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Preparation of Silver Sulfide-Coated Nickel Sulfide Monodispersed Fine Particles for Use in Solid-State Nickel Ion Selective Electrodes

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A nickel ion-selective electrode (Ni(II)-ISE) was fabricated using monodispersed fine silver sulfide (Ag_2S)-coated nickel sulfide (NiS) particles 5 μm in diameter. The NiS particles were prepared by a method which involved the homogeneous precipitation from a mixed solution of thioacetamide with and without urea and nickel nitrate at 70°C or 90°C over a 3 h period. The surface coating with the NiS particles with an Ag_2S layer was carried out by an ion-exchange method, in which the NiS particles were dispersed into ethanol containing silver nitrate at 0°C for 0.5 h or 2.5 h. The amount of Ag_2S coating the surface of the NiS particles increased with an increase in the time used for the coating reaction. The Ag_2S content in the Ag_2S-coated NiS particles obtained at 2.5 h of the coating reaction was 7.4 wt%, and the thickness of the Ag_2S layer was estimated to be 50 nm. The resulting Ag_2S-coated NiS particles were pressed into a pellet, and the pellet was then sintered at 500°C under an atmosphere of N_2 for 3 h. The Ni(II)-ISE was fabricated using the pellet as the sensing membrane. An Ni(II)-ISE based on a mixture of Ag_2S and NiS particles was also fabricated in a manner similar to that based on the Ag_2S-coated NiS particles for comparison. The Ni(II)-ISE fabricated using the Ag_2S-coated NiS particles (coating time: 2.5 h) showed a near-Nernstitian response to Ni(II) in the concentration range from 10^{-3} to 10^{-1} M. This electrode showed a much better response than the electrode fabricated using the mixture of Ag_2S and NiS particles.

1. Introduction

Recently, monodispersed ultrafine particles, the morphology, chemical composition and crystal structure of which are identical and the size distribution of which is very narrow, have been the subject of much attention for the preparation of nanocomposite materials.(1) Such materials can be packed regularly and closely, and the microstructure of the resulting materials is homogeneous. Ultrafine particles of metals and metal compounds are also promising as sensors for gases. The adsorption and desorption of gases on the ultrafine particles cause morphological changes, rearrangements of the lattice, oscillations and fast oxidation-reduction reactions because of their large specific surface area, soft lattice and many other unique characteristics. Tamaki *et al.* reported a NO_2 gas sensor using fine particles of tungsten oxide as the sensor material.(2) They investigated the effect of particle size on the sensitivity to NO_2 gas species and concluded that sensitivity to NO_2 is primarily determined by the grain size of WO_3. Yanase *et al.* found that a reversible change in the optical absorption spectra of ultrafine silver particles dispersed in a porous silica film occurred due to atmospheric changes in the gases.(3) They concluded that this phenomenon may be due to adsorption of oxygen and desorption of CO, which caused coagulation of the ultrafine particles of Ag.

On the other hand, solid particles of metal sulfide are used for solid-state heavy metal ion-selective electrodes (ISEs). A potentiometric method based on such ISEs has great potential for use as a powerful on-line analytical method for heavy metal ions and is currently of interest in the fields of hydrometallurgy, chemical plating, and other related chemical industrial processes. However, only three heavy metal ISEs for Cd(II), Cu(II) and Pb(II), which are based on mixtures of Ag_2S and the corresponding metal sulfide, have been commercialized to date, although many efforts have been made with respect to the preparation of the heavy metal ISEs.(4–14) Some recent patents have been issued for heavy metal ISEs for Zn(II), Ni(II) and others based on metal sulfides,(15) but these have not yet been commercialized. This may be because reproducibility of the Zn(II) and Ni(II) ISEs is insufficient to permit their commercialization from the viewpoint of performance and fabrication.

The mechanism of response of the heavy metal ISEs based on a sensing membrane which consists of Ag_2S and metal sulfide (MS) can be regarded as the same as an electrode of the third kind.(16) Namely, the ISE basically responds directly to Ag(I) at the surface of the ISE membrane, because the sensing membrane is a solid electrolyte, while Ag(I) carries charges in the membrane. The potential of the electrode can be expressed as follows:

$$E = E^0_{\mathrm{Ag/Ag^+}} + \frac{2.303RT}{F} \log a_{\mathrm{Ag^+}}, \tag{1}$$

where $E^0_{\mathrm{Ag/Ag^+}}$ is the standard potential of the electrode for the Ag/Ag^+ couple, and $a_{\mathrm{Ag^+}}$ is the activity of Ag(I).

The Ag(I) activity at the electrode surface is determined by the following dissolution equilibrium of Ag_2S and MS between the membrane phase and its adjacent solution phase and is expressed by eq. (4):

$$Ag_2S \rightleftarrows 2Ag^+ + S^{2-}, \tag{2}$$

$$MS \rightleftarrows M^{2+} + S^{2-}, \tag{3}$$

$$a_{Ag^+} = \sqrt{\frac{K_{sp,Ag_2S}}{K_{sp,MS}} a_{M^{2+}}}\ , \tag{4}$$

where $K_{sp,MS}$ and K_{sp,Ag_2S} are the solubility products of MS and Ag_2S, respectively, and $a_{M^{2+}}$ is the activity of the metal ion, M(II).

Therefore the potential of the electrode is related to the activity of the metal ion in a sample solution, as follows:

$$E = E^0_{Ag/Ag^+} + \frac{2.303RT}{2F} \log \frac{K_{sp,Ag_2S}}{K_{sp,MS}} + \frac{2.303RT}{2F} \log a_{M^{2+}}. \tag{5}$$

According to the response mechanism described, other heavy metal ISEs for Zn(II) and Ni(II) could be expected to be fabricated using Ag_2S and MS. However, although the preparations of such ISEs have been reported as patents, the ISEs have not yet been commercialized.

The following three conditions need to be satisfied for heavy metal ISEs based on a mixture of metal sulfide and silver sulfide.(16)

1) The solubility product of MS, $K_{sp,MS}$, must be much larger than that of Ag_2S, K_{sp,Ag_2S}.

