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Analytical Study of the Lead Ion-selective Ceramic Membrane Electrode

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The lead(II) ion-selective ceramic membrane electrode developed by sintering a mixture of lead, silver, and cuprous sulfides showed sensitivity, selectivity, and other response characteristics well suited to analytical utilization. The Nernstian slope was obtained over a concentration range from 10^{-1} to 10^{-6}M Pb^{2+} in activity, and the analytical range had a concentration of 10^{-1}—10^{-7}M when the membrane contained less than 30 wt% of cuprous sulfide and more than 1 wt% of lead sulfide. Among the common ions, silver, cupric, mercury(II), ferric, sulfide and iodide ions interfered seriously. About 10 times as many cadmium and bromide ions and more than 1000 times as many alkali metal, alkaline earth metal, zinc, aluminum, nickel, manganese(II), cobalt, and nitrate ions did not interfere with the lead ion, however. The electrode potentials did not change over a pH range from 2 to the pH at which the precipitation of lead hydroxide occurred. The electrode was safely used at temperatures from 0 to 95°C, and the potentials of the membrane satisfied the Nernstian equation within the limits of experimental error. The membrane electrode responded to activity changes very quickly: the rate of those changes was twice that in a lead sulfide-silver sulfide two-component ceramic electrode. A continuous potential measurement for 5 months promised long-term stability and accuracy. The rapid response rate and the long lifetime suggest that the continuous monitoring of some changing systems is feasible.

Ion-selective solid-state membrane electrodes can be classified conveniently into the following main groups: a single crystal membrane electrode, such as a fluoride ion-selective europium-doped lanthanum fluoride electrode:[1] a compacted polycrystalline electrode, where the membrane consists of a disc of a water-insoluble active material: a heterogeneous-membrane electrode, the so-called Pungor type, in which the active material is impregnated in an inert binder or matrix such as silicone rubber, and a glass electrode similar in principle and structure to a conventional glass pH electrode.[4]

For the lead ion-selective solid-state membrane electrode, a compacted polycrystalline electrode[5] has recently been developed by Orion Research, Inc.: here the membrane consists of lead sulfide incorporated with silver sulfide. A lead sulfide-impregnated silicone rubber membrane electrode[6] has since been prepared.

No electrode membrane has, however, yet been obtained by a sintering process, although a halide ion-sensitive electrode membrane was made by casting silver halide[7] and/or by hot-pressing a mixture of silver halide and a powdered thermoplastic polymer.

In our laboratory, a new type of cuprous sulfide ceramic membrane electrode which can be used for the measurement of cupric ion activity[9] has been prepared, and subsequently a lead sulfide ceramic electrode membrane incorporated with silver and cuprous sulfides has been developed.[10] The lead ion-selective electrode membrane obtained by a hot-pressing method permited lead-ion determination over a concentration range from 10^{-1} to 10^{-7} mol/*l*. In a previous paper, the relationship of the potential *vs.* the concentration curves and the compositions of the ceramic membranes was described. The present work was undertaken to provide some quantitative information regarding the analytical usefulness of a ceramic membrane electrode containing a mixture of lead, silver, and cuprous sulfides as the membrane for measuring the lead-ion concentration.

Experimental

Apparatus. An Orion model 801 digital pH meter was used for all the potentiometric measurements. The reference electrode was a Horiba Seisakusho model 2530-05T saturated calomel electrode to prevent contamination from a test solution.

The electric furnace for the preparation of the raw materials and the hot-pressing apparatus for making an electrode membrane were the same as previously reported.[10]

Chemicals. The lead, silver, copper, and sulfur were commercially-available materials, as pure as possible. The raw materials, PbS, Ag_2S, and Cu_2S, for preparing the membranes were obtained by the direct reaction of the corresponding metal with sulfur, as has previously been described.[10]

A stock solution of the 0.1M Pb^{2+} ion was prepared by direct weighing from Nakarai reagent-grade $Pb(NO_3)_2$ and was stored in polyethylene reagent bottles. A series of standard solutions of the lead ion was prepared by the suitable dilution of the stock solution, keeping the ionic strength of 0.1M by the addition of appropriate volumes of a 1M sodium nitrate solution. All the other chemicals were of Nakarai reagent grade and were used without further purification. The nitric acid and sodium hydroxide solutions were used to adjust the pH of the standard solutions. All the solutions were prepared from water which had been both deionized and distilled.

