Cadmium and Silver Sulfide-impregnated Silicone Rubber Membranes as Selective Electrodes for Cadmium Ions

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Silicone rubber membranes impregnated with mixtures of cadmium sulfide and silver sulfide were developed as selective electrodes for cadmium ions in a solution. Both co-precipitated and sintered mixtures could be used as the active materials for the electrode membrane, but here the membrane which contained a mixture in which cadmium sulfide had been added to silver sulfide after they had been precipitated individually did not show the satisfactory response characteristics. The Nernstian slope was obtained in the activity range from 10^{-1} to 10^{-5} M Cd^{2+}, while the analytical range was from 10^{-1} to 10^{-6} M. These potentials did not change at pH values from 2.5 to 7.5. Among common ions, silver, copper(II), mercury(II), iron(III), sulfide, and iodide ions interfered seriously. About 10—100 times as many lead and bromide ions and more than 1000 times as many alkali metals, alkaline earth metals, zinc, aluminum, nickel, manganese(II), cobalt, nitrate, and perchlorate ions were tolerated in coexistence with cadmium ions.

Many attempts have recently been made to obtain the precipitate-impregnated membranes as selective electrodes.[1] Pungor[2] developed silver salt-impregnated silicone rubber membrane electrodes for chloride, bromide, iodide, sulfide, and silver ions.

As for ion-selective electrodes for cations other than silver ions, various kinds of precipitate-impregnated membranes were made. These membrane electrodes, however, proved unsatisfactory for potentiometric measurements, either because they did not give the desired response or because they had no selectivity toward particular ions in a solution.

Copper(I) sulfide-impregnated silicone rubber membrane electrodes have been developed for copper(II) ions in our laboratory.[3] The internal electrode and internal solution have been eliminated by attaching the membrane to the surface of a metal directly. Lead sulfide-impregnated silicone rubber membrane electrodes for lead ions have also been described in a previous paper,[4] in which an investigation of the soaking effect of the membrane before the measurement has been presented.

On the other hand, a cadmium ion-selective compressed membrane electrode, the membrane of which comprised an intimate mixture of silver sulfide and cadmium sulfide, has been developed by Frant and Ross.[1] Subsequently, a cadmium ion-selective ceramic membrane electrode has been prepared by applying a hot-pressing method; this membrane contains cadmium sulfide, silver sulfide, and copper(I) sulfide.[5]

The present paper will describe the development of selective electrodes for cadmium ions using cadmium and silver sulfide-impregnated silicone rubber membranes, which have the same construction as has been described in the previous papers. It will also discuss the incorporation effect of silver sulfide.

Experimental

Apparatus and Reagents. An Orion Model 801 digital pH/mV meter was used to make the potentiometric measurements. A Horiba Seisakusho 2530-05T saturated calomel electrode was used as the reference electrode. The silicone rubber was obtained from the Shin-Etsu Chemical Co., and all the reagents were Nakarai Chemical reagent-grade materials and were used without further purification.

Preparation of Cadmium and Silver Sulfide-impregnated Silicone Rubber Membrane Electrodes. The preparation of the active materials can be divided roughly into the following two methods; the co-precipitation method, which consists of bubbling hydrogen sulfide through an aqueous solution containing cadmium and silver nitrates in order to precipitate a mixture of silver and cadmium sulfides at room temperature, and the sintering method, which consists of the sintering of the mixture of cadmium and silver sulfides at 300—500 °C for 3 hr in a stream of hydrogen sulfide at 50—100 ml min^{-1}. The silver sulfide for the sintered mixture was prepared by the direct reaction of silver metal powder and sulfur in a nitrogen gas stream, as has previously been described.[6] The cadmium sulfide was made by bubbling hydrogen sulfide through an aqueous solution of cadmium nitrate at room temperature.

The sulfide-mixture thus sintered was ground to a particle size of less than 10 μm. The powdered mixture of cadmium and silver sulfides was then mixed with 25 w/w% of silicone rubber. A platinum plate (1 mm thick) or wire (1 mm in diameter) which was directly connected with a leading wire was coated with the mixture to a thickness of about 0.5 mm. After being polymerized, the membrane was held in a plastic holder filled with epoxy resin.

The membrane electrode was then soaked in a 10^{-2} M aqueous solution of cadmium nitrate at 25 °C for a week.

