

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

Youichi Shimizu,* Miho Okimoto, and Noriko Souda

Department of Applied Chemistry, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan

All solid-state sulfur oxides (SO_x) sensor devices combined with a sodium ionic conductor (Na₅DySi₄O₁₂) disk and metal sulfide-sensing electrodes synthesized via solution routes have been systematically investigated for the detection of SO₂ in the range of 20–200 ppm at 150–400°C. Among the various sulfide-sensing electrodes tested, the metal monosulfide-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 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.

Introduction

Sulfur oxides (SO₂ and SO₃) as emissions from gasoline or diesel engines, power stations, and other industrial plants, and so on are typical air pollutants as well as one of the major sources of acid rain or smog. Thus, continuous on-site monitoring of SO_x has become 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 crystal,¹⁶ and so on, have been investigated. Among them, 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/Na₂SO₄,⁶ CaF₂/CaSO₄,¹⁰ and NASICON/

Na₂SO₄¹¹ have been demonstrated. However, these sensors still need relatively high operating temperatures and/or appear to have chemical instability in the alkali metal sulfates used as the solid electrolyte or auxiliary phase. Previously the use of the metal sulfide electrodes, such as MoS₂¹² or Ag₂S–MoS_x,¹³ was tested; instead of conventional metal sulfates for the auxiliary phases of CaF₂ or Ag-β-alumina-based solid electrolyte sulfur gas sensors, respectively, they seemed to bring about better sensing performance at a 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 a solid electrolyte and a metal sulfide electrode.

Recently, it was found that the Na₅DySi₄O₁₂ (NaDyCON)-based sodium ion conductor showed a relatively higher chemical stability under an acidic condition as well as higher ionic conductivity at lower temperatures, and it was also revealed that metal sulfides have worked as sensing electrodes for a NaDyCON-based solid electrolyte SO₂ sensor.¹⁷ In this study, a NaDyCON-based solid electrolyte electrochemical sensor has been

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*shims@tobara.isc.kyutech.ac.jp

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systematically investigated using metal monosulfides, disulfides, and thiospinels as a sensing electrode for the detection of SO_2 . As a result, it turned out that the metal monosulfide, especially the $\text{Pb}_{1-x}\text{Cd}_x\text{S}$ ($x = 0.1, 0.2$)-based device, showed good sensing properties to SO_2 at 400°C .

Experimental Procedure

Preparation of Sensor Materials

Solid electrolyte disks of NaDyCON were prepared by a solution sol-gel method^{17,18}: Aqueous solutions of $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, and $\text{Dy}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 disks, and then finally sintered at 1000 – 1050°C for 6 h in air.

Metal monosulfides (MS: $\text{M} = \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Pb}, \text{Cd}_{1-x}\text{Ni}_x\text{S}, \text{Pb}_{1-x}\text{M}'_x\text{S}$; $\text{M}' = \text{Cd}, \text{Ni}, x = 0$ – 0.1) and Ag_2S were prepared by a homogeneous precipitation method^{19,20}: aqueous solutions of metal chlorides were mixed with urea at room temperature, and then thioacetamide 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 disulfides ($\text{M}'_2\text{S}_2$; $\text{M}' = \text{Ni}, \text{Ru}$) and Bi_2S_3 were prepared by the ammonium sulfide method²⁰: an ammonium sulfide aqueous solution was slowly added to the aqueous solution of metal chlorides at room temperature, which was stirred at room temperature for 1 h and then adjusted to $\text{pH} < 7$ with HCl to obtain 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 ($\text{Ni}_3\text{S}_4, \text{Co}_3\text{S}_4, \text{AlNi}_2\text{S}_4, \text{FeNi}_2\text{S}_4, \text{CoNi}_2\text{S}_4$) were prepared by a pH-controlled precipitation method^{21,22}: thioacetamide 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 12 h, 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., Osaka, Japan; SnS, WS_2 ; Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) were also used as the sensing electrode material.

The products obtained were characterized by X-ray diffraction analysis (XRD: JDX-3500K, JEOL Ltd., Tokyo, Japan) using $\text{CuK}\alpha 1$ radiation, and scanning

electron microscopy (SEM: JSM-6320F, JEOL Ltd.), and so on.

