Polarographic Studies of Some Metal Ions in Fused LiCl-KCl and NaF-KF-LiF Eutectics by Using Improved Molybdenum Microelectrode of Dipping Type

Polarographic Studies of Some Metal Ions in Fused LiCl-KCl and NaF-KF-LiF Eutectics by Using Improved Molybdenum Microelectrode of Dipping Type*

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Synopsis

In the first place, polarographic studies of various metallic ions in fused LiCl-KCl eutectic at 450°C were carried out by using improved molybdenum microelectrode of dipping type. By using a spiral molybdenum wire or a chlorine reference electrode as anode, effects of temperature, concentration of reducible species, microelectrode area and gas bubbling rate over the microelectrode surface were examined with Zn(II) as an example. The limiting current was independent of the gas bubbling rate from 0.5 to 3.5 sec/bubble and directly proportional to the microelectrode area and to the concentration of Zn(II). From the result of the temperature dependence of limiting current, the activation energy of the electrode process at the voltage showing limiting current was determined as 4.6 kcal/mole of Zn(II). This value may show that the limiting current obtained by this electrode is diffusion-controlled. From the polarographic behavior of Zn(II), it was concluded that this electrode reaction should be completely irreversible, because the relationship of $\log(i_d-i)/i$ vs. E was linear, the slope being 150 mV at 450°C. Following the above fundamental studies, polarographic behaviors of Tl(I), Cu(II), Cd(II), Al(III) and U(IV) were examined mainly on the relation between i~E curves and half-wave potentials.

In the second place, polarographic studies of lead(II) ion in fused KF-NaF-LiF eutectic at 650°C were carried out by improving the microelectrode mentioned above. The polarogram obtained showed an S-shaped form without a bend, and resembled that in the fused chloride. The relation between applied voltage and $\log(i_d-i)/i$ was linear. The half-wave potential was -0.55 ± 0.01 V vs. the molybdenum anode and the limiting current was proportional to the concentration of lead(II) ion ranging from 1.95~4.60 mmoles per 1000 g fused salt.

I. Introduction

Recently, the fused salt electrolysis is increasingly used for metallurgical researches and refining of metals, but fundamental studies on the electrochemical behavior of metal ions in the fused salts are comparatively few and many uncertain

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points on the electrode reaction or on the state of the metal ions in fused salt solution remain to be solved. In order to clarify these points, the polarographic method is useful. Polarographic studies in fused salt have been far less developed than those in aqueous solution, and the pioneering works were first reported in 1948 almost simultaneously by American and Russian investigators[1]-[3]. The present authors have also reported the results of studies on polarography, using a dropping mercury electrode and a few metal ions in a fused salt (m.p. 120 C) of a ternary system of KCl-LiCl-$AlCl_3$, as the low-melting solvent[4]. However, the dropping mercury electrode cannot be used for high-melting fused salts and, even in the case of low-melting fused salt, its application to metals is limited due to the narrow range of potential of the polarogram obtained. Consequently, the use of a solid microelectrode is considered to be necessary. In a solid microelectrode there are stationary, rotating, vibrating and dipping type. Some changes in the surface of electrodes cannot be avoided by the deposition of reduction product and this is especially marked in a stationary electrode. Evacuation of external atmosphere is difficult with a rotating or a vibrating electrode. For these reasons, the dipping type was used in the present work.

This type of electrode has been used by some workers in earlier days[5]-[7]. Hills and Oxley[7] stated that the polarogram obtained with platinum microelectrode of the dipping type was similar to that obtained with the dropping mercury electrode, and that the relationship between the applied voltage and $\log(i_d\text{-}i)/i$ was linear. Further, they stated that the surface area of the electrode and the process of diffusion were more easily seen in a flat electrode than in a needle-shaped one, and that the former was more convenient for the theoretical analysis using the Ilkovic equation. Flat electrode, however, cannot be used for a long time due to drastic corrosion of lead glass used for sealing the platinum wire in the fused salt.

