Sulfide Active Materials for Lead (II)  
Ion-Selective Electrodes

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Lead (II) ion-selective electrode membranes with solid state membranes were prepared by pressing and sintering mixtures of various ratios of lead sulfide and silver sulfide, and their potential response to lead ion was measured. These data and the standard potentials which were obtained by extrapolating the potential vs. logarithm activity curves were compared with the observed characteristic properties of lead sulfide-silver sulfide mixed crystals which were studied by powder X-ray diffraction and electrical conductivity measurements. According to these results, it will be suggested that the solid solution will be formed by dissolving silver sulfide in lead sulfide lattice and will play an important role in the performance of lead (II) ion-selective electrodes and that the addition of 0.5 mol% silver sulfide to lead sulfide will be sufficient to form active materials for such electrodes.

1 Introduction
Recently lead (II) ion-selective electrodes with sulfide membranes have been developed and widely used for potentiometric determination of lead (II) ion [1]. The active materials of such electrodes consist of mixed sulfide of lead and silver. However, the role of silver sulfide in the active materials has not been adequately clarified though the potential response mechanisms of such electrodes have been presented by several authors [1,4,9].

In this paper, lead ion-selective electrodes were prepared by pressing and sintering mixtures of various ratios of lead sulfide and silver sulfide, and their potential response to lead ion was measured by a usual method. These data were compared with the characteristic properties of lead sulfide-silver sulfide mixed crystals, which were studied by powder X-ray diffraction and electrical conductivity techniques.

2 Experimental
2.1 Preparations of ion-selective electrodes

The cross section of lead ion-selective electrode membranes prepared is shown in Fig. 1. The disk-shaped solid state membranes were fastened directly to copper lead wire with the conductive silver paste and then mounted using polyester resin. An internal solution and an internal electrode were eliminated to avoid internal contamination and to simplify the structure of the electrode.

The lead sulfide and silver sulfide active materials were synthesized by direct reactions between the elements, that is, stoichiometric mixtures of metallic lead or silver and elemental sulfur were reacted in a highly evacuated Pyrex glass tube at 350°C for 24 h, and the sulfides obtained were then crushed and heated again.

Fig. 1 Cross-section of lead (II) ion-selective electrode prepared
in a similar tube with sulfur in another portion of the tube to control the stoichiometric ratio of the sulfides to excess sulfur.

The powdered mixtures of various compositions of the lead sulfide and silver sulfide obtained in this manner were moulded to the disk of 11 mm diameter and 2 mm thickness at a pressure of $5 \times 10^7$ kg/cm$^2$ and were sintered at temperatures of 400 to 600$^\circ$C for 2 h, in a N$_2$ atmosphere to prepare the electrode membranes.

2.2 Potential measurements

Potential measurements with prepared electrodes were carried out at $25 \pm 1^\circ$C by the conventional method. Test solutions containing various concentrations of lead ion were prepared by dilution of a stock solution of 1 M lead ion which was made from lead nitrate of analytical reagent grade and twice-distilled water. No indifferent salt was added to maintain a constant ionic strength of the test solution, so that lead ion activities were calculated according to the theoretical equation of Debye–Hückel, using the effective diameter values of the hydrated lead ion in Kieland's table$^3$.

3 Results and Discussion

3.1 Potential response properties

The potential–logarithmic activity curve which was measured with the electrode having pure lead sulfide as an active material is shown in Fig. 2 as curve 1. The slope of this curve was in the range of 20 to 28 mV/decade which is smaller than the theoretical value of 29.5 mV/decade, and a response time of 2 to 3 h was required to reach the constant potential value with in the range of 1 mV, so that the electrode cannot be used as an indicator for lead ion.

The behavior of the electrode with the membrane containing 0.05 mol% silver sulfide was almost similar to that of pure lead sulfide. The potential–logarithmic activity curve is shown in Fig. 2 as curve 2. The slope was 11 to 23 mV/decade and the response time was 3 to 4 h.

When the silver sulfide content was 0.25 mol%, the electrode began to show good response to lead ion after using it for one week after preparation. The potential–logarithmic activity curve is shown in Fig. 2 as curve 3. Its slope agreed with the theoretical value of 29.5 mV/decade and its response time was within 1 min.

In the case of 0.5 mol% silver sulfide content, the behavior of the electrode was almost similar to that of 0.25 mol%, except that the reproducible potential values were achieved 2 days after preparation (curve 4 in Fig. 2).

