AlNi₂S₄, FeNi₂S₄, and CoNi₂S₄, at 400°C, while those based on RuS₂, Bi₂S₃ and, Ni₃S₄ electrodes, showed good sensing properties and stability to SO₂ at 400°C, although their response times were as slow as 11-17 min.

In the electrode materials tested, PbS-, CdS- based elements showed relatively good SO₂ response at 400°C. The partial substitution of metal cation in the transition metal sulfides is expected to an appearance of anomalous valence of the transition metals, anion defects. This is expected to give large modification of the electrocatalytic activities. Thus, we tried to the solid solution type Pb_{1-x}M_xS

and $\text{Cd}_{1-x}\text{M}_x\text{S}$. Thus, $\text{Pb}_{1-x}\text{M}_x\text{S}$, $\text{Cd}_{1-x}\text{M}_x\text{S}$ (M: Cd, Ni, $x = 0 - 0.3$) families were further tested as sensing electrode materials.

Figure 4 shows the SO_2 sensing properties of the element using $\text{Pb}_{0.8}\text{Cd}_{0.2}\text{S}$ electrode at 400°C . The device showed good and reversible EMF responses to SO_2 at 400°C . The EMF response was linear to the logarithm of SO_2 concentration ($\log P_{\text{SO}_2}$) between 40 and 400 ppm with the slope of as high as -79 mV / decade at 400°C . The 90 % response time to 100 ppm SO_2 was about 15 min at 400°C .

Table 2 summarizes the SO_2 sensing performance for the sensor devices attached with PbS-based electrodes, such as $\text{Pb}_{1-x}\text{Cd}_x\text{S}$ and $\text{Pb}_{1-x}\text{Ni}_x\text{S}$ ($x = 0.1 - 0.3$), respectively, the all sulfides were stable even in 2N H_2SO_4 solution at room temperature. At 400°C , the $\text{Pb}_{0.8}\text{Cd}_{0.2}\text{S}$ and $\text{Pb}_{0.9}\text{Ni}_{0.1}\text{S}$ -based elements showed the highest accuracy (slope: -78 to -80 mV/decade) but relatively slow response rate. On the other hand, the electrode with the $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{S}$ electrode showed rather fast response and recovery times to SO_2 , although the slope was as low as -19 mV / decade at 400°C . It was also found that $\text{Pb}_{1-x}\text{Ni}_x\text{S}$ systems gave improvement of SO_2 sensing property of the accuracy (slope) by the partial substitution of Ni into PbS at 400°C .

Table 3 summarizes the SO_2 sensing performance for the sensor devices attached with CdS-based electrodes, such as, $\text{Cd}_{1-x}\text{Ni}_x\text{S}$ ($x = 0.1, 0.2, 0.3$). In the $\text{Cd}_{1-x}\text{Ni}_x\text{S}$ system, not so good improvement was observed by the partial substitution of Ni into CdS at $300 - 400^\circ\text{C}$.

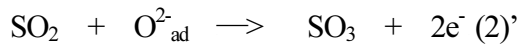
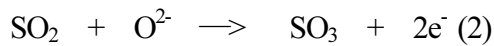
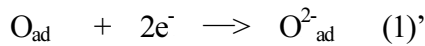
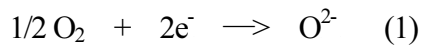
The reason for the dependence of the sensor response properties on the electrode material was not clear yet, but it seems come from the electro-catalytic activity and/or sorption-desorption behavior of the reaction gases to the sulfide electrodes used. Further investigation is now in progress.

It was further found that the $\text{Pb}_{0.8}\text{Cd}_{0.2}\text{S}$ element gave good selectivity to SO_2 at 400°C . Figure 5 shows SO_2 selectivity of the device attached with a $\text{Pb}_{0.8}\text{Cd}_{0.2}\text{S}$ electrode at 400°C . The device showed good and EMF responses to SO_2 between 40 and 400 ppm at 400°C . The $\text{Pb}_{0.8}\text{Cd}_{0.2}\text{S}$ based element hardly responded to O_2 , NO_2 and CO_2 , although it had a sensitivity to NO . The investigations of close sensitivity and effect of humidity etc. are now in progress.