Measurement of Potentials The potentials developed by the membrane electrode in the test solution were measured with a saturated calomel electrode as the reference electrode at 25±0.1 °C. The slope of the straight line of E *vs.* log $a_{Cd^{2+}}$ and the concentration range for the obedience to Nernst's law were investigated in order to evaluate the validity of the electrode membrane.

Magnetic stirring was employed at a constant rate to insure good reproducibility. Between measurements, the

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[1] R. A. Durst (Ed.), "Ion-Selective Electrodes," N. B. S. Spec. Publ. 348, U. S. Printing Office, Washington, (1970).

[2] E. Pungor, *Anal. Chem.*, **39**, A28 (1967).

[3] H. Hirata and K. Date, *Talanta*, **17**, 883 (1970).

[4] H. Hirata and K. Date, *Anal. Chem.*, **43**, 279 (1971).

[5] H. Hirata and K. Higashiyama, *Z. Anal. Chem.*, **257**, 104 (1971).

[6] H. Hirata and K. Higashiyama, *Anal. Chim. Acta*, **54**, 415 (1971).

electrode pair was rinsed several times with distilled water. The outer chamber of the double-junction reference electrode was drained and filled daily prior to the measurements of the potentials with 0.1 M of potassium nitrate solution.

No potential changes were observed on filling. Standard solutions containing 10^{-4} M or less of Cd^{+2} should be prepared whenever their potentials are measured. Otherwise, deviations from the Nernst law may arise through the adsorption of the solution on the wall of a beaker and the contamination of the solution.

Results and Discussion

The copper(II) sulfide-impregnated silicone rubber membrane selectively responded to cupric ions,[3] although copper(II) sulfide was a crystal with a high-electron conductivity.[7] However, the copper(II) sulfide-compressed membrane did not respond to cupric ions unless silver sulfide was added. Lead sulfide is also a semiconducting polar crystal with a high-electron conductivity at room temperature.[8] Nevertheless, the lead sulfide-impregnated silicone rubber membrane electrode responded to lead ions and showed a good selectivity, as has been described in a previous paper.[4] However, a pure lead sulfide sintered or compressed membrane, in which no trace of silver could be detected by emission spectroscopy, proved inert to lead ions in a solution. On the basis of the above results, the differentiation in the behavior of heterogeneous and homogeneous membrane electrodes seems to involve not only mechanical but also electrochemical problems.

The pure cadmium sulfide used was an insulator at room temperature, so that the cadmium sulfide-impregnated silicone rubber membrane electrode provided no meaningful response as an ion-selective electrode for cadmium ions. When the pure cadmium sulfide was sintered in a nitrogen gas stream including a slight amount of oxygen, pulverized, and impregnated in silicone rubber, the membrane thus obtained could act as a semiconductor. Its conductivity is supposed to be induced by the presence of a slight excess of cadmium produced by oxidation of cadmium sulfide. The potentials produced by the electrode membrane were unsteady and sensitive to the presence of static charges and visible light. This electrode membrane could not provide the Nernstian slope at all.

In the case of cadmium sulfide mixed with a metal sulfide other than silver sulfide, such as a cadmium sulfide-cuprous sulfide system, the sintered mixture-impregnated silicone rubber membrane electrode did not exhibit any effective response toward cadmium ions, although the membrane had semiconductive characteristics because of the conductivity of cuprous sulfide.

When cadmium sulfide was incorporated with silver sulfide in the silicone rubber membrane, the electrode fabricated from the membrane showed sensitive and stable potentials toward cadmium ions. Figure 1 shows the relationship between the potentials and the activities of cadmium ions by the silicone rubber membrane electrodes containing a mixture of cadmium sulfide and silver sulfide prepared by the precipitation method.