Sensor Devices

Figure 1 shows a schematic diagram of SO_2 sensor devices using the NaDyCON disk and a metal sulfide electrode. A paste prepared with sulfides and turpentine oil was painted onto the surface of the NaDyCON disk, 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 disk 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, that is, SO_2 diluted with nitrogen, by mixing with nitrogen or dry synthetic air ($\text{N}_2 + \text{O}_2$ gas mixture). The sensor response, EMF, was measured with a digital electrometer (Advantest, R8240, Tokyo, Japan) at a total flow rate of $100 \text{ cm}^3/\text{min}$.

Results and Discussion

Sensor Materials and Elements

XRD pattern of the prepared NaDyCON disk sintered at 1000°C revealed that well crystallized and al-

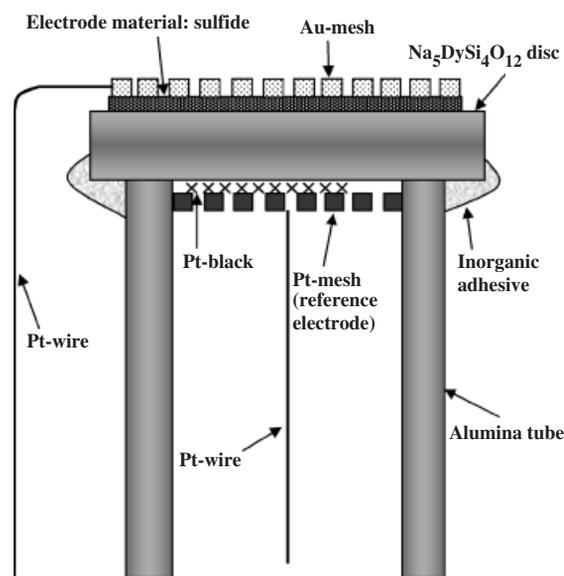


Fig. 1. Schematic diagram of solid electrolyte sulfur dioxide sensor devices using a sulfide-sensing electrode.

most single-phase NaDyCON could be obtained. The densities of the disks 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 disk measured by an AC impedance method with Au electrodes was about $1.0 \times 10^{-1} \text{ S/cm}^1$ at 300°C , which is comparable with that of the $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NASICON) disks.

Figure 2 shows XRD patterns of the three types of sulfides synthesized by the wet-chemical preparation processes. The well-crystallized and almost single-phase metal monosulfide (NiS), metal disulfide (NiS_2), and thiospinel (Ni_3S_4) could be observed. The other metal monosulfides, disulfides, and thiospinels thus prepared showed well-crystallized and almost single-phase sulfides.

SEM image of the sensor device using the NaDyCON disk and the CdS revealed that the electrode formed a porous structure and was tightly fixed on the surface of the NaDyCON disk. The thickness of the CdS layer was about $2 \mu\text{m}$ as shown in Fig. 3. It was also revealed that the NaDyCON disk was relatively dense without any large pores.

SO_x -Sensing Properties

As most of the metal sulfide could be synthesized via wet-chemical routes, the effects of metal sulfides on SO_2 -sensing properties were investigated first. Most of the devices with metal sulfide showed no response to SO_2 at temperatures between 150°C and 250°C . At temperatures of $300\text{--}400^\circ\text{C}$, the devices based on metal sulfide-based elements showed SO_2 responses with different values of the slope and the response time. Table I shows the sensing performance of the SO_2 sensors using various kinds of metal sulfide electrodes, which were stable even in a 2N H_2SO_4 solution at room temperature. For the types of sulfides, metal monosulfides were found to be the most promising materials for a SO_2 sensor, such that CdS-, SnS-, PbS-based elements showed good sensing properties to SO_2 , although NiS-, GeS-based elements showed poor or no SO_2 response. For example, the device attached to an SnS electrode showed good and reversible EMF responses to SO_2 at 400°C . The EMF response was linear to the logarithm of SO_2 concentration ($\log P_{SO_2}$) between 20 and 200 ppm, with the slope of -49 mV/decade at 400°C . The 90% response time to 200 ppm SO_2 was about 7 min at 400°C . A poor response to SO_2 was obtained with the elements using electrodes of metal disulf-