Preparation of the Ceramic Membrane. The ceramic membrane was obtained by the following two methods:

(1) A mixture of lead, silver, and cuprous sulfides was compressed and then sintered at 350—500°C for 3 hr in a hydrogen sulfide gas stream, and

(2) A mixture of lead, silver, and cuprous sulfides was

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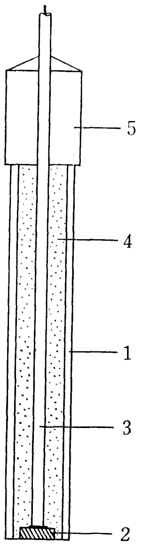

Fig. 1. Cross-section of lead ion selective ceramic membrane electrode.
1. stem 2. ceramic membrane 3. leading wire
4. insulator (epoxy resin) 5. cap

compressed and subsequently hot-pressed at 350—400°C for 2 hr under a pressure of 3—7 ton cm^{-2}.

Preparation of the Electrode. A cross-section of the lead(II) ion-selective ceramic membrane electrode is shown in Fig. 1. The ceramic membrane was fastened directly with a leading wire, and then mounted with epoxy resin adhesive in a stem of unbreakable epoxy resin, which is highly resistant to acids, bases, and organic solvents. The internal electrode and solution which are commonly used in usual selective electrodes, such as a glass pH electrode or a liquid ion-exchanger electrode, were eliminated in order to avoid any internal contamination of the membrane and in order to simplify the structure of the electrode. Then, the membrane surface was polished with diamond paste and washed with an ultrasonic wave cleaner.

Procedure. Potentiometric measurements for drawing the calibration curves were carried out in the conventional manner. The potentials developed by the membrane electrode were measured at 25.0±0.1°C with a saturated calomel electrode as the reference electrode. Magnetic stirring was employed. The electrode potentials were attained rapidly, and in every case the equilibrium potentials were read within 2 min after the immersion of the electrodes into the standard solution. The reproducibility for different solutions with the same lead-ion concentration was within ±0.5 mV if the electrode surface was kept clean and the stirring rate was constant.

Dynamic response curves were obtained after the rapid concentration or dilution of the standard solution by the addition of more concentrated lead nitrate or 0.1 M sodium nitrate solutions. In all cases, the resulting potentials *vs.* time curves were smooth and reproducible after the initial mixing period (the pH and ionic strength were kept constant).

Results and Discussion

Response of the Membrane Electrode to the Lead(II) Ion. In general, the mechanism of the response of solid-state electrodes is not so well understood as that of glass or liquid ion-exchanger membrane electrodes; by an analogical consideration of the glass membrane electrode, the ion-exchange theory[11] has been applied directly to the solid-state membrane electrode. Pungor[3] demonstrated with radiochemical methods that the rate of the iodide-ion exchange at the membrane-solution interface was very fast when a silver iodide-impregnated silicone rubber membrane was used. Buck[12] has presented such a theory assuming a rapid, reversible ion exchange at the membrane interfaces and mobile defects within the membrane crystal. While it is at least highly probable that these are necessary conditions for the operation of a solid-state ion-selective membrane electrode, experimental evidence supporting this theory has not been available for many solids now in use as membrane materials. It is especially very difficult to adapt this theory to a complicated mixed crystalline membrane electrode such as the present ceramic membrane electrode.