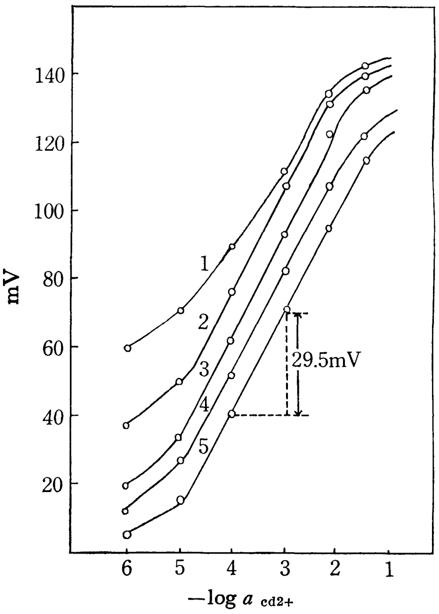

Fig. 1. Relationship between electrode potential and activity of cadmium ion. Weight ratio of CdS to Ag_2S. 1. 80 to 20, 2. 60 to 40, 3. 20 to 80, 4. 10 to 90, 5. 5 to 95.

Only the membranes containing an intimate and uniform mixture of silver sulfide and cadmium sulfide obtained by the co-precipitation method showed very satisfactory potential changes in relation to the concentration of cadmium ions. However, sufficient potential changes were not observed with the membrane containing a mixture of cadmium and silver sulfides which had been separately precipitated. The differentiation of the structure of the two mixtures has, however, not yet been clarified enough.

The co-precipitate-impregnated membrane electrode yielded a linear response toward cadmium ions over a concentration range of 10^{-1}—10^{-5} M cadmium nitrate, with an observed slope of 29.5 mV per log Cd^{2+} unit at 25 °C; this is in good agreement with the Nernst law. The analytical concentration range by this electrode was 10^{-1}—10^{-6} M. However, the best membrane of the impregnated silicone rubber electrode is less sensitive than the compressed or sintered membrane electrodes.[5] In general, the response characteristics, such as the sensitivity and response rate, of a precipitate-impregnated silicone rubber membrane electrode seems to be inferior to those of a precipitate-compressed or a precipitate-sintered membrane electrode.

As for the composition of the active materials, more than 60 w/w % of cadmium sulfide and less than 40 w/w % of silver sulfide could not provide sufficient potential changes or high response rates to the changes in the cadmium ion concentration.

When the mixture of cadmium sulfide and silver sulfide obtained by the sintering method was used as an active material, the silicone rubber membrane showed almost the same response characteristics as the co-precipitate-impregnated one. However, the sufficient

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[7] H. Devaux and J. Cayrel, *C. R. Acad. Sci. Paris*, **198**, 1339 (1934).

[8] R. L. Petritz and W. W. Scanlon, *Phys. Rev.*, **97**, 1620 (1955).

potential changes were not observed with the membrane containing the mixture of cadmium and silver sulfides which had been separately prepared by the reaction of the corresponding metal and sulfur.

The response time of the measuring cell was a few sec for 10^{-2} M Cd^{+2} and about ten min for a 10^{-6} M solution. The membrane had to be soaked in a 10^{-2} M cadmium nitrate solution for more than 5 days after its preparation. However, once the membrane was soaked, the potentials were stable and steady even if the membrane was exposed to air for more than two weeks.

When the fraction of the silicone rubber in the membrane was more than 50% by weight, the potentials were unsteady and unstable, so that it could not be measured. When it was decreased to less than 50%, the time required for soaking in the solution of cadmium nitrate decreased and the potentials became more stable; potential properties similar to those shown in Fig. 1 were thus obtained. However, the lower the fraction of silicone rubber in the membrane, the lower the adhesive force.

Effect of Temperature. The co-precipitate- or the sintered mixture-impregnated silicone rubber membrane electrodes are affected by changes in the temperature. The single potential of a reference electrode changes slowly with the temperature because of changes in the solubility equilibrium on which the electrode potential depends. The potential of the silicone rubber membrane electrode for cadmium ions also varies with the temperature, as is indicated by the Nernst factor, 2.303 $RT/2F$, within the limits of experimental error. The electrodes could be safely used at temperatures between 0 and 60 °C.

Influence of pH. The desirable pH of a solution was adjusted with newly-prepared buffer solutions. Figure 2 shows the influence of pH on the potentials of cadmium ion-selective silicone rubber membrane electrodes in 10^{-2} and 10^{-4} M Cd^{+2} solutions.

The potentials did not change between pH 2.5 to 7.5. They decreased sharply, however, when the pH increased above 7.5, for the precipitation of $Cd(OH)_2$ occurred. Of course, the pH at which the precipitation begins depends on the concentration of cadmium ions. The resulting curves in Fig. 2 also show that the measurable pH-range is independent of the presence of silicone rubber. The cadmium sulfide content in the membrane did not affect the range of pH, either.