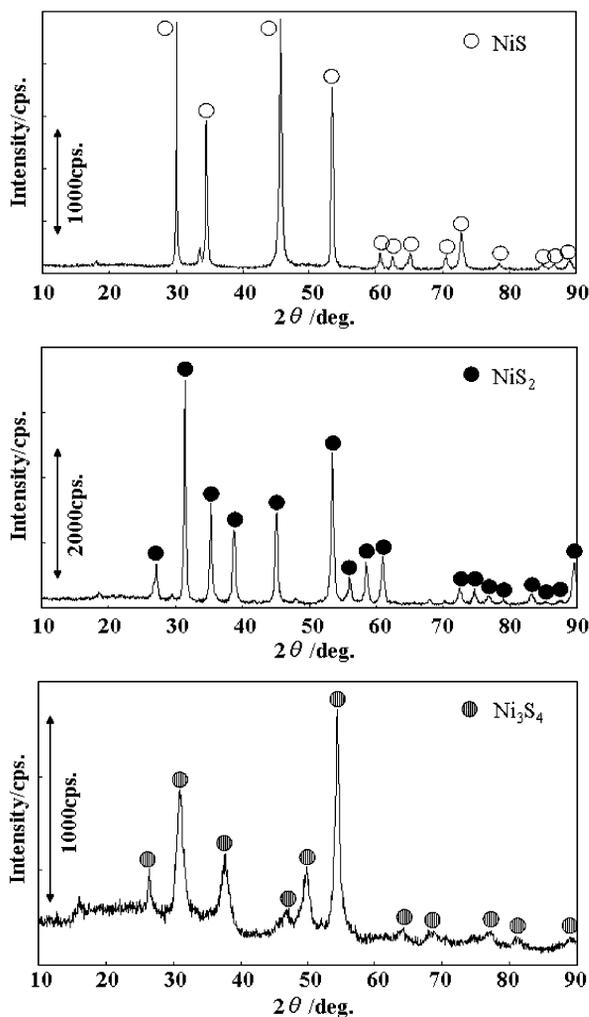


Fig. 2. X-ray diffraction patterns of a monosulfide (NiS), a disulfide (NiS_2), and a thiospinel (Ni_3S_4) synthesized by wet-chemical methods.

ides or thiospinels, such as NiS_2 , MoS_2 , WS_2 , or AlNi_2S_4 , FeNi_2S_4 , and CoNi_2S_4 , at 400°C , while those based on RuS_2 , Bi_2S_3 , and Ni_3S_4 electrodes showed good sensing properties and stability for SO_2 at 400°C , although their response times were as slow as 11–17 min.

In the electrode materials tested, PbS-, CdS-based elements showed a relatively good SO_2 response at 400°C . The partial substitution of metal cation in the transition metal sulfides is expected to occur due to an appearance of anomalous valence of the transition metals, anion defects. This is expected to confer large modification in electrocatalytic activities. Thus, we tried to use the

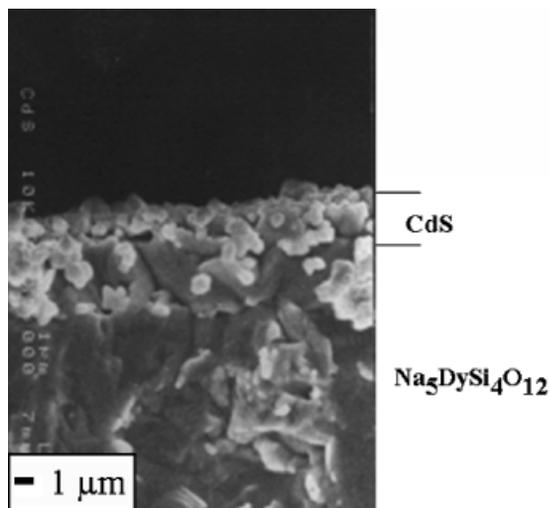


Fig. 3. Scanning electron microscopy image of the cross-section of the sensor device using a $\text{Na}_5\text{DySi}_4\text{O}_{12}$ electrolyte and a CdS electrode.

solid solution type $\text{Pb}_{1-x}\text{M}_x\text{S}$ 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 a $\text{Pb}_{0.8}\text{Cd}_{0.2}\text{S}$ 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 II summarizes the SO_2 -sensing performance for the sensor devices attached to 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; all the sulfides were stable even in the 2 N 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 a 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 led to improvement in the SO_2 -sensing property of the accuracy (slope) by the partial substitution of Ni into PbS at 400°C .

Table III summarizes the SO_2 -sensing performance for the sensor devices attached to 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 $300-400^\circ\text{C}$.

Table I. Sensing Performance to SO_2 of the Device Using Various Types of Metal Sulfides at 400°C

Electrode material	ΔE^* (mV)	Slope (mV/decade)	Response time [†]	Performance of sensor [‡]
NiS	-86	+19	15	Δ
CdS	-405	-94	4	O
GeS	0	0	-	X
SnS	-217	-49	7 [§]	O
PbS	-287	-20	7 [§]	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

* $\Delta E = E_{100 \text{ ppm}} - E_{\text{Air}}$.