3.3 Mechanism of potentiometric sensing

For the most of the sensor devices tested, the slope of the line for ΔE vs. $\log P_{\text{SO}_2}$ was largely depending on the electrode materials, and the element type. Thus, the sensing mechanism seems to be come from not the conventional Nernst' type but probably the mixed potential one²⁴.

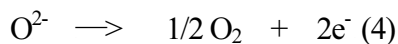
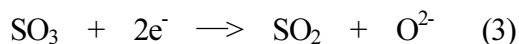
When the sensing electrode is exposed to SO_2 gas including oxygen or adsorbed oxygen, the electrochemical oxidation (1), (1)' and electrochemical SO_2 oxidation (2), (2)' take place simultaneously.



These two reactions form a local cell and determine the mixed electrode potential. Figure 6 (a) depicts schematic polarization curves for both the anodic and the cathodic reactions.

As a sensor device, the sensing signal should be more accurate value, i.e., the slope of ΔE vs. $\log P_{\text{SO}_2}$ should be larger. When we consider about the cases (I), (II), and (III) in the new Figure 6 (a),

the mixed potentials gave the larger slope in the order to (I) > (II) > (III). On the other hand, the value of the slope E vs. $\log I$ at the small current area means Tafel slope of the anodic reaction (1), which shows the electrocatalytic activity to the reaction (1) or (1)'. The electrocatalytic activity is to be (III), (II), and (I) in that order. In our previous studies, the electrocatalytic activities of the metal sulfides to the oxygen reduction were thiospinels, disulfides, and monosulfides, in that order^{20,22}. For that reason, the monosulfide groups of CdS, SnS, and PbS, which have larger Tafel slopes, thus these gave the large slope in ΔE vs. $\log P_{SO_2}$ plots. If the electrochemical reaction was different due to the electrocatalytic activities, the case electrochemical reduction (3), (3)' and electrochemical oxidation (4), (4)' take place, instead of the reactions (1),(1)' or (2),(2)', respectively, as shown in Fig. 6 (b).



However, the sensing mechanisms of the present electrochemical device still need further investigations.

4. Conclusion

A solid electrolyte SOx sensor device using NaDyCON and metal sulfide- based electrode was found to exhibit good performance for the potentiometric sensing to SO_2 at 400°C. The EMF responses were linear to the logarithm of SO_2 concentration between 40 - 400 ppm SO_2 . The device using the $Pb_{0.8}Cd_{0.2}S$ and $Pb_{0.9}Cd_{0.1}S$ electrode gave good SO_2 sensing properties.

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References

- ¹M. Gauthier and A. Chamberland, "Solid-State Detectors for the Potentiometric Determination of Gaseous Oxides – I. Measurement in Air–," *J. Electrochem. Soc.*, 124 [10] 1579 -1583 (1977).
- ²Y. Saito, T. Maruyama, Y. Matsumoto, and Y. Yano, "Electromotive Force of the SO₂-O₂-SO₃ Concentration Cell Using NASICON"; pp.326-331 in Proc. of the Int. Meet. on Chemical Sensors, Fukuoka, Sep. 19-22 (1983). Edited by T. Seiyama, K. Fueki, J. Shiokawa, and S. Suzuki. Kodansha/Elsevier, Tokyo 1983.
- ³Y. Saito, T. Maruyama, Y. Matsumoto, K. Kobayashi, and Y. Yano, " Applicability of Sodium Sulfate as a Solid Electrolyte for a Sulfur Oxides Sensor," *Solid State Ionic*, 14 [4] 273- 281 (1984).
- ⁴N. Imanaka, Y. Yamaguchi, G. Adachi, and J. Shiokawa, "Sodium Sulfate Mixed with Rare Earth Sulfates (Ln = Y and Gd) and Silicon Dioxide as a Solid Electrolyte for a Sulfur Dioxide Detector," *Bull. Chem. Soc. Jpn.*, 58 [1] 5-8 (1985).
- ⁵Q. G. Liu and W. L. Worrell, "Electrical Conductivity of Li₂SO₄-Ag₂SO₄ Solid Electrolytes," *Solid State Ionics*, 18&19 [1] 524 -528 (1986).