On the operation mechanism for an electrode such as a silver sulfide - cupric sulfide - compacted membrane electrode, Rechnitz *et al.*[13] suggested that this membrane was an ionic conductor which allowed the silver ion to pass and that this electrode transported the charge by the movement of silver ions, but the potential was determined indirectly by means of the availability of S^{2-}, which, in turn, was fixed by the activity of the divalent metal in contact with the membrane. Certainly, a pure lead sulfide ceramic membrane, in which no trace of silver could be detected by qualitative emission spectroscopy, as has previously been reported, proved non-responsive to the lead ion, but an impure lead sulfide ceramic membrane containing less than 0.01 wt% of silver was rather more sensitive than a pure one, and a membrane with 1% of silver sulfide added exhibited 27 mV for each ten-fold change in the lead-ion activity. Nevertheless, a very pure lead sulfide-impregnated silicone rubber membrane electrode was readily sensitive to lead ion activity without any trace of silver sulfide and showed sufficient selectivity among other cations or anions in spite of the fact that pure lead sulfide was not an ionic but an electronic semiconductor.

Recently, Brand and Rechnitz[14] have made impedance measurements of the electrode membranes. In the case of an electrode fabricated from a compacted disc containing a mixture of lead and silver sulfides, it was found that there was no net ion transport across the membrane cell, and that charges were built up at the membrane-solution interface, producing a capacitative effect. Such ion-blocking at the interface includes the absence of an ion-exchange reaction (ionic conduction within the membrane) or the absence of a charge-transfer reaction (electronic conduction within the membrane).

However, it is quite difficult, from the above point of view, to clarify the specific ion-selectivity and the effect of incorporation by silver sulfide.

Further investigations of the mechanism of the mixed crystalline membrane electrode were not, however,

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carried out in the present study.

Calibration Curves. The experimental cell can be represented as:

$$\text{Lead ion-sensitive electrode}\ \Big|\ \text{test solution}\ \mu=0.1\ (\text{NaNO}_3)\ \Big\|\ 0.1\,\text{M}\ \text{NaNO}_3\ \Big|\ \text{SCE}$$

The potential of this cell is given by:

$$E = \text{constant} + 2.303(RT/2F)\log a_{\text{Pb}^{2+}},$$

where the "constant" is the sum of the potentials at the leading wire-membrane contact interface, the saturated calomel electrode and the liquid-junction potential between a test solution and the reference electrode, and the potential across the membrane, when the silver-ion activity in the test solution is unity. Since the measurements were carried out at a constant ionic strength of 0.1 M, the junction potential was kept approximately constant.

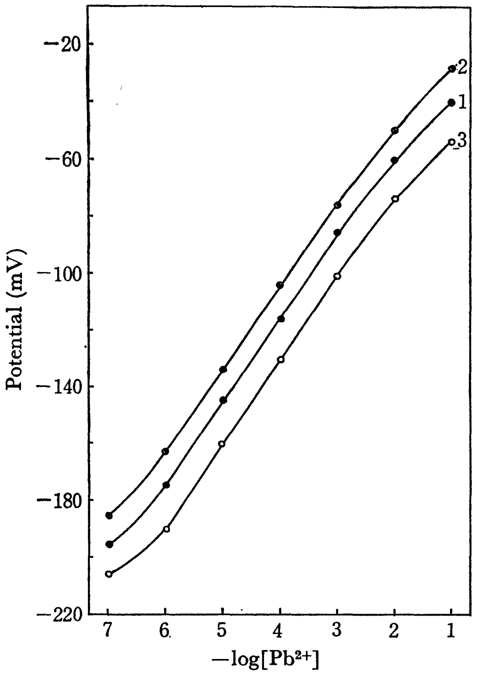

Fig. 2. Potential *vs.* concentration curves for the membranes prepared by hot-pressing method (at 370°C, for 2hr and under a pressure of 7 ton cm^{-2}).