[†]90% response time to 100 ppm SO_2 .

[‡]O, excellent; Δ, fair; X, Poor; US, unstable.

[§]90% response time to 200 ppm SO_2 .

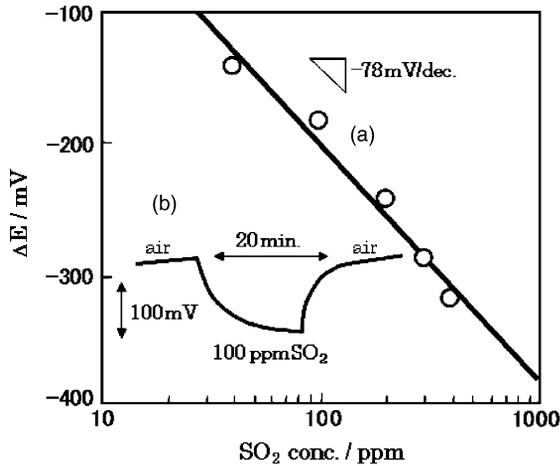


Fig. 4. Sensing performance to sulfur dioxide (SO₂) of the device using Pb_{0.8}Cd_{0.2}S electrode at 400°C. (a) ΔE versus SO₂ concentration. (b) Response transient to 100 ppm SO₂.

The reason for the dependence of the sensor response properties on the electrode material is not yet clear, but it seems to arise 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.

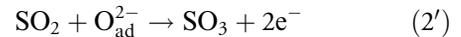
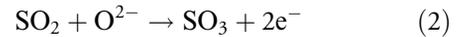
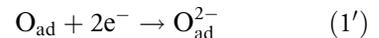
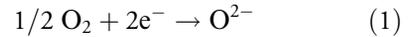
It was further found that the Pb_{0.8}Cd_{0.2}S element gave good selectivity to SO₂ at 400°C. Figure 5 shows the SO₂ selectivity of the device attached to a Pb_{0.8}Cd_{0.2}S electrode at 400°C. The device showed good and EMF responses to SO₂ between 40 and 400 ppm at 400°C. The Pb_{0.8}Cd_{0.2}S-based element hardly responded to O₂, NO₂, and CO₂, although it had a sensitivity to NO. Investigations of close sensitiv-

ity and the effect of humidity, and so on, are now in progress.

Mechanism of Potentiometric Sensing

For most of the sensor devices tested, the slope of the line for ΔE versus log P_{SO₂} was largely dependent on the electrode materials, and the element type. Thus, the sensing mechanism seems to arise not from the conventional Nernst' type but probably the mixed potential one.²⁴

When the sensing electrode is exposed to SO₂ gas including oxygen or adsorbed oxygen, the electrochemical oxidation (1), (1') and electrochemical SO₂ 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 a more accurate value, that is, the slope of ΔE versus log P_{SO₂} should be larger. When we consider cases (I)–(III) in the new Fig. 6(a), the mixed potentials gave a larger slope in the order of (I) > (II) > (III). On the other hand, the value of the slope E versus log I at the small current area means a Tafel slope of the anodic

Table II. Sensing Performance to SO₂ of the Device Using Pb-Based Metal-Sulfide Electrodes at 400°C

Electrode material	ΔE* (mV)	Slope (mV/decade)	Response time [†]	Performance of sensor [‡]
PbS	-287	-20	7	Δ
Pb _{0.9} Cd _{0.1} S	-81	-19	3	○
Pb _{0.8} Cd _{0.2} S	-184	-78	15	○
Pb _{0.9} Ni _{0.1} S	-244	-80	17	○
Pb _{0.8} Ni _{0.2} S	-127	-24	15	Δ
Pb _{0.7} Ni _{0.3} S	-75	-49	15	Δ

* ΔE = E_{100 ppm} - E_{Air}.

[†] 90% response time to 100 ppm SO₂.

[‡] ○, excellent; Δ, fair.

Table III. Sensing Performance to SO₂ of the Device Based on Metal-Sulfide Electrodes at 400°C

Electrode material	AE* (mV)	Slope (mV/decade)	Response time [†]	Performance of sensor [‡]
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

*ΔE = E_{100 ppm} - E_{Air}

[†]90% response time to 100 ppm SO₂.