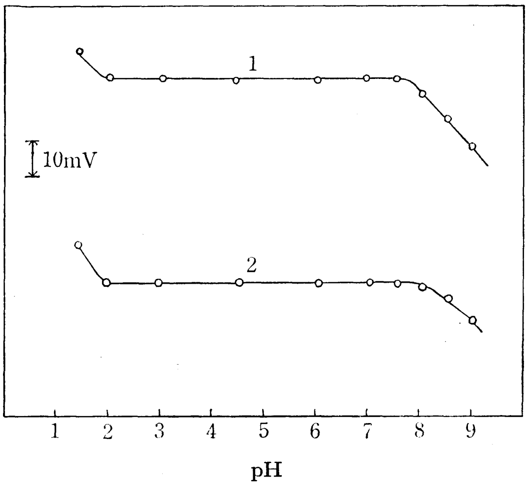

Fig. 2. Influence of pH. 1. 10^{-2} M Cd^{2+}, 2. 10^{-4} M Cd^{2+}

Dynamic Response Rate. When an ion-selective membrane electrode is used for the concentration control of a reaction process or as an indicator electrode in the potentiometric titration, the dynamic response characteristics are very important factors. The cadmium ion-selective precipitate-impregnated silicone rubber membrane electrode was evaluated by exposing the electrode to a rapid change in cadmium-ion concentration (exactly twofold) and recording the e.m.f. *vs.* time function. Some typical response curves are represented in Fig. 3. In the observed concentration range, the co-precipitate-impregnated electrode was found to establish the equilibrium reading rather rapidly after the applied concentration was changed. The sintered mixture-impregnated membrane electrode could equilibrate more quickly than the co-precipitate-impregnated one.

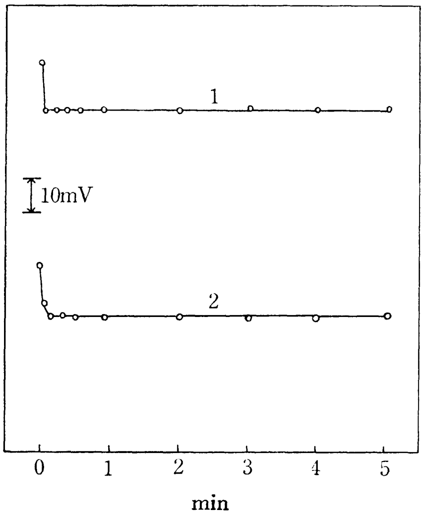

Fig. 3. Dynamic response rate.
1. 10^{-2} M—5×10^{-3} M, 2. 10^{-4} M—5×10^{-5} M

All of the curves thus obtained were smooth and of an identical shape; the e.m.f. values expected on the basis of the calibration curves were attained in all cases. The response rate of the electrode used depends on the stirring method, the efficiency of the solution mixing, and the cleanliness of the membrane surface, but is independent of the initial ion concentration over the entire range studied.

However, when the impregnated silicone rubber membrane contained a mixture in which cadmium sulfide had been added to silver sulfide after they had been precipitated individually, the electrode fabricated from this membrane did not show a fast dynamic response rate.

Selectivity. No electrode is entirely selective toward a particular ion in a solution, and the presence of the other ions may seriously impair electrode performance. It is, therefore, important to be aware of such interferences. An approximate selectivity constant can be derived experimentally from the ratio of ionic concentrations where the interfering ions cause a deviation from the expected theoretical slope, 2.303 $RT/2F$. Tests of the effects of several ions on the membrane electrodes were made in solutions containing 10^{-4} M of cadmium ions. The concentration ratios of common ions to cadmium ions were varied from 1 to 1000. Among common ions, silver, copper(II), mercury(II), iron(III), sulfide, and iodide ions interfered seriously. About 10—100 times as many lead and bromide ions and more than 1000 times as many alkali metals, alkaline earth metals, zinc, aluminum, nickel, manganese(II), cobalt, nitrate, and perchlorate ions were tolerated in coexistence with cadmium ions.

The numerical selectivity ratios of the electrode for cadmium ions with respect to these common ions were not evaluated, but in view of these findings it is clear that this electrode is well suited for the selective analytical measurement of cadmium ion activity in a wide variety of practical systems.

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