2) The root of the value of $K_{sp,MS}$ must be sufficiently small compared to the level of M(II) in the sample solution. Otherwise the potential of the ISE is determined by the activity of M(II) produced from the dissolution of MS.

3) The sulfide of the membrane phase should equilibrate rapidly with M(II) in the sample solution for the electrode to have a reasonable response time. Namely, a rapid reaction rate between Ag(I) and M(II) at the surface of the electrode membrane is required.

If an Ni(II)-ISE based on NiS and Ag_2S is fabricated, conditions (1) and (2) are satisfied for the NiS. The solubility product of NiS is reported to be $10^{-24.0}$, which is similar to that of PbS ($10^{-26.6}$) (see Table 1).(17) The rest of the conditions (3) appear to be restricted by the ion-exchange kinetics and mass transfer of ions at the surface of the electrode. Although data on the rate of the ion-exchange between Ag(I) and Ni(II) could not be observed, the order of magnitude of the rate of the ion-exchange reaction may be estimated from the rate constant of complex formation of the metal ions and water exchange. These rate constants of the two reactions have been reported and are listed in Table 2 for several metal ions. As can be seen from Table 2, both the rate constants for complex formation and water-exchange reactions for Ni(II) are smaller by four orders of magnitude than those for Cu(II), Cd(II) and Pb(II). This indicates that Ni(II) is a relatively inert ion and that the ion-exchange reaction between Ag(I) and Ni(II) is expected to be slower than that of the other metal ions. The time constant (half-life time) of the water-exchange reaction is calculated

Table 1
Selectivity coefficients of the Ni(II) ion-selective electrode*.

Divalent ions	Selectivity coefficients: $k_{\mathrm{Ni,M}}^{\mathrm{pot}}$		Solubility Product of MS**
	Theoretical Value***	Observed value	
Ni^{2+}	-	-	$10^{-24.0}$
Cu^{2+}	10^{10}	9.0×10^5	$10^{-34.0}$
Pb^{2+}	398	0.25	$10^{-26.6}$
Co^{2+}	0.79	0.011	$10^{-23.9}$
Zn^{2+}	0.63	3.53	$10^{-23.8}$

*A sensing membrane was prepared using Ag_2S-coated NiS particles at a 2.5 h coating time (electrode 2). ** Taken from ref. (17). ***Calculated from eq. (11).

Table 2
Rate constants of complex formation and water exchange for some metal ions.

Metal ions	Rate constant	
	Complex formation* ($mol^{-1} dm^3 s^{-1}$)	Water exchange (s^{-1})
Cu(II)	3.0×10^9 a)	4.4×10^9 e)
Cd(II)	4.0×10^9 b)	1.1×10^8 **f)
Pb(II)	3.0×10^9 c)	-
Ni(II)	1.9×10^5 d)	3.8×10^4 g)

*Ligand of the complex: Ethylenediaminetetraacetic acid
**Solvent: Methanol

to be on the order of 100 μs for Ni(II), while it is 1–10 ns for Cu(II) and Cd(II) from the data shown in Table 2. If the rate-determining step of the ion-exchange reaction is mass transfer, the time constant is dependent on the diffusion coefficients and diffusion distance as follows:

$$t \approx l^2/D, \qquad (6)$$

where D and l are the diffusion coefficient and diffusion distance, respectively. Since most ionic species in solution are on the order of 10^{-5} cm^2 s^{-1}, the time constant is calculated to be 1 ms and 0.1 μs for diffusion distances of 1 μm and 100 nm, respectively, from eq. (6).

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a) K. Kato: Bull. Chem. Soc. Jpn. **33** (1960) 600.
b) N. Tanaka, R. Tamamushi and M. Kodama: Z. Phys. Chem. (Frankfurt am Main) **14** (1958) 141.
c) T. Takahashi, T. Koiso and N. Tanaka: Nippon Kagaku Zasshi **91** (1970) 236.
d) J. C. Cassatt and R. G. Wilkins: J. Am. Chem. Soc. **90** (1968) 6045.
e) D. H. Powell, L. Helm and A. E. Merbach: J. Chem. Phys. **95** (1991) 9258.
f) S. Yamada and R. E. Verral: J. Phys. Chem. **85** (1981) 3145.
g) Y. Ducomun, K. E. Newnan and A. E. Merbach: Inorg. Chem. **19** (1980) 3696.

This time constant for molecular diffusion changes significantly with the diffusion distance. In this case, the diffusion distance can be regarded as the distance between areas of Ag_2S and MS on the surface of the membrane. Therefore, condition (3) appears to be dependent on the particle size and homogeneity of distribution of NiS and Ag_2S particles. Figure 1 shows schematic models of an electrode membrane. If the particles of NiS and Ag_2S, which are in the size range of several hundred micrometers, are distributed nonuniformly as shown in Fig. 1(a), the ion-exchange between Ni(II) and Ag(I), which is generated from the dissolution from NiS and Ag_2S, cannot be equilibrated rapidly due to the long distance for molecular diffusion. On the other hand, if monodispersed fine particles of NiS and Ag_2S in the nanometer level range or monodispersed Ag_2S-coated NiS fine particles with a coating layer at the nanometer level are distributed uniformly as shown in Figs. 1(b) and (c), the diffusion distance of Ni(II) and Ag(I) becomes shorter by two or three orders of magnitude. Therefore, the ion-exchange reaction between Ni(II) and Ag(I) is estimated to be fast and the ion-exchange equilibrium will be rapidly established. Thus the Ni(II)-ISE based on the membrane shown in Figs. 1 (b) and (c) can satisfy condition (3), and a good response can be expected by overcoming the slow kinetic properties of Ni(II).

Kim *et al.* have recently reported an interesting method for preparation of monodispersed ultrafine ZnS particles of nanometer-scale size by a homogeneous precipitation method(18) and of Ag_2S-coated ZnS particles with a nanometer-scale coating layer by an ion-exchange method.(19)

Based on the above expectation, in this study we attempted to fabricate an Ni(II)-ISE by preparing monodispersed ultrafine particles of NiS and Ag_2S and Ag_2S-coated NiS particles according to the method reported by Kim *et al.* The performance of the fabricated Ni(II)-ISE was also evaluated and is described herein.