- ⁶R. Akila and K. T. Jacob, " An SO_x ($X = 2, 3$) Sensor Using B-Alumina/ Na_2SO_4 Couple," *Sensors and Actuators*, 16 [4] 311-323 (1989).
- ⁷Y. Yan, Y. Shimizu, N. Miura, and N. Yamazoe, Solid-State sensor for Sulfur Oxides Based on Stabilized Zirconia and Metal Sulphate, *Chem. Lett.*, 635-638 (1992).
- ⁸Y. Yan, N. Miura, and N. Yamazoe, Conduction and Working Mechanism of sulfur Dioxide Sensor Utilizing Stabilized Zirconia and Metal Sulfate," *J. Electrochem. Soc.*, 143 [2] 609-613 (1996).
- ⁹L. Wang and R. V. Kumar, "A New SO_2 Gas Sensor Based on an Mg^{2+} Conducting Solid Electrolyte, " *J. Electroanal. Chem.*, 543 [2] 103-114 (2003).
- ¹⁰K. T. Jacob, M. Iwase, and Y. Waseda, " A Galvanic Sensor for SO_3/SO_2 based on the $\text{CaF}_2/\text{CaSO}_4$ Couple ," *Solid State Ionics*, 23 [4] 245-252 (1987).
- ¹¹G. Rog, A. Kozłowska-Rog, K. Zakula, W. Bogusz, and W. Pycior, "Calcium β "-Alumina and Nasicon Electrolytes in Galvanic Cells with Solid Reference Electrodes for Detection of Sulfphur Oxides in Gases, " *J. Appl. Electrochem.*, 21, 308-312 (1991).
- ¹²M. Taniguchi, M. Wakihara, T. Uchida, K. Hirakawa, and J. Nii, "Sulfur Gas Sensor Using a Calcium Fluoride Solid Electrolyte ," *J. Electrochem. Soc.*, 135 [1] 217-221 (1988).
- ¹³J. Kirchnerova, C. W. Bale, and J. M. Skeaff, " Potentiometric Gaseous Sulfur Sensor Based on Silver Beta-Alumina Solid Electrolyte," *Solid State Ionics*, 91 [3/4] 257-264 (1996).
- ¹⁴Y. Shimizu, N. Matsunaga, T. Hyodo, and M. Egashira, " Improvement of SO_2 Sensing Properties of WO_3 by Noble Metal Loading ," *Sensors and Actuators B*, 77 [1/2] 35-40 (2001).
- ¹⁵C-Y. Chiou, T-C. Chou, "Amperometric SO_2 Gas Sensors Based on Solid Polymer Electrolytes," *Sensors and Actuators B*, 87 [1] 1-7 (2002).

- ¹⁶K. H. Karmarkar and G. G. Guilbault, "A New Design And Coatings for Piezoelectric Crystals in Measurement of Trace Amounts of Sulfur Dioxide," *Anal. Chim. Acta*, 71 [2] 419-424 (1974).
- ¹⁷N. Souda and Y. Shimizu, "Sensing Properties of Solid Electrolyte SO_x Sensor Using Metal-Sulfide Electrode," *J. Mater. Sci.*, 38 (21), 4301-4305 (2003).
- ¹⁸Y. Shimizu, Y. Azuma, and S. Michishita, "Sol-Gel Synthesis of NASICON-Discs from Aqueous Solution," *J. Mater. Chem.*, 7 [8] 1487-1490 (1997).
- ¹⁹J. Grau and M. Akinc, "Synthesis of Nickel Sulfide Powders by Thioacetamide in the Presence of Urea," *J. Am. Ceram. Soc.*, 80 [4] 941-951 (1997).
- ²⁰Y. Shimizu, T. Yano, H. Suzuki, S. Kouno, and T. Izumi, "Sol-Gel Processing and Oxygen Electrocatalytic Properties of Metal-Sulfides," *ITE Letters*, 4 [6] 752-758 (2003).
- ²¹Y. Shimizu and T. Yano, "A Solution Route to Synthesize Nickel Thiospinels," *Chem. Lett.* [10] 1028-1029 (2001).
- ²²T. Ueda and Y. Shimizu, "Electrocatalytic Properties of Nickel-Based Thiospinels for PEFC," *ITE Letters*, 5 [5] 454-458 (2004).
- ²³R. D. Shannon, B. E. Taylor, T. E. Gier, H-Y. Chen, and T. Berzins, "Ionic Conductivity in Sodium Yttrium Silicon Oxide (Na₅YSi₄O₁₂)-Type Silicates," *Inorg. Chem.* 17 [4] 958-964 (1978).
- ²⁴N. Miura, G. Liu, and N. Yamazoe, "High-Temperature Potentiometric/Amperometric NO_x Sensors Combining Stabilized Zirconia with Mixed-metal Oxide Electrode," *Sensors and Actuators B*, 52, 169-178 (1998).