When the active materials contained 1.0 to 75.0 mol% silver sulfide, the electrodes gave the Nernstian response to lead ion immediately after their preparation. The potential–logarithmic activity curves showed the theoretical slope and the response time was in the range of 1 to 2 min (curves 5, 6, 7 and 8 in Fig. 2).

In the case of 85 and 95 mol% of silver sulfide content, the potential–logarithmic activity curves showed the theoretical slope of 29.5 mV/decade, but the response times were 30 min and 1 to 2 h, respectively.

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![Potential–logarithmic activity curves of lead (II) ion-selective electrodes prepared with PbS–Ag$_2$S mixed sulfide active materials](image-url)

Fig. 2 Potential–logarithmic activity curves of lead (II) ion-selective electrodes prepared with PbS–Ag$_2$S mixed sulfide active materials

1: Pure PbS, 2: Mixed sulfide contained 0.05 mole% Ag$_2$S, 3: 0.25%, 4: 0.5%, 5: 1%, 6: 10%, 7: 40%, 8: 75%, 9: 85%, 10: 95%
Table 1 Potential response properties of lead (II) ion-selective electrodes prepared with PbS-Ag\textsubscript{2}S mixed sulfide active materials

<table>
<thead>
<tr>
<th>Ag\textsubscript{2}S content (mol %)</th>
<th>Sintering temp. of active materials (°C)</th>
<th>Response range for Pb\textsuperscript{2+} soln. (−log (a_{\text{Pb}^{2+}}))</th>
<th>Response time in 10\textsuperscript{−1} M Pb\textsuperscript{2+} (min)</th>
<th>Response time in 10\textsuperscript{−4} M Pb\textsuperscript{2+} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>580</td>
<td>1−5</td>
<td>20−28</td>
<td>3−4h</td>
</tr>
<tr>
<td>0.05</td>
<td>580</td>
<td>1−4</td>
<td>16−23</td>
<td>3−4h</td>
</tr>
<tr>
<td>0.25</td>
<td>580</td>
<td>1−5</td>
<td>29.5</td>
<td>1 min</td>
</tr>
<tr>
<td>0.5</td>
<td>580</td>
<td>1−5</td>
<td>29.5</td>
<td>1 min</td>
</tr>
<tr>
<td>1</td>
<td>580</td>
<td>1−4</td>
<td>29.5</td>
<td>1 min</td>
</tr>
<tr>
<td>10</td>
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<td>1−4</td>
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<td>1−2 min</td>
</tr>
<tr>
<td>40</td>
<td>450</td>
<td>1−4</td>
<td>29.5</td>
<td>1−2 min</td>
</tr>
<tr>
<td>75</td>
<td>400</td>
<td>1−5</td>
<td>29.5</td>
<td>1 min</td>
</tr>
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<td>85</td>
<td>425</td>
<td>1−5</td>
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<td>30 min</td>
</tr>
<tr>
<td>95</td>
<td>450</td>
<td>1−5</td>
<td>29.5</td>
<td>1−2 min</td>
</tr>
<tr>
<td>99</td>
<td>450</td>
<td>−</td>
<td>−</td>
<td>5−6 h</td>
</tr>
<tr>
<td>100</td>
<td>450</td>
<td>−</td>
<td>−</td>
<td>7−8 h</td>
</tr>
</tbody>
</table>

The above mentioned data are summarized in Table 1. The electrodes prepared with active materials containing 0.25 to 95 mol% silver sulfide gave the Nernstian response, while the electrodes constructed from pure lead sulfide or silver sulfide alone did not show the theoretical response to lead ion. The potential responses were very fast in the range of 0.25 to 75 mol% silver sulfide content but were very slow outside of this range.

3.2 Characteristic properties of active materials

The powder X-ray diffraction patterns of the active materials containing various amounts of silver sulfide in the lead sulfide are shown in Fig. 3. The numerals in this figure represent mol% of silver sulfide. In these patterns, the dotted peaks may be attributed to lead sulfide and the other peaks to silver sulfide, so that a new phase cannot be found in the lead sulfide-silver sulfide system.

The electrical conductivities of lead sulfide containing silver sulfide were measured by the conventional method using a 1 kHz impedance bridge, YEW BV-Z-13A, and were plotted with respect to silver sulfide content as shown in Fig. 4. According to these results, the electrical conductivities of lead sulfide suddenly increase on addition of a small amount of silver sulfide and reach a maximum value at 0.5 mol% silver
the active materials will become mixtures of this solid solution and a second solid solution formed by dissolving lead sulfide into the silver sulfide lattice. When the silver sulfide is present at more than about 80 mol\%, the second solid solution may be the predominant one.