2. Materials and Methods

2.1 *Reagents and apparatus*

Thioacetamide (TAA) and $Ni(NO_3)_2$ were purchased from Wako Pure Chemical Industries Ltd. The compounds $AgNO_3$, HNO_3 (60%) and NaOH were purchased from

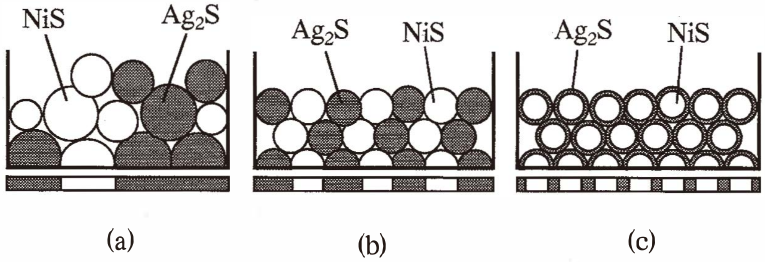

Fig. 1. Schematic models of electrode membranes. (a) large and rough Ag_2S and NiS particles, (b) monodispersed fine Ag_2S and NiS particles and (c) monodispersed fine Ag_2S-coated NiS particles.

Kishida Chemical Co., Ltd. The Ag_2S and NiS (99.999 %) were purchased from Wako Pure Chemical Industries Ltd. and Cerac Inc., respectively. All other chemicals were of analytical reagent grade except for those specified.

The crystal phases of synthesized products were examined using an X-ray diffractometer (XRD; XD-D1, Shimadzu Co., Ltd.). The morphology of synthesized products was observed by scanning electron microscopy (SEM; S-900, Hitachi Co., Ltd.). Distributions of elemental nickel and silver in the Ag_2S-coated NiS particles were observed with an energy-dispersive X-ray microanalyzer (EDX; S-2300, Hitachi Co., Ltd.). Potentiometric measurements of the fabricated Ni(II)-ISE were carried out at room temperature using a potentiometer (IOL-50, Denki Kagaku Keiki Co., Ltd.) with a double junction type Ag/AgCl reference electrode (4083, Denki Kagaku Keiki Co., Ltd.).

2.2 *Synthesis of silver sulfide and nickel sulfide particles*

Fine particles of the metal sulfides (MS) for the sensing membrane of the electrode were prepared from the nitrate salts of the corresponding metal and TAA as follows. Solutions of 0.4 M $AgNO_3$ (250 ml) and 0.1 M $Ni(NO_3)_2$ (250 ml) solutions were prepared by dissolving each of the salts in distilled water. The pH of the solutions was adjusted to 1.52 (±0.01) with HNO_3. After filtration through a cellulose nitrate membrane filter (pore size: 0.1 μm), the solution was heated in a 500 ml flask at 70 or 90°C for 15 min in a thermostated water bath. A specified amount of TAA was then added into the solution to initiate the precipitation reaction. For the synthesis of the NiS particles, TAA with and without urea was added to the $Ni(NO_3)_2$ solution. TAA is hydrolyzed in an acidic solution, and hydrogen sulfide is liberated, as shown in eq. (7). The fraction of sulfide ion, S^{2-}, which can react with metal ion to produce metal sulfide is dependent on the pH of the solution according to the equilibria in eqs. (8) and (9). Urea was added to increase the fraction of sulfide ion. Metal sulfide particles were precipitated over time as reaction (7) proceeded.

$$CH_3C(S)NH_2 + H_2O \rightarrow CH_3C(O)NH_2 + H_2S, \tag{7}$$

$$H_2S \rightleftarrows HS^- + H^+, \tag{8}$$

$$HS^- \rightleftarrows S^{2-} + H^+. \tag{9}$$

After 1 or 3 h, the thermostated water bath was removed and the flask was cooled. The products were repeatedly washed with distilled water using ultrasonic agitation and centrifugation, and, finally, washed with ethanol. The products were dried at 100°C under reduced pressure for 1 h. The reaction conditions and concentration of reagents are shown in Table 3.

2.3 *Preparation of Ag_2S-coated NiS particles*

In the case of the preparation of Ag_2S-coated NiS particles, 0.401 g (0.0044 mol) of the NiS particles, which were synthesized using TAA and urea (sample C in Table 3), were suspended in 200 ml of ethanol in a 200 ml Erlenmeyer flask. Ultrasonic agitation was then applied for 20 min to disperse the NiS particles. The flask was placed in an ice bath at 0°C for 15 min, and 0.375 g (0.0022 mol) of $AgNO_3$ was then added to the flask in the form of

Table 3
Reaction conditions, yields and crystal phase of products.

Sample No.	Metal Nitrate	Concentration (M) $M(NO_3)_n$	TAA	Urea	Time (h)	Temperature (°C)	Yield (%)	Crystal phase
A	$AgNO_3$	0.04	0.4	0	1	70	93	β-Ag_2S
B	$Ni(NO_3)_2$	0.1	0.8	0	3	70	3.2	amorphous
C	$Ni(NO_3)_2$	0.1	0.8	0.6	3	90	97	$NiS_{1.03}$

a solid. The solution was stirred by a magnetic stirrer for 0.5 h or 2.5 h. During stirring, an ion-exchange reaction occurred between Ag(I) dissolved in the ethanol and Ni(II) on the surface of the NiS particles according to eq. (10), and thus the surface of the NiS particles was coated with Ag_2S,

$$NiS + 2Ag(I) \rightarrow Ag_2S + Ni(II)\,. \tag{10}$$

After the coating reaction, the products were washed with distilled water until Ag(I) was no longer detected in the wash water and were dried at 100°C under reduced pressure. The weight percent of Ag_2S in the Ag_2S-coated NiS particles was calculated from the amount of Ag(I) remaining in the solution by potentiometric titration with a 0.1 M NaI standard solution.