Figure captions

Fig. 1 Schematic diagram of solid electrolyte SO₂ sensor devices using sulfide sensing electrode.

Fig. 2 XRD patterns of a mono-sulfide (NiS) , a di-sulfide (NiS₂) , and a thiospinel (Ni₃S₄) synthesized by wet-chemical methods.

Fig. 3 SEM image of the cress section of the sensor device using Na₅DySi₄O₁₂ electrolyte and CdS electrode.

Fig. 4 Sensing performance to SO₂ of the device using Pb_{0.8}Cd_{0.2}S electrode at 400°C.

(a) ΔE vs. SO₂ concentration.

(b) Response transient to 100ppm SO₂.

Fig. 5 Selectivity of the SO₂ sensor using Pb_{0.8}Cd_{0.2}S electrode at 400°C.

Fig. 6 Schematic polarization curves for cathodic and anodic electrochemical reactions of the sulfide based electrode.

Table 1 Sensing performance to SO_2 of the device using various type of metal-sulfides at 400°C .

Electrode Material	ΔE ^{a)} [mV]	Slope [mV/dec.]	Response time ^{b)}	Performance of sensor ^{d)}
NiS	-86	+19	15	Δ
CdS	-405	-94	4	O
GeS	0	0	-	X
SnS	-217	-49	7 ^{c)}	O
PbS	-287	-20	7 ^{c)}	O
NiS ₂	0	0	-	X
MoS ₂	-300	-12	10	X
WS ₂	-176	-11	14	X
RuS ₂	-123	-48	12	Δ
Bi ₂ S ₃	-200	+73	11	Δ
AlNi ₂ S ₄	50	0	17	X
FeNi ₂ S ₄	-168	0	12	X
CoNi ₂ S ₄	-259	-197	15	US
Ni ₃ S ₄	-188	-34	17	Δ

a) $\Delta E = E_{100\text{ppm}} - E_{\text{Air}}$, b) 90% response time to 100 ppm SO_2 ,

c) 90% response time to 200 ppm SO_2 ,

d) O : excellent, Δ : fair, X : poor, US: unstable

Table 2 Sensing performance to SO₂ of the device using Pb-based metal-sulfide electrodes at 400°C.

Electrode Material	ΔE ^{a)} [mV]	Slope [mV/dec.]	Response time ^{b)}	Performance of sensor ^{d)}
PbS	-287	-20	7	Δ
Pb _{0.9} Cd _{0.1} S	-81	-19	3	O
Pb _{0.8} Cd _{0.2} S	-184	-78	15	O
Pb _{0.9} Ni _{0.1} S	-244	-80	17	O
Pb _{0.8} Ni _{0.2} S	-127	-24	15	Δ
Pb _{0.7} Ni _{0.3} S	-75	-49	15	Δ

a) $\Delta E = E_{100\text{ppm}} - E_{\text{Air}}$, b) 90% response time to 100 ppm SO₂,

c) O : excellent, Δ : fair

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Table 3 Sensing performance to SO₂ of the device using Cd-based metal-sulfide electrodes at 400°C.