In order to eliminate such defects, the form of needle-shaped electrode was improved, and some fundamental examinations were made of polarography of various metal ions in aqueous solution[8]. It was thereby seen that (i) constant polarograms were obtained with such an electrode; (ii) the wave height was proportional to the concentration of reducible species; (iii) the current-voltage curve of E vs. $\log(i_d\text{-}i)/i$ showed linearity; (iv) the half-wave potential did not vary with varying concentration of the reducible species and the rate of change of the applied voltage. These results showed that the improved electrode could be used

(1) Yu. Lialikov and V. Karmazin, Zavodskaya Lab., **14** (1948), 144.
(2) N. Nachtrieb and M. Steinberg, J. Am. Chem. Soc., **70** (1948), 2613.
(3) Yu. K. Delimarskii, E.M. Skovets and L.S. Berenblyum, Zhur. Fiz. Khim., **22** (1948), 1108.
(4) H. Gotô, S. Suzuki and M. Saitô, J. Chem. Soc. Japan, **83** (1962), 883.
(5) Yu. Lialikov and V. Karmazin, Zavodskaya Lab., **14** (1948), 144; Zhur. Anal. Khim., **8** (1953), 38.
(6) S.N. Frengas, J. Chem. Soc. London, 1956, 534.
(7) G.J. Hills and J.E. Oxley, Z. anal. Chem., **207** (1960), 5.
(8) H. Gotô, S. Suzuki and M. Saitô, J. Chem. Soc. Japan, **84** (1963), 41.

for polarography in aqueous solution.

The present report concerns the examination of the adaptability of this improved electrode to the polarography in fused salts.

II. Polarography in fused potassium chloride and lithium chloride eutectic

1. Experimental apparatus and reagents

(1) Polarographic instrument: Yanagimoto pen-recording DC polarograph of the polarization rate of 3.2 mV/sec.

(2) Electrolytic cell: Quartz cell, 40 mm in diameter and 300 mm in length, as shown in Fig. 1(A).

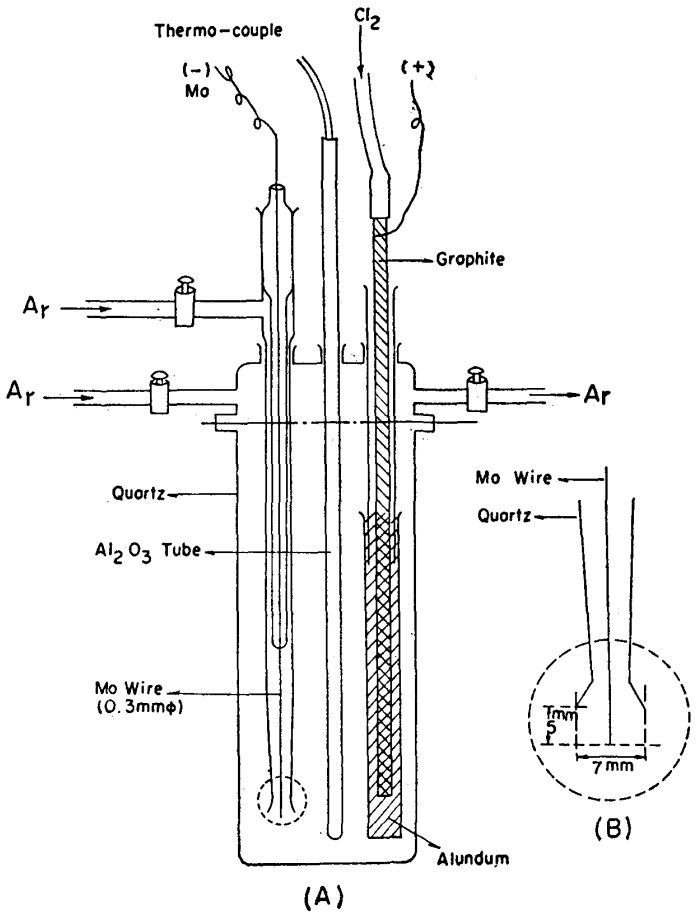

Fig. 1. Cell assembly used in fused chloride salt polarography.

(3) Electric furnace and control of its temperature: The electric furnace used was a double heating furnace of vertical type, wound with iron-chromium wire (1 mm ϕ). In order to obtain uniform temperature of the furnace, a copper tube of 4 mm in thickness was inserted. The temperature of the outer furnace was raised nearly to the required one with transformer (100 V, 10 amp) and the inner furnace was maintained at the required temperature with the accuracy of ± 2°C by an automatic temperature controller. Unless otherwise noted, the experiment was carried

out at 450°±2°C.