2.4 *Preparation of sensing membranes and fabrication of electrodes*

The Ag_2S-coated NiS particles (0.3 g) were pressed into a 10 mm diameter pellet about 2 mm thick by uniaxial pressing at 2 t/cm^2 for 1 min. For comparison, the mixture of the synthesized or commercial NiS and Ag_2S particles at the given ratio was also pressed into a pellet. The resulting pellet was sintered at 500°C under nitrogen atmosphere for 3 h. The temperature of the electric furnace was increased at a rate of 10°C/min until it reached 500°C. A silver wire was attached using a silver paste adhesive on one side of the pellet. The resulting pellet was used as the sensing membrane of the electrode. The electrode was fabricated by fixing the pellet on the end of an acrylic pipe 10 mm in diameter using sealant adhesive. The surface of the electrode was polished to a mirror plane with diamond polishing compound (1/4 μm, Buehler) paste on a filter paper after polishing with emery paper (No. 1000).

2.5 *Evaluation of the performance of the electrode*

The potential of the fabricated electrode was measured by immersing the electrode with a reference electrode into a series of standard solutions of $Ni(NO_3)_2$ in the concentration range from 10^{-4} to 10^{-1} M. The ionic strength of the sample solution was adjusted by adding 0.1 M KNO_3 to the solution. The solution was stirred by a magnetic stirrer at about 200 rev min^{-1} during the measurement. The effect of pH on the electrode potential was examined by measuring the potential of the sample solution at different pHs. The pH of the sample solution was changed by the addition of small volumes of HNO_3 or NaOH solutions. The selectivity coefficients of the electrode for Ni(II) against several divalent ions, $k^{\mathrm{pot}}_{\mathrm{Ni,M}}$, were determined by the separate solution method.

3. Results and Discussion

3.1 *Morphology of synthesized Ag_2S and NiS particles*

Table 3 shows the conditions of preparation and crystal phases of the products determined by XRD. The crystal phase of the Ag_2S particles obtained in this study was monoclinic β-Ag_2S, which is the stable form at low temperature (sample A). No diffraction peak was observed for the NiS particles which were synthesized using only TAA (sample B). It was found by EDX analysis that the NiS particles contained nickel and sulfur at nearly a 1:1 molar ratio. These observations indicate that the NiS particles obtained using only TAA might be an amorphous α-NiS phase. The NiS particles synthesized using TAA and urea (sample C) were identified as hexagonal $NiS_{1.03}$ from the XRD pattern. This hexagonal $NiS_{1.03}$ is called the β-NiS phase and is the most stable form of the crystal phases of NiS. The SEM micrographs of the Ag_2S and NiS particles synthesized in this work are shown in Fig. 2, along with the commercial samples. The particle sizes of the commercial Ag_2S and NiS particles are about 50–100 μm and about 10–100 μm, respectively. These particles are of an irregular shape, rather than spherical, and are aggregated. On the other hand, the size of the synthesized Ag_2S particles (sample A) is about 1 μm, and much smaller than that of the commercial Ag_2S particles, as can be seen from Fig. 2. The size of the NiS particles synthesized using only the TAA (sample B) was about 500 nm, and that of the NiS particles synthesized using TAA and urea (sample C) was about 5 μm. These results indicate that the sizes of Ag_2S and NiS particles synthesized by homogeneous precipitation are very small and that the size distribution is uniform. This large difference in the morphology and particle size between α-NiS and β-NiS particles may be the result of the additional use of urea for the synthesis of the NiS particles and the high reaction temperature. Urea is hydrolyzed to ammonia and carbon dioxide, similarly to TAA, in the synthesis of the NiS particles. The product of the hydrolysis reaction, ammonia, increases the pH of the solution and, as a result, the fraction of S^{2-} increases. The increase in the fraction of S^{2-} may lead to an accelerated crystal growth of the NiS particles and may generate the difference in the crystal phase, namely, the α-form and β-form, and the morphology. Indeed, a high reaction temperature promotes the hydrolysis of TAA and urea, so that the yield of the β-NiS particles (97 %) is significantly larger than that of the α-NiS particles (3.2 %), shown in Table 3. Grau *et al.* reported that when the reaction temperature is 70°C, a direct reaction of Ni(II) with TAA without hydrolysis to generate S^{2-} is dominant and that the product is amorphous NiS.(20, 21) They also reported that when the reacting temperature is 90°C, the hydrolysis reaction of TAA is fast and the main product is $NiS_{1.03}$.

3.2 *Morphology of Ag_2S-coated NiS particles*

The SEM micrographs of Ag_2S-coated NiS particles obtained using the synthesized β-NiS particles and their raw NiS particles are shown in Fig. 3. As shown in Fig. 3(a), the raw

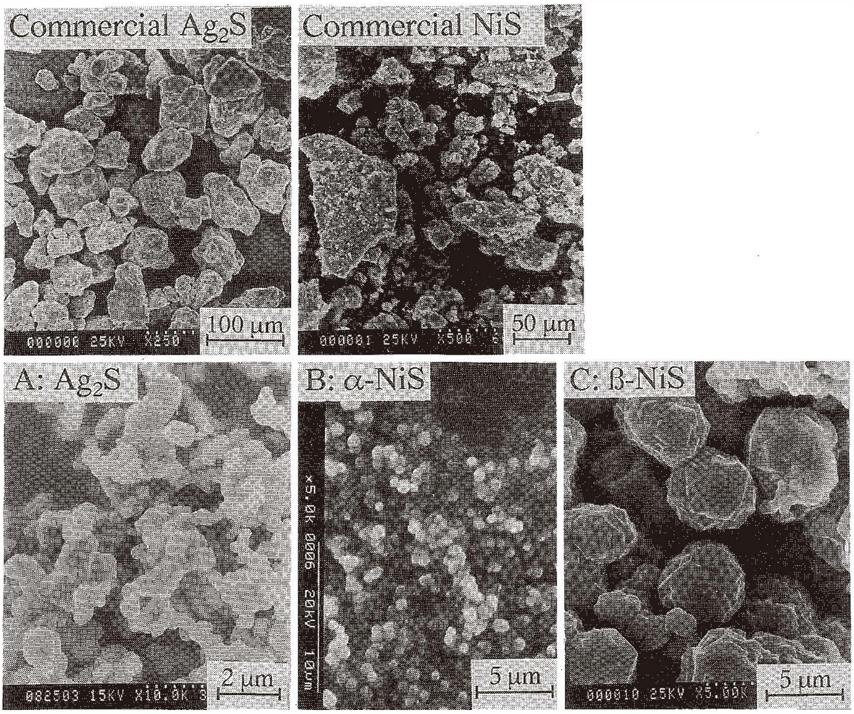

Fig. 2. SEM micrographs of commercial and synthesized metal sulfide particles. Reaction conditions are from Table 2.