Electrode Material	ΔE ^{a)} [mV]	Slope [mV/dec.]	Response time ^{b)}	Performance of sensor ^{c)}
CdS	-405	-94	4	O
Cd _{0.9} Ni _{0.1} S	-165	-12	10	Δ
Cd _{0.8} Ni _{0.2} S	-116	3	16	X
Cd _{0.7} Ni _{0.3} S	101	12	14	Δ

a) $\Delta E = E_{100\text{ppm}} - E_{\text{Air}}$, b) 90% response time to 100 ppm SO₂,

c) O : excellent, Δ : fair, X : poor

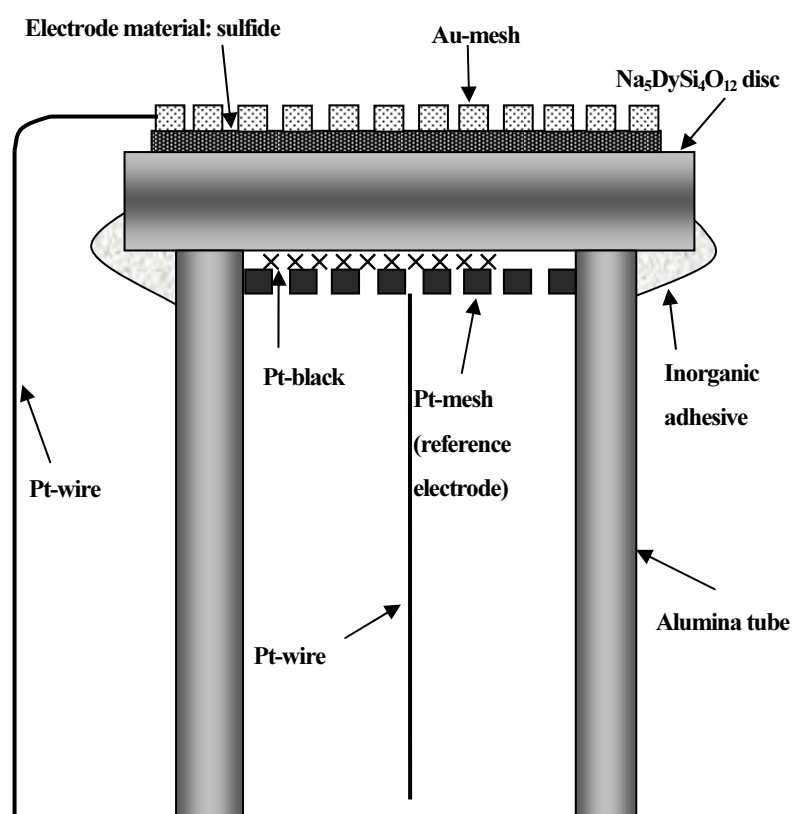


Fig. 1 Schematic diagram of solid electrolyte SO₂ sensor devices using sulfide sensing electrode.