1.	PbS 30%	Ag_2S 65%	Cu_2S 5%
2.	PbS 50%	Ag_2S 40%	Cu_2S 10%
3.	PbS 80%	Ag_2S 16%	Cu_2S 4%

The actual potential of the ceramic membrane electrode *vs.* the saturated calomel electrode as a function of the lead-ion concentration is demonstrated in Fig 2. A straight line has been drawn, over a range of lead-ion activities from 10^{-1} to 10^{-6}M, with a slope of 29.5 mV per log [Pb^{2+}] unit. This value is in agreement with that predicted by the Nernst relationship. The experimental results suggest that the ceramic electrode membrane material used in the indicator electrode and the applied sintering process were very effective. Moreover, the analytical range of this electrode, as depicted in Fig. 2, was a concentration of 10^{-1}—10^{-7} mol/*l*.

Dynamic Response Characteristics. When an ion-selective membrane electrode is utilized for the concentration control of a reaction process or as an indicator electrode in the potentiometric titration, the dynamic-response characteristic is a very important factor. The response characteristics of the lead ion-sensitive membrane electrode were evaluated by exposing the electrode to a rapid change in lead-ion concentration (approximately twofold) and by recording the resulting e.m.f. *vs.* time function. The dynamic-response experiment was carried out with hot-pressed ceramic membranes containing 30, 50, and 80 wt% of lead sulfide. Some of the resulting response curves typical of the results obtained, are represented in Fig. 3.

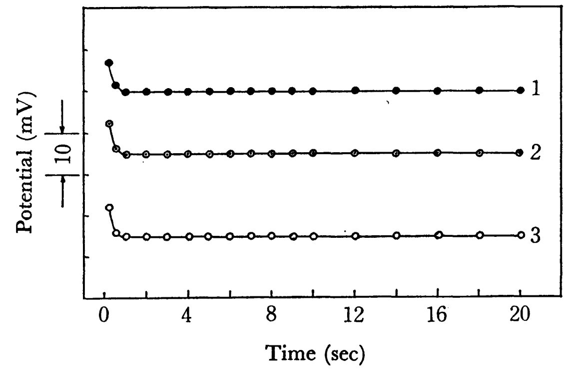

Fig. 3. Dynamic response curves.
Membranes for the curves 1, 2, and 3 are identical with those numbered in Fig. 2 in the compositions and preparation conditions respectively.

All the curves were smooth and of an identical shape; the expected (on the basis of calibration curves) e.m.f. value was attained in all cases. The response half-time $t_{1/2}$ of the electrode used depends on the stirring method, the efficiency of the solution mixing, and the cleanliness of the electrode surface, but it is independent of the initial lead-ion concentrations over the entire range studied. The response half-times obtained are of an order of less than one second for the present experimental conditions and are probably determined mainly by the mixing efficiency. Since the electrode used is an extremely low-solubility ceramic ionic semiconductor (the electrical resistance is less than 100 ohm-cm), the rapid response to changes in the lead-ion concentration is not unexpected. The high response rate of this electrode suggests that a continuous monitoring of lead-ion activities in aqueous solutions would be feasible.

Influence of pH. Figure 4 shows the influence of the pH on the lead ion-selective ceramic membrane electrodes in 10^{-2}, 10^{-4}, and 10^{-6}M Pb^{2+} solutions. The potentials did not change at pH values below 6.5. They did, however, decrease sharply when the pH increased above 6.5, for the precipitation of $Pb(OH)_2$ occurred. Of course, the pH at which the precipitation begins depends on the concentration of the lead ion. The resulting curves in Fig. 4 also show that the measurable pH range is independent of the lead-sulfide content in the membrane. However, the membrane containing much more than 50% of lead sulfide dissolved and the potential become unstable at a lead-ion concentration lower than 10^{-6} mol/*l*, when it was