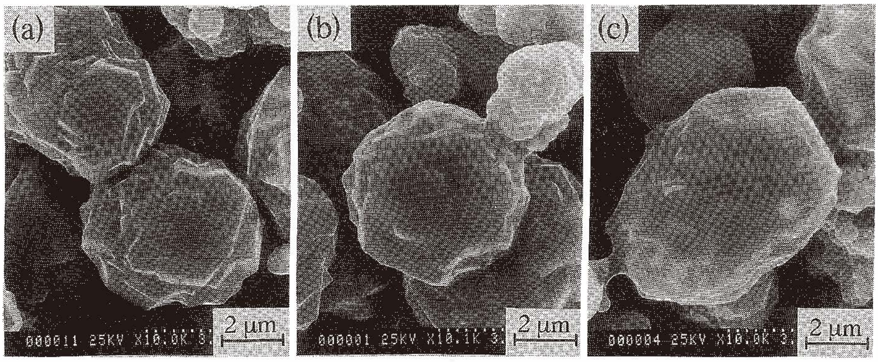

Fig. 3. SEM micrographs of Ag_2S-coated NiS particles. (a) raw NiS particles, (b) Ag_2S-coated NiS particles (coating time 0.5 h) and (c) Ag_2S-coated NiS particles (coating time 2.5 h). Conditions of the coating reaction: amount of NiS particles: 0.0044 mol; amount of $AgNO_3$: 0.0022 mol; reaction temperature: 0°C; solvent and volume: ethanol and 100 ml.

NiS particles are nearly spherical and uniform with a particle size of about 5 μm, but are somewhat angular. Figures 3(b) and (c) show the SEM micrographs of the Ag_2S-coated NiS particles obtained at different coating times. When the coating time was 0.5 h, the angularity of the particles was not very marked. When the coating time was 2.5 h, the surface of the NiS particles appeared to be smooth and coated with a thin layer of Ag_2S. The XRD patterns of the raw NiS particles and the Ag_2S-coated NiS particles prepared at different coating times are shown in Fig. 4. When the coating time was 0.5 h, the XRD pattern of the Ag_2S-coated NiS particles was nearly the same as that of the raw NiS particles. When the coating time was 2.5 h, a new peak was observed at 37° in the pattern which was identified as the β-Ag_2S phase. The appearance of this peak indicates that the NiS particles are coated with the Ag_2S layer. Unfortunately, silver was not identified by EDX analysis in the element distribution of the Ag_2S-coated NiS particles. This may be because the amount of Ag_2S coated on the NiS particles is very small and is below the detection limit of the EDX apparatus. However, the amount of Ag_2S coated on the NiS particles could be estimated by measuring the $AgNO_3$ which remained after the coating

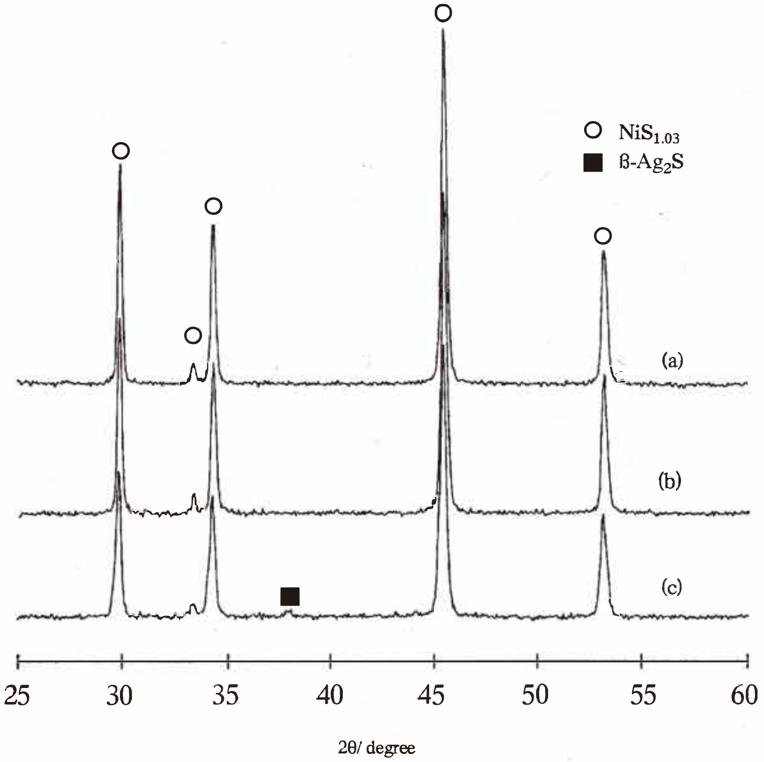

Fig. 4. X-ray diffraction patterns of raw NiS and Ag_2S-coated NiS particles. (a) raw NiS particles, (b) Ag_2S-coated NiS particles (coating time 0.5 h), and (c) Ag_2S-coated NiS particles (coating time 2.5 h).

reaction by potentiometric titration. The amounts of $AgNO_3$ consumed by the coating reaction were 1.0×10^{-4} and 2.5×10^{-4} mol for the case of reaction times of 0.5 h and 2.5 h, respectively. Therefore, the NiS particles are calculated to be coated with an Ag_2S layer of 3.0 and 7.4 wt% for the case of reaction times of 0.5 h and 2.5 h, respectively. The thicknesses of the Ag_2S layers on the NiS particles are also calculated to be 25 nm and 50 nm for the two cases, respectively, assuming that the raw NiS particles are spheres 5 μm in diameter.