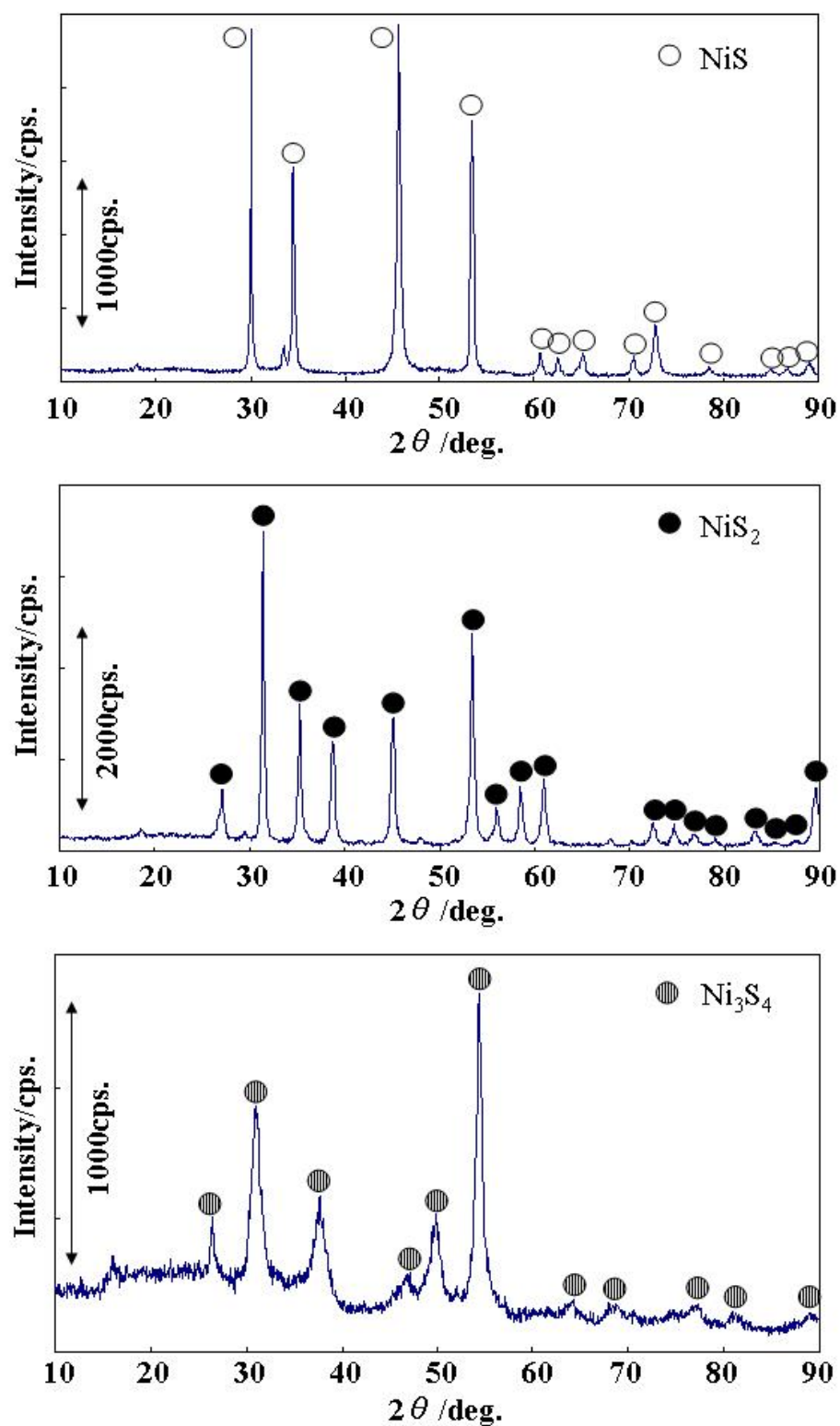


Fig. 2 XRD patterns of a mono-sulfide (NiS), a di-sulfide (NiS₂), and a thiospinel (Ni₃S₄)

synthesized by wet-chemical methods.

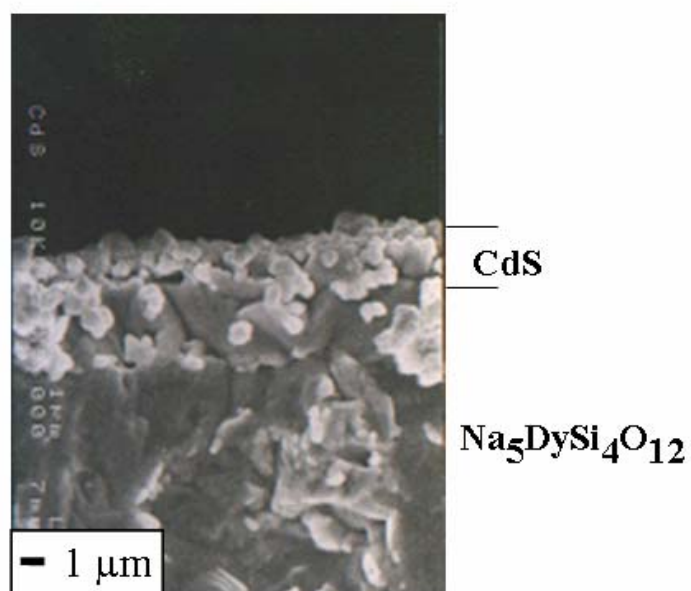


Fig. 3 SEM image of the cross section of the sensor device using Na₅DySi₄O₁₂ electrolyte and CdS electrode.