(4) Molybdenum microelectrode of dipping type: Molybdenum wire (0.3 mm ϕ) was sealed in the end of a hard glass tube of 2 mm in diameter as shown in Fig. 1 (A), and this was inserted into a quartz tube. The lower part of the quartz tube was narrowed and the tip coming into contact with the solution was opened into a hole of 7 mm in diameter with the angle of about 45° as shown in Fig. 1(B). The molybdenum electrode was extruded by 0.1~0.5 mm from the top of the bubble formed by passage of argon gas. This form was adopted in order to maintain the surface area of molybdenum coming into contact with the solution constant against the change in gas flow rate and to minimize the oscillations. By making the electrode into this shape, its sensitivity was increased several folds over the existing type.

The electrode used for the present experiment was found to satisfy the above-mentioned conditions when it was extruded by 5 mm from the tip of the quartz tube, and such an electrode gave satisfactory polarograms. The electrode surface was polished with emery paper No. 05, washed with aqua regia for a few seconds, and rinsed well with distilled water. Moisture on the surface was removed with a filter paper and a fully dried electrode was used.

(5) Reference electrode: A chlorine reference electrode has been used as a standard electrode for the electrochemical studies in fused chloride bath by many workers[9]-[14].

In the present work, the chlorine reference electrode as shown in Fig. 1(A) was used. The electrode consisting of a tubular graphite (nuclear reactor grade), 2 mm in inner- and 6 mm in outer-diameter, was inserted into an Alundum tube of 18 mm in outer-diameter and 1 mm in thickness, and fully purified chlorine gas was passed at a constant rate (1~2 bubbles/sec) through the top of the graphite,

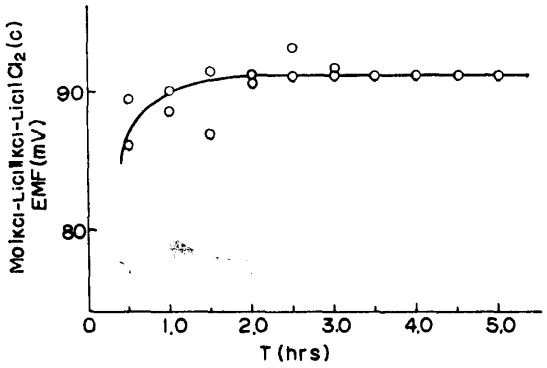

Fig. 2. Stability of chlorine electrode.

(9) R. Lorenz, *Die Elektrolyse Geschmolzener Salze*, Krapp, Halle am Saale (1905).
(10) W. Hildebrand, J. Am. Chem. Soc., **52** (1930), 4655.
(11) E.J. Salstrom, T. J. Kew and T.M. Powell, ibid., **58** (1936), 1848 .
(12) P. Drossbach, J. Electrochem. Soc., **103** (1956), 700.
(13) K.H. Stern, J. Phys. Chem., **60** (1956), 679.
(14) M. Takahashi, J. Electrochem. Soc. Japan, **25** (1958), 432.

and the electrode was used when its potential was sufficiently stable. The examination of the stability of this electrode showed that a reversible potential was attained in 2 hours as shown in Fig. 2.

(6) Reagents: All special grade. Metal oxides were prepared from corresponding salts by the conventional method[15]. Potassium uranium pentafluoride was prepared in the following way[16]: Potassium fluoride, hydrofluoric acid and formic acid were added to the solution of uranyl nitrate, reduction was effected by irradiation of sunlight, and the precipitated green potassium uranium fluoride was collected by filtration. The precipitate was heated at 100~125°C for 1~2 weeks and a completely dried one was used.

(7) Preparation and purification of the eutectic salt of potassium chloride and lithium chloride: Since potassium chloride is very hygroscopic, various methods have been devised[7][17][18] for making water-free eutectic salt of potassium chloride and lithium chloride. After examination of these methods, it was seen that the eutectic salts prepared by the following methods, (A) and (B), were most suitable.