3.3 *Effects of particle size and crystal structure of metal sulfide on the potential response of the electrode*

Figure 5 shows the potential response of the electrodes which were fabricated from the mixture of synthesized Ag_2S particles and α-NiS particles or the commercial NiS particles at various weight ratios. In the case of the electrode which was fabricated using the commercial NiS particles, the electrode does not show a Nernstian response to Ni(II), as shown in Fig. 5(1). Interestingly, at concentrations lower than 10^{-3} M, the electrode showed an anionic response. The reason for the non-Nernstian response of the electrode is not clear at this stage of the investigation, but the large size of the commercial NiS particles and the nonuniform mixture of NiS and Ag_2S particles may be one of the reasons, as

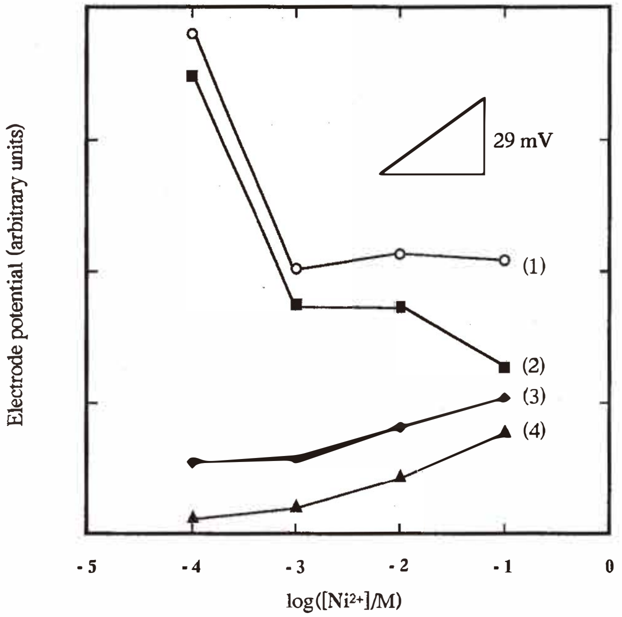

Fig. 5. Response of electrodes fabricated using a mixture of synthesized Ag_2S particles and synthesized NiS (α-type) or commercial NiS (γ-type) particles. Type and weight percent of NiS particles: (1) commercial NiS(50 wt%); (2) synthesized α-NiS(33 wt%); (3) synthesized α-NiS(50 wt%); and (4) synthesized α-NiS(67 wt%).

described in the introduction. In the case of the electrode which was fabricated using the synthesized α-NiS particles, when the weight ratio of the NiS particles was greater than 50 wt%, the electrodes showed a reasonable cationic response to Ni(II) in the concentration range from 10^{-3} to 10^{-1} M. This improvement of the potential response with an increase in the weight ratio of the NiS particles may be due to the exposed part of the NiS area in the surface of the electrode becoming larger with an increase in the weight ratio of the NiS particles.

Figure 6 shows the potential response of the electrodes which were fabricated using the mixture of synthesized Ag_2S and β-NiS particles instead of α-NiS at various weight ratios. All the electrodes show a cationic response to Ni(II), although there are differences in the degree of response depending on the weight ratio of the NiS particles, as shown in Fig. 6. The response of the electrode which was fabricated using the β-NiS particles was somewhat better than that fabricated using the α-NiS particles. As described in the previous section, the α-NiS particles synthesized in this work were much smaller than the β-NiS particles. This suggests that the α-NiS particles may provide advantageous properties for the potential of the electrodes with respect to the homogeneity of the mixture with the Ag_2S particles. However, the potential response of the electrode fabricated by the β-NiS particles was, in fact, better than that by the α-NiS particles. Since α-NiS particles are amorphous, the pellet prepared by pressing the particles could not be packed very densely,

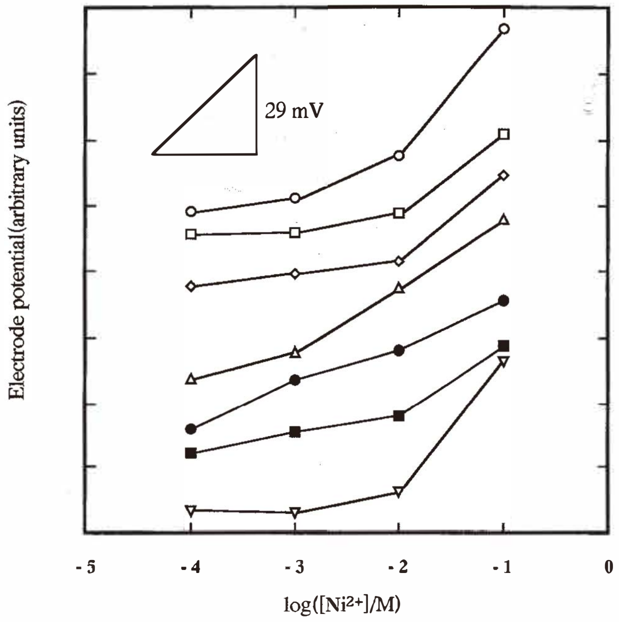

Fig. 6. Response of the electrodes fabricated using a mixture of synthesized Ag_2S and β-NiS particles at different weight ratios. Weight percent of β-NiS particles, ○:25 wt%; □: 33 wt%; ◇: 50 wt%; △: 67 wt%; ●: 75 wt%; ■: 80 wt%; ▽: 91 wt%.

even when pressures higher than 2 t/cm^2 were applied. The first reason for the poor response of the electrode prepared from the α–NiS may be due to lower density of the pellet. The second reason may be that the α-NiS particles contain sulfur as an impurity, even when the particles are extensively washed with water and ethanol. The presence of a sulfur impurity was confirmed by the evolution of vapor containing sulfur in our experiment when the pellet was sintered. Grau *et al.* reported that the α-NiS particles prepared by TAA contained significant amounts of carbon, excess sulfur and hydrogen by chemical analysis and thermogravimetric measurments.(20,21) A third reason may be that the solubility product of α-NiS, which is reported to be $10^{-18.5}$, is larger by five orders of magnitude than that of β-NiS, which is reported to be $10^{-24.0}$,(17) because the value of $K_{sp,MS}$ must be sufficiently smaller for the heavy metal ISE to show a good response as described in the introduction.