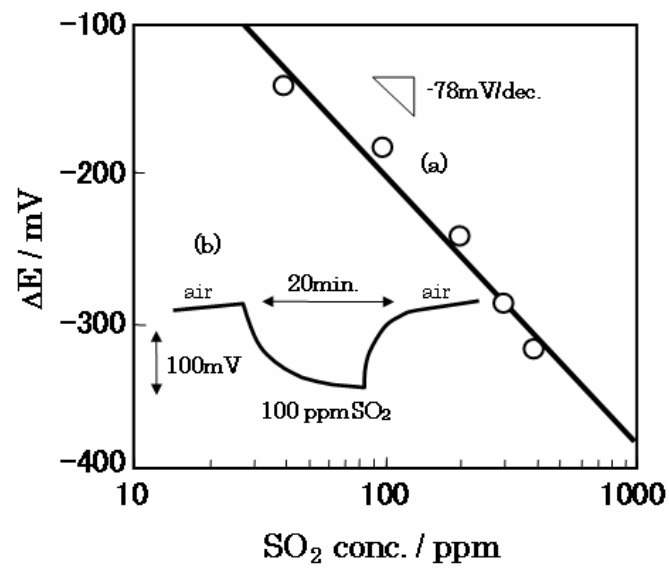


Fig. 4 Sensing performance to SO_2 of the device using $\text{Pb}_{0.8}\text{Cd}_{0.2}\text{S}$ electrode at 400°C .

(a) ΔE vs. SO_2 concentration.

(b) Response transient to 100 ppm SO_2 .

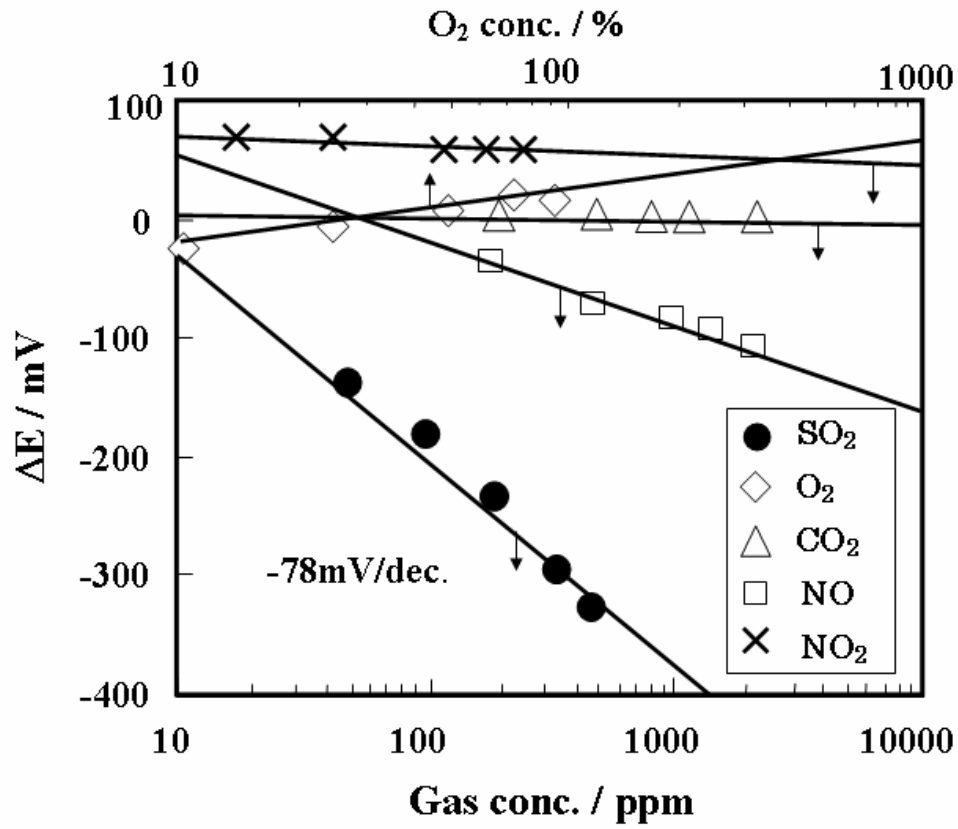


Fig. 5 Selectivity of the SO_2 sensor using $\text{Pb}_{0.8}\text{Cd}_{0.2}\text{S}$ electrode at 400°C .