Method (A): Potassium chloride and lithium chloride were separately dried in a vacuum desiccator at 10^{-2} to 10^{-3} mmHg for 1~2 weeks. The mixture of 51 mole per cent potassium chloride and 49 mole per cent lithium chloride was placed in a fusion cell and heated in an electric furnace, while passing dry chlorine gas. The temperature was raised to 500°C and maintained for 2~3 hours to remove volatile impurities and water. The furnace temperature was finally raised to 650~700°C to fuse the salts and then maintained for 1.5~3.0 hours. The fused salt was transferred to an electric furnace maintained at 450°C and argon gas was passed vigorously through the salts to remove chlorine.

Method (B): A calculated amount of fully dried lithium perchlorate was taken in the fusion cell and the temperature was gradually raised to 380~400°C

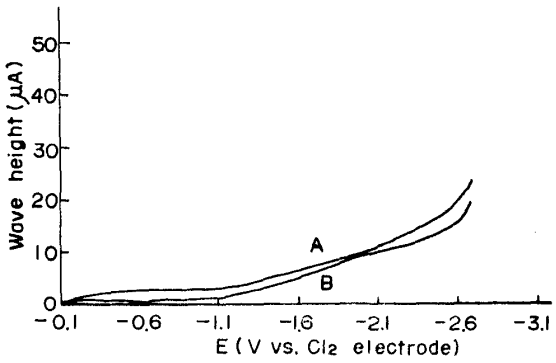

Fig. 3. Residual current of fused LiCl-KCl eutectic
A: method A B: method B

(15) E.H. Archibald, *The Preparation of Pure Inorganic Substances*, John Wiley and Sons Inc., New York (1932).
(16) S.K. Kanta, Chem. Eng. Progr. Symp. Ser., **50** (1954). No. 12, 63.
(17) H.A. Laitinen, W.S. Ferguson and R.A. Osteryoung, J. Electrochem. Soc., **104** (1957), 516.
(18) D.L. Marich and D.N. Hume, ibid., **107** (1960), 354.

to effect complete decomposition. A calculated amount of potassium chloride was added to it and the mixture was treated as in (A), with passage of dry chlorine. The subsequent treatment was the same as in (A).

Residual current curves of the fused salts prepared by these two methods are shown in Fig. 3. Terminal voltage rise is about –2.6 V vs. the chlorine electrode in both cases but the fused salt prepared by the method (B) gives a slightly better result. Although there is no danger, the procedure of pyrolysis of lithium perchlorate is difficult and this method is considered not to be suitable as a general method for the preparation of fused salts.

2. Experimental method

(1) Preparation of sample solution: Solubilities of various metal oxides in the eutectic fused salt are comparatively small[19]. Consequently, the sample solution was prepared in the following way. A definite amount of the oxide was added directly to the purified fused salt at the experimental temperature, and chlorine gas was passed through the fused salt to dissolve the oxide. Then, argon gas was passed vigorously through the fused salt for 10～20 minutes to remove chlorine.

(2) Measurement: Polarographic analyses were carried out 5～6 times for each sample at a constant temperature. Unless otherwise noted, the experiment was carried out at 450°±2°C.

3. Experimental results and considerations

(1) Polarography of zinc(II) ion

(i) Polarographic wave of zinc(II) ion: As shown in Fig. 4, the polarographic

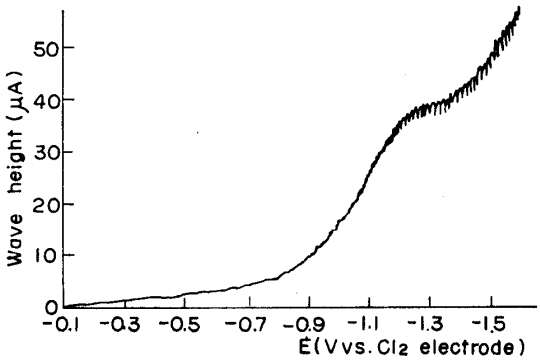

Fig. 4. Polarographic wave of Zn^{2+} ion in fused LiCl-KCl eutectic.

wave of zinc(II) ion differs from that of platinum(II) ion obtained by Hills et al.[7], which showed a sudden rise from the decomposition voltage and a large oscillation. The wave form obtained with zinc(II) ion in the present case was similar to that obtained with dropping mercury electrode.