3.4 *Potential response of electrode fabricated using Ag_2S-coated NiS particles*

Two electrodes were fabricated using the two different Ag_2S-coated NiS particles with respect to the coating time. The coating time for the Ag_2S-coated NiS particles used for one electrode was 0.5 h and that for the other was 2.5 h. The former electrode is designated electrode 1, and the latter, electrode 2. The potential response of the two electrodes was examined for a series of standard solutions of Ni(II). The results are shown in Fig. 7. As

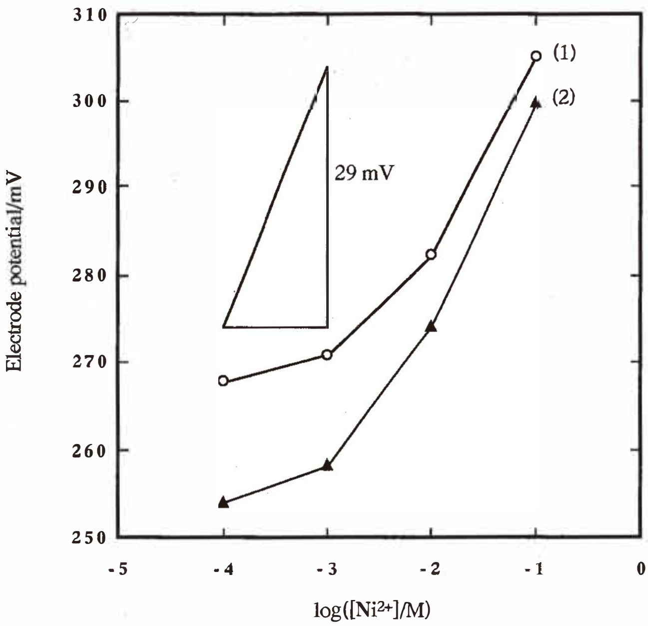

Fig. 7. Potential response of the electrodes fabricated using Ag_2S-coated NiS particles. Electrode (1): coating time 0.5 h, and electrode (2): coating time 2.5 h.

can be seen from Fig. 7, both electrodes show a near Nernstian response in the concentration range from 10^{-3} to 10^{-1} M. In particular, the slopes of the calibration curves of electrode 1 and 2 in the concentration range between 10^{-2} and 10^{-1} M are 22.8 and 25.5 mV/decade, respectively, while the slope for the electrode fabricated using the mixture of NiS and Ag_2S particles was 19.9 mV/decade in the concentration range between 10^{-3} and 10^{-1} M, as described in the previous section. The superior response of the electrodes which were fabricated using the Ag_2S-coated NiS particles compared to those fabricated using the mixture of NiS and Ag_2S particles may be due to the Ag_2S layer being as thin as 50 nm at the surface of the former electrode. Electrode 2 is superior to electrode 1 with respect to the slope sensitivity and to the lower limit of detection, as can be seen from Fig. 7. The poorer response of electrode 1 may be due to the smaller amount of Ag_2S coated on the surface of the NiS particles used for electrode 1 so that the sensing membrane does not contain sufficient Ag_2S to provide Ag(I) conducting pathways through the membrane. Indeed, the potential of electrode 1 was sluggish and subject to electronic noise, while the potential of electrode 2 was stable and its potential drift was less than 0.2 mV/h for 10^{-1} M Ni(II) solution. The potential stability of electrode 2 was as good as that of the commercial Pb(II)-ISE, 0.7 mV/h, which was measured in this work. The electrode which was fabricated using the Ag_2S-coated NiS particles showed a good response, as predicted in the introduction. The evaluation of the performance of electrode 2 follows.

3.5 *Effect of pH on the potential response of the electrode and the selectivity*

The effect of pH on the potential response of electrode 2 was examined, since the potential of the Ni(II)-ISE is expected to be affected by pH due to hydrolysis of the Ni(II) solution and formation of HS^- or H_2S at the surface of the electrode. As can be seen from Fig. 8, the increasing tendency of the potential is observed in the pH region below pH 4, and a decrease in potential is observed in the region of pH higher than about pH 8. The potential increase at a lower pH may be due to the formation of HS^- or H_2S at the surface of the electrode, which arises from the protonation of sulfide ion generated by the dissolution of the equilibrium amount of Ag_2S or NiS from the sensing membrane of the electrode. This phenomenon is often observed for the solid-state ISEs based on the metal sulfides, such as Cu(II)-, Cd(II)- and Pb(II)-ISE.(16) The potential decrease at the lower pH is due to the hydrolysis of Ni(II) in the sample solution, which causes a decrease in the activity of Ni(II). As a result, this electrode can be used in the pH region from pH 5 to pH 8.

Values for the selectivity coefficient of electrode 2 for Ni(II) against several metal ions, $k^{\mathrm{pot}}_{\mathrm{Ni,M}}$, were obtained by the separate solution method and are listed in Table 1. The selectivity coefficient of the heavy metal ISE based on the metal sulfide is related to the values of solubility product of the metal sulfide, expressed by eq. (11)(16)

$$k^{\mathrm{pot}}_{\mathrm{Ni,M}} = \frac{K_{\mathrm{sp,NiS}}}{K_{\mathrm{sp,MS}}}, \tag{11}$$

where $K_{\mathrm{sp,NiS}}$ and $K_{\mathrm{sp,MS}}$ were solubility products of NiS and the sulfide of the objective

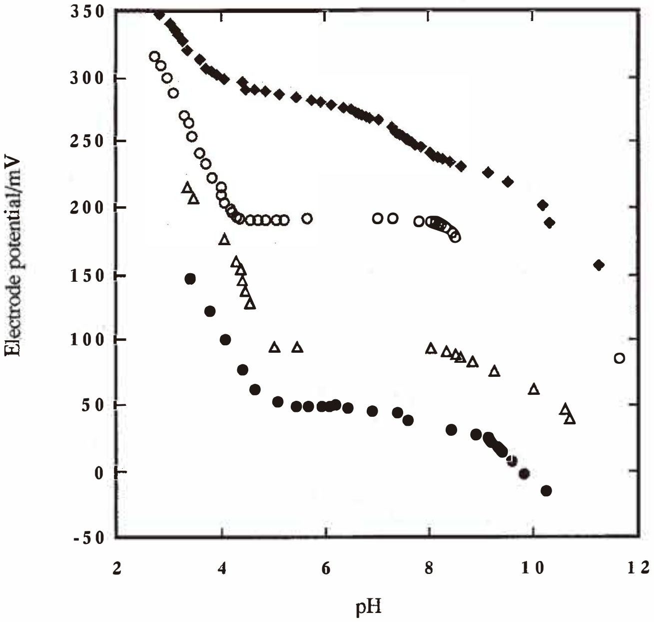

Fig. 8. Effect of pH on the potential of the electrodes. A sensing membrane was prepared using Ag_2S-coated NiS particles at a coating time of 2.5 h (electrode 2). Concentration of Ni^{2+}, ◆: 10^{-1} M; ○: 10^{-2} M; △: 10^{-3} M; ●: 10^{-4} M.