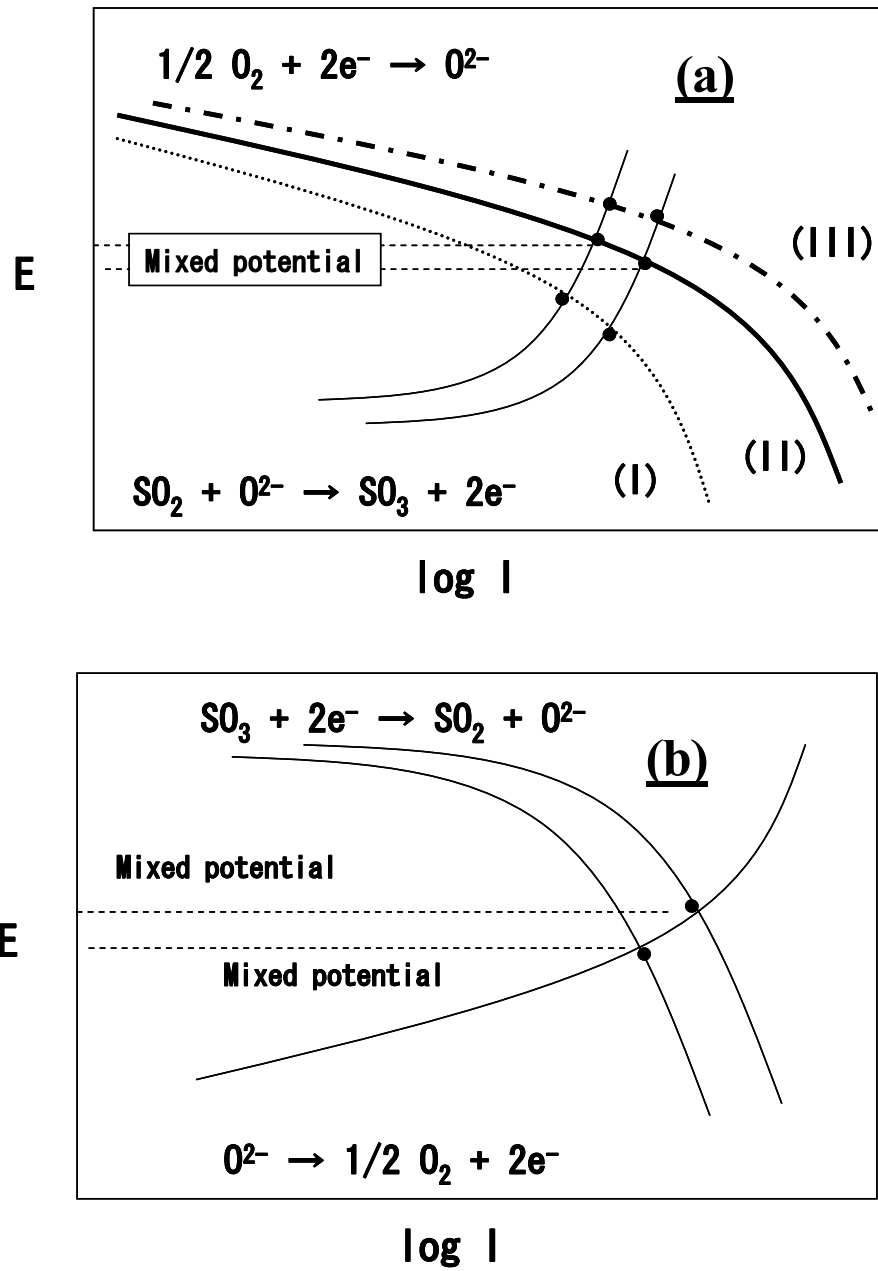


Fig. 6 Schematic polarization curves for cathodic and anodic electrochemical reactions of the sulfide based electrode.