(ii) Relationship between the rate of argon gas passed over the cathode surface and the limiting current: Results obtained with aqueous solution[8] were appli-

(19) H.A. Laitinen and B.B. Bhaita, J. Electrochem. Soc., **107** (1960), 705.

cable also to the present case. The limiting current tended to increase with increasing flow rate of gas but was almost unaffected and remained constant in the range of gas flow rate of 0.5～3.5 sec/bubble. However, the increase of gas flow rate resulted not only in the increase of wave height but also in the deterioration of the wave form and so a constant limiting current became hardly obtainable. This may be due to the difficulty of obtaining a constant diffusion layer by the irregular stirring of the solution near the electrode surface, accompanying the increase of gas flow rate, as was found in the experiment with aqueous solution. With regard to the relationship between the gas flow rate and the wave height, Hills et al. stated that the latter was independent of the former in the range of 0.3～3.0 sec/bubble.

(iii) Relationship between the cathode surface area and the limiting current: Relationship between the cathode surface area and the limiting current obtained by using 1.1 mmoles zinc per 1000 g fused salt as the reducible species is shown in Table 1. In this case, the accurate surface area of the cathode was obtained by

Table 1. Relationship between cathode surface area and limiting current*

Cathode surface area (mm^2)	Limiting current (μA)	Limiting current/ Cathode surface area ($\mu A/mm^2$)
4.70	17.8	3.78
4.70	18.2	3.87
7.85	29.0	3.70
7.85	30.0	3.32
		av. 3.79

* The concentration of Zn(II) ion in 1000 g molten medium was 1.1 mmoles.

measuring the area of reduction product deposited on the surface after electrolysis at a voltage giving the constant limiting current until the reduction product was clearly observed on the electrode surface. As will be seen from Table 1, the limiting current is directly proportional to the cathode surface.

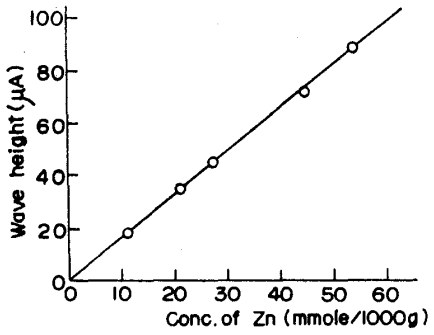

Fig. 5. Relationship between concentration of Zn^{2+} ion and limiting current.

(iv) Relationship between the concentration of zinc(II) ion and the limiting current: Zinc ion concentration in the range of 1.1～5.4 mmoles per 1000g fused

salt was used and the result is shown in Fig. 5. The surface area of the cathode used was 4.7mm². As will be seen from Fig. 5, the limiting current is directly proportional to the concentration in the above range. The half-wave potential of zinc(II) ion is -1.10 ± 0.05 V vs. the chlorine electrode, and remains constant irrespective of the concentration and of the rate of change of the applied voltage.

(v) Limiting current constant of zinc(II) ion in the fused salt of potassium chloride and lithium chloride eutectic at 450°C: From the experimental results described in (ii) to (iv), the limiting current (i_d) of the polarographic wave of zinc (II) ion can be expressed by the following equation under the above-mentioned experimental conditions:

$$i_d = K \cdot A \cdot C, \tag{1}$$

where A is the cathode surface area, C the concentration of reducible species and K a proportionality factor (limiting current constant).

The value of limiting current constant calculated from Eq. (1) was $3.46\pm0.04\mu$ A/mmole·mm² at 450°C for zinc(II) ion as shown in Table 2.

Table 2. Limiting current constant of Zn(II) ion in fused KCl-LiCl eutectic*.

Concentration of Zn(II) ion (mmole/1000g)	Limiting current (μA)	Limiting current constant (K)
1.11	18.0±0.5	3.46
2.15	35.0±1.0	3.45
2.76	45.0±1.0	3.46
4.42	71.0±2.0	3.42
5.41	89.0±2.0	3.54

* The cathode surface area was 4.70 mm² and the temperature 450±2°C.