Accordingly, it may be suggested that the first solid solution made by dissolving silver sulfide in lead sulfide will play an important role in the performance of lead (II) ion-selective electrodes and that the addition of 0.5 mol\% silver sulfide to lead sulfide is sufficient to form active materials for such electrodes.

4 Summary

(1) Lead (II) ion-selective electrodes prepared with PbS-Ag,S mixed sulfide active materials containing 0.25 to 95 mol\% silver sulfide give the Nernstian response, while the electrodes constructed from pure lead sulfide or silver sulfide alone do not show the theoretical response to lead ion. The potential responses are very fast in the range of 0.25 to 75 mol\% silver sulfide content but are very slow outside of this range.

(2) According to a powder X-ray diffraction measurement, no new phase can be found in the lead sulfide-silver sulfide system.

(3) Electrical conductivities of lead sulfide suddenly increase on addition of a small amount of silver sulfide and reach a maximum value at 0.5 mol\% silver sulfide content.

(4) Standard potentials of these electrodes prepared give nearly constant values of −52 to −56 mV vs. SCE in the range of 0.5 to 75 mol\% silver sulfide content and become more noble at contents outside of this range.

(5) These results may indicate that a solid solution will be formed by dissolving silver sulfide in the lead sulfide lattice and that its solid solubility limit will be about 0.5 mol\%.

Accordingly, it may be suggested that this solid solution will play an important role in the performance of lead (II) ion-selective electrodes and that the addition of 0.5 mol\% silver sulfide to lead sulfide is sufficient to form active materials for such electrodes.

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第1回工業電解用電極材料技術懇談会

先に本誌（1978年12月号P.647、p.687）に掲載されたように、工業電解用電極材料技術懇談会が1979年1月より発足し、第1回懇談会が1979年1月15日午後7時30分に横浜国立大学エネルギー材料研究施設で開催された。約50名の参加者が参加された。まず高橋雄雄懇談会主査の挨拶があり、懇談会設立の趣旨、今後の運営方針が述べられた。

当日のプログラムの最初は鴨川武教授（横浜国立大学）の「鉛アノードに関する諸問題」と題する講演であった。ダイカル合金などに使用する高純度鉛の製造のために、析出鉛中の鉛の混入を防止することが大きな問題となった時期があった。鉛アノード表面に生成するPbO2が塊状脱落し、電解液に浮遊してカソードに析出することが原因である。

この時期に鴨川教授は浮遊PbO2粒子の電解浴中における挙動を詳細に調べ、カソードへの析出の抑制に対するマッガン添加の効果および亜酸化マッガンの抑制効果の作用機構を明らかにした。

電解材料の合目的な開発のためには単にアノードの電極特性や寿命だけでなく、システム全体への影響を考慮する必要があり、電極周辺技術への配慮がいかに大切であるかを、ご自分の経験を織り込んで指摘された点が今後の電解の活躍に大きな示唆を与えた。

次いで柴崎一教授（横浜国立大学）が「電着二酸化鉛電極の現状と将来」と題して講演された。不溶性アノード材料の現状と一般的な条件および現在使われている材料の特性、電着二酸化鉛電極製造法（電着方法、電着条件、電解法、電解の性質、電着形態、結晶相、機械的性質）、用途および応用などについて広範にわたって解説された。電解の実物を取り扱う中から、長年にわたる経験を背景に興味深い話をされ、懇談会参加者一同得られた所大であった。

今回は初めての試みであり、懇談会は無断である上に、講演後の自由討論は厳選のパーソナリティを揺さぶる人々が行うという趣向であった。会場での討論は、時には懇談会最終の1時間にわたり、個別の意見交換、懇談会場としても大いに有効であった。

懇談会における高橋雄雄の話でも、現在高橋の技術水準に達している工業電解技術の省エネルギー化の観点から、電極材料の新技術についても新しい電極材料の出現によって新たな展開が期待される分野が多くあることが指摘された。

この懇談会は本年中にあと3回開催予定であるという第2回は5月10日に横浜国立大学で開催することになっている。今後も会員各位のご協力を、なおお願いする次第である。

（懇談会幹事 東京大学 増子 昇）