SHORT COMMUNICATIONS

The Polarography of Lead(II) Ions in Fused Sodium Fluoride-Potassium Fluoride-Lithium Fluoride Ternary Eutectic

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So far, it has not been possible to carry out the polarography of metal ions in a medium of fused fluoride salts because of the generally high melting points of fluoride salts and because of their strongly corrosive action. However, a good polarogram of a metal ion was obtained by using a eutectic mixture of sodium fluoride-potassium fluoride-lithium fluoride as the fused salt solvent, as proposed by Bergman et al.[1] The advantage of this solvent are its good thermal stability, the wide span of its electrolytic decomposition potential, its high conductivity and fluidity, and the commercial availability of its components as reagent-grade salts. Further, its melting point is the lowest of all the fluorides, and its chemical reactivity is such that a high pure alumina can be utilized as construction material. The properties of the solvent thus permit, in theory, a study of the electrochemistry of a wide variety of solutes with a minimum of interference from solvent effects and with only moderate experimental difficulty as high-temperature work goes.

In the present work, the dipping-type microelectrode, described in a previous report,[2] was modified for the fluoride bath, as is shown in Fig. 1, and the polarogram of the lead(II) ions in this solvent was obtained.

The fused salt was prepared in the following way: Sodium fluoride, potassium fluoride and lithium fluoride were separately dried in a vacuum desiccator at $10^{-2}\sim10^{-3}$ mmHg for 1~2 weeks. A mixture of 11.5 mol. % of sodium fluoride, 42 mol. % of potassium fluoride and 46.5 mol. % of lithium fluoride was placed in an alumina cell and heated in an electric furnace while being evacuated to $10^{-2}\sim10^{-3}$ mmHg. The temperature was raised to fuse the salts and was maintained at 850~900°C for 1.5~3.0 hr. The furnace temperature was then adjusted to 650±2°C.

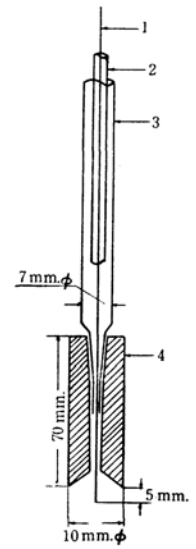

Fig. 1. Dipping type Mo microelectrode for fluoride bath.
1. Mo wire (0.3 mm. ϕ) 3. Quartz glass
2. Borosilicate glass 4. Graphite ring

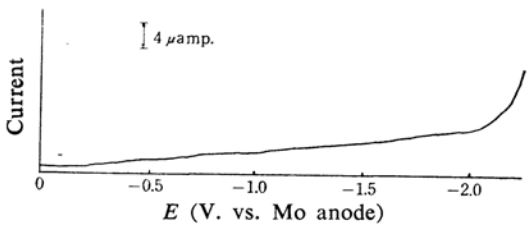

Fig. 2. Residual current curve of fused NaF-KF-LiF eutectic at 650°C.

The residual current curve obtained is shown in Fig. 2. The terminal voltage rise occurred at about −2.1 V. vs. the Mo anode.

1) A. G. Bergman and E. P. Dergnnov, *Compt. rend. acad. sci. U. R. S. S.*, **31**, 754 (1941).
2) H. Gotô, S. Suzuki and M. Saitô, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 332 (1963).

A typical polarogram of lead(II) ions is shown in Fig. 3; the wave form is similar to that described in a previous report.[2] The corresponding log plot is shown in Fig. 4. It was found that there is a linear relationship between the applied voltage and $\log(i_d-i)/i$, in spite of the fact that plotting the applied voltage against $\log(i_d-i)$ did not produce a straight line.

The half wave potential was -0.55 V. vs. the Mo anode.

The concentration of lead(II) ions, in the range of 1.95~4.60 mmol./1000 g. fused salt, was found to be directly proportional to the limiting current.

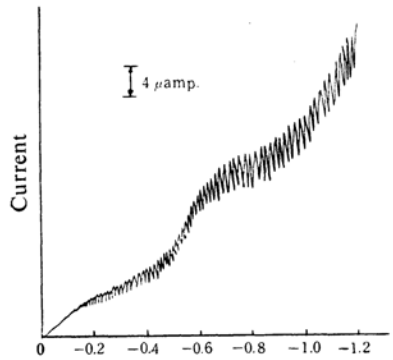

Fig. 3. Polarogram of Pb(II) ion in fused NaF-KF-LiF eutectic at 650°C.

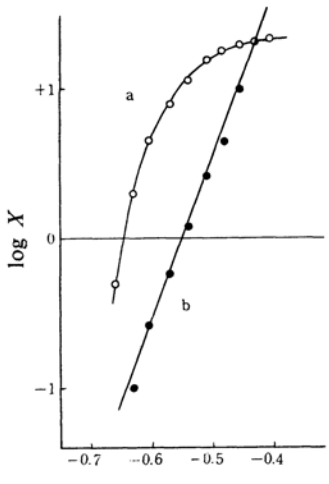

Fig. 4. Log plot of the current-voltage curve of Pb(II) ion.
a: $E\sim\log(i_d-i)$
b: $E\sim\log(i_d-i/i)$

Consequently, it is thought that the procedure described here may be useful for the study of the electrochemical behavior of metal ions in a medium of fused fluoride salt.

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