[‡]O, excellent; Δ, fair; X, poor.

SO₂, sulfur dioxide.

reaction (1), which shows electrocatalytic activity to reaction (1) or (1'). The electrocatalytic activity was 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 this reason, the monosulfide groups of CdS, SnS, and PbS, which have larger Tafel slopes, thus these yielded a large slope in ΔE versus log P_{SO₂} plots. If the electrochemical reaction was different due to the electrocatalytic activities, the case electrochemical reduction (3), (3') and electrochemical oxidation (4), (4') took place, instead of the reactions (1), (1') or (2), (2'), respectively, as shown in Fig. 6(b)

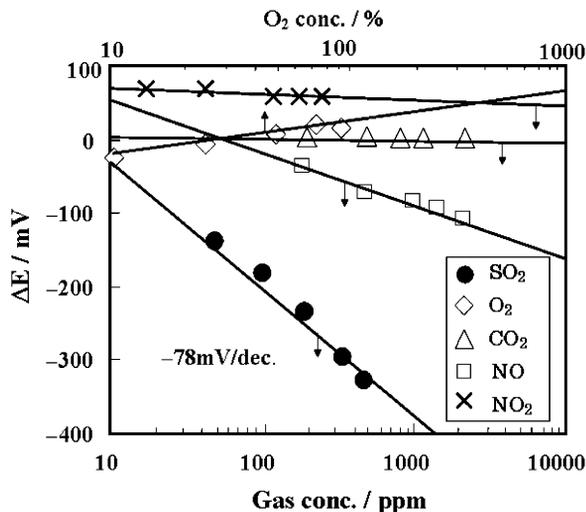
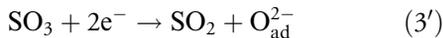
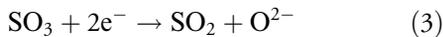
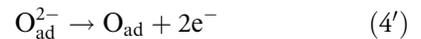
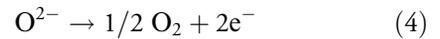


Fig. 5. Selectivity of a sulfur dioxide (SO₂) sensor using a Pb_{0.8}Cd_{0.2}S electrode at 400°C.



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

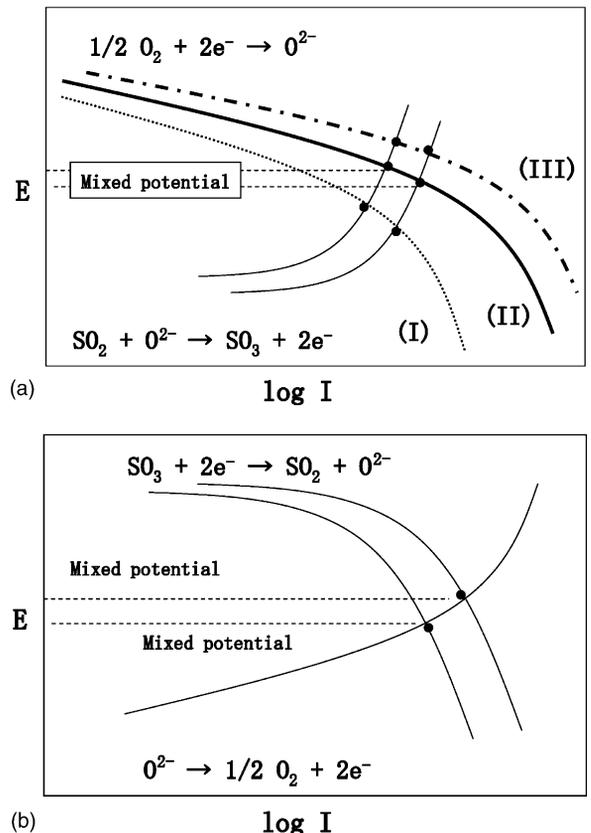


Fig. 6. Schematic polarization curves for cathodic and anodic electrochemical reactions of the sulfide-based electrode.

Conclusion

A solid electrolyte SO_x sensor device using NaDyCON and a metal sulfide-based electrode was found to exhibit good performance for potentiometric sensing to SO₂ at 400°C. The EMF responses were linear to the logarithm of SO₂ concentration between 40 and 400 ppm SO₂. The device using the Pb_{0.8}Cd_{0.2}S and Pb_{0.9}Cd_{0.1}S electrode yielded good SO₂-sensing properties.

Acknowledgments

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