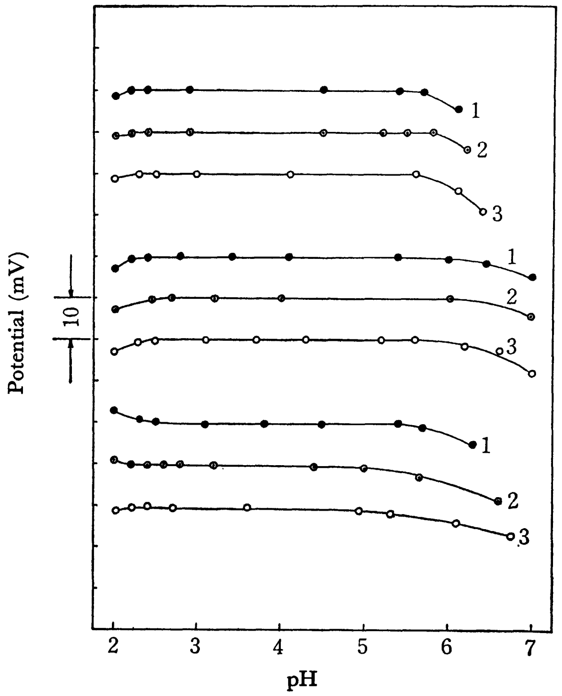

Fig. 4. Influence of the pH.
Membranes corresponding to the numbers of the curves are the same as those of Fig. 2 in their preparation conditions and compositions.

exposed in a solution with a pH below 2 for a long time.

Selectivity. No electrode is entirely selective towards a particular ion, and the presence of 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 ion causes deviation from the expected theoretical (2.303 $\boldsymbol{R}T/2F$) slope.[3]

Tests of the effects of several ions *e.g.* Ag^+, Cu^{2+}, Hg^+, S^{2-}, Fe^{3+}, I^-, Cd^{2+}, Br^-, alkali metal, alkaline earth metal, Zn^{2+}, Al^{3+}, Ni^{2+}, *etc.* on the lead ion-selective ceramic membrane prepared by the hot-pressing method were made in solutions containing 10^{-4}M of lead ions. The concentration ratios of common ions to lead ion were varied from 1 to 1000, Among the common ions, silver, cupric, mercury(I), ferric, sulfide, and iodide ions interfered seriously. About 10 times as many cadmium and bromide ions and more than 1000 times as much alkali metal, alkaline earth metal, zinc, aluminum, nickel, manganese(II), cobalt, and nitrate did not interfere with the lead ion. The lead-sulfide content in the ceramic membrane was independent of the selectivity in the present experimental range.

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

Effect of the Temperature. The electrode was safely used at temperatures from 0 to 95°C, and the potentials of the membrane satisfied the Nernstian equation within the limits of experimental error.

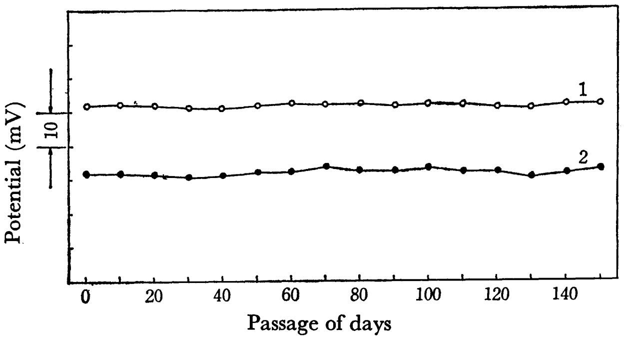

Fig. 5. Long term stability of the membranes hot-pressed at 370°C, for 2hr and under 7 ton cm^{-2}, containing
1. PbS 30% Ag_2S 65% Cu_2S 5%
2. PbS 50% Ag_2S 40% Cu_2S 10%

Lifetime. A continuous potential measurement was made using a hot-pressed ceramic membrane electrode in a specially-designed sample circulation cell. Figure 5 demonstrates that the ceramic membrane electrode had a very long lifetime and that the long-term stability and accuracy was well suited to the continuous monitoring of lead-ion activities in an aqueous solution in relation to the rapid response to changes in the lead-ion concentrations.

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