metal ion, respectively. The theoretical selectivity coefficient as calculated from eq. (11) and the solubility product of the metal sulfides reported are also listed in Table 1. The observed selectivity coefficients against Co(II) and Pb(II) are somewhat smaller than the theoretical values, as can be seen from Table 1. In particular, the observed selectivity coefficient against Cu(II) is smaller than the theoretical value by four or five orders of magnitude. This may be due to the formation of CuS on the surface of the electrode as a result of the ion exchange of the Cu(II) in the solution with the Ni(II) on the NiS particles during the potential measurement for the Cu(II) solution, because the solubility product of CuS is much smaller than that of NiS. Once the surface of the sensing membrane is covered with the CuS, the Ni(II)-ISE is converted to a Cu(II)-ISE. As a result, the interference from Cu(II) is apparently smaller than that expected from the solubility product values. The difference in the selectivity coefficient from the theoretical value has been pointed out by Hulanicki and Lewenstam(22) based on the mechanism of response of the electrode, which was described in the introduction. Since the CuS layer which formed on the electrode surface can be removed easily by polishing the electrode on a filter paper, the response of the electrode to Ni(II) was reproducible after the measurement of the selectivity coefficient for Cu(II).

4. Conclusions

We conclude that condition (3) described in the introduction was not satisfied for an Ni(II)-ISE based on NiS and Ag_2S because the ion-exchange reaction between Ag(I) and Ni(II) at the surface of the electrode appeared to be slow due to the inert nature of Ni(II) compared with Cu(II), Pb(II) and Cd(II). Since the rate-determining step of the ion-exchange reaction is thought to be a mass transfer step, if the diffusion distance of Ag(I) and Ni(II) could be shortened, the ion-exchange reaction would be expected to proceed rapidly.

To shorten the diffusion distance, two approaches were attempted, one involving the preparation of fine particles of NiS and Ag_2S and the other the preparation of Ag_2S-coated NiS particles. An Ni(II)-ISE was fabricated using a mixture of monodispersed ultrafine particles of NiS and Ag_2S, which were prepared by homogeneous precipitation from a mixed solution of thioacetamide with and without urea and nickel nitrate to realize model (b) as shown in Fig. 1. However, the response of the electrode was not as good as we expected. This may be due to the size of the NiS particles prepared in this work being 5 μm in diameter, which was considerably larger than the nanometer level that we expected from the results reported by Kim *et al.* The larger particle size of the NiS particles is due to the crystal growth of NiS being faster than that of ZnS. On the other hand, an Ni(II)-ISE was fabricated using the Ag_2S-coated NiS particles to realize model (c) in Fig. 1. The detection limit of the electrode was 10^{-3} M, an insufficient performance compared with the commercial ISEs, but this electrode showed a near-Nernstian response. By controlling the crystal growth of the NiS particles, many fine sulfide particles could be used to prepare an electrode with sufficient performance to achieve models (b) and (c).

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References

1 A. Kato and H. Arai, CHO-BIRYUSHI (Ultrafine particles) (in Japanese) (Asakura Shoten, Tokyo, 1993) Chapt. 1.
2 J. Tamaki, Z. Zhang, K. Fujimori, M. Akiyama, T. Harada, N. Miura and N. Yamazoe: J. Electrochem. Soc. **141** (1994) 2207.
3 A. Yanase, H. Komiyama and K. Tanaka: Jpn. J. Appl. Phys. **27** No. 2 (1988) L164.
4 M. Koebel: Anal. Chem. **46** (1974) 1559.
5 K. Ito, N. Matsuda, S. Ikeda and G. Nakagawa: Denki Kagaku **48** (1980) 16.
6 S. Ikeda, N. Matsuda, G. Nakagawa and K. Ito: Denki Kagaku **47** (1979) 281.
7 N. Matsuda, G. Nakagawa, S. Ikeda and K. Ito: Denki Kagaku **48** (1980) 199.
8 G. O. Neto, S. H. P. Serrano and E. F. A. Neves: Anal. Lett. **20** (1987) 1363.
9 B. Hoyer: Talanta **38** (1991) 115.
10 R. Demarco: Marine Chem. **55** (1996) 389.

11 Y. Tani, M. Soma, E. G. Harsanyi and Y. Umezawa: Anal. Chim. Acta **395** (1999) 53.

12 S. Sakura and R. Virtanen: Bull. Chem. Soc. Jpn. **54** (1981) 1360.

13 K. Uosaki, Y. Shigematsu, H. Kita and Y. Umezawa: Anal. Chem. **61** (1989) 1980.

14 S. Ito, Y. Asano and H. Wada: Talanta **44** (1997) 697.

15 K. Higashiyama: Japanese patent bulletin S52-41679 (1977).

16 R. E. Durst: Ion-Selective Electrodes (National Bureau Standards Special Publication **314** Washington, 1969) Chapt. 2.

17 A. Ringbom: Complexation in Analytical Chemistry (John Wiley and Sons Inc., New York, 1963).

18 Y. D. Kim, T. Yoneima, S. Nagashima and A. Kato: J. Chem. Soc. Japan **1995** (1995)707.

19 Y. D. Kim, S. Ishizaki and A. Kato: J. Mater. Sci. Lett. **15** (1996) 943.

20 J. Grau and M. Akinc: J. Am. Ceram. Soc. **79** (1996) 1073.

21 J. Grau and M. Akinc: J. Am. Ceram. Soc. **80** (1997) 941.

22 A. Hulanicki and A. Lewenstam: Talanta **23** (1976) 661.