(vi) Effect of temperature on limiting current and activation energy of electrode reaction process at the voltage showing the limiting current: Examina-

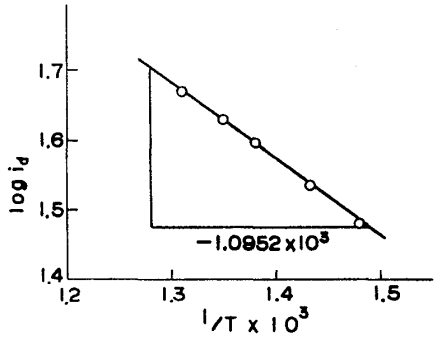

Fig. 6. Relationship between the reciprocal of absolute temperature and the logarithm of limiting current.

tion of the effect of temperature on the limiting current in the range of 400~490°C was carried out and a linear relation was obtained between the reciprocal of absolute

temperature and the logarithm of limiting current as shown in Fig. 6. The slope of the straight line is $-1.0952\times10^{3}\mathrm{deg}^{-1}$.

The following relationship between the limiting current and the temperature has already been recognized[20]-[22].

$$\ln i_d = A - B/T \tag{2}$$

Put $$A = \ln K \tag{3}$$

and $$B = Q/R \tag{4}$$

then $$i_d = K\cdot\exp(-Q/RT)\,, \tag{5}$$

where Q is the activation energy of the electrode reaction process at the voltage showing the limiting current (hereafter abbreviated to the activation energy), R the gas constant and T the absolute temperature. From Fig. 6 and Eq.(5) the activation energy of 4.6 kcal/mole was obtained.

The values of activation energies reported by the similar experiments are as follows: 5.6 kcal for nickel(II) ion in fused potassium chloride and lithium chloride eutectic at 415°C[20]; 6.3 kcal for copper(II) ion; 5.9 kcal for cadmium(II) ion; 4.5 kcal for lead(II) ion; 3.0 kcal for nickel(II) ion; 4.5 kcal for cobalt(II) ion in fused potassium chloride and sodium chloride eutectic at around 700°C[23]. The value of 9.5 kcal for zinc(II) ion in fused eutectic salt of sodium nitrate, potassium nitrate and ammonium nitrate at around 160°C has also been reported[24], and about 5.0 kcal for the value of self-diffusion of sodium and nitrate ions in fused sodium nitrate[25].

From the fact that the value of 4.6 kcal for zinc(II) ion obtained in the present experiment is comparable to the values reported to date as above, and from the

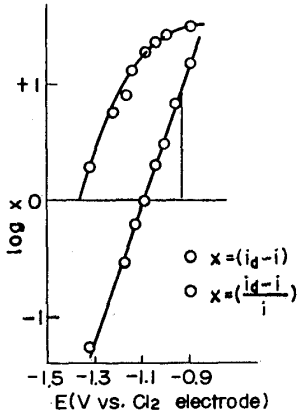

Fig. 7. Log plots current-voltage curve of Zn(II) ion.

(20) E.D. Black and T. Devries, Anal. Chem., **27** (1955), 906.
(21) Yu. K. Delimarskii and K.M. Kalabalina, Ukr. Khim. Zh., **23** (1957), 584.
(22) K.M. Kalabalina and Yu. K. Delimarskii, Dopovidi, AN URSR, (1957), No. 6, 562.
(23) Yu. K. Delimarskii and V.V. Kuzumovich, Zhur. Neorg. Khim., **4** (1959), 1263.
(24) N.H. Nachtrieb and M. Steinberg, J. Am. Chem. Soc., **72** (1950), 3558.
(25) E.R. Van Artsdalen, D. Brown, A. Dworking and F.J. Miller, ibid., **78** (1956), 1772.
(26) N.G. Chovnyk, Zhur. Fiz. Khim., **30** (1956), 227.

experimental results described in (iii), the limiting current obtained in this experiment should be diffusion-controlled.

(vii) Current-voltage curve of zinc(II) ion: The current-voltage curve of the polarographic wave of zinc(II) ion described in (i) is shown in Fig. 7. It is seen that the relation of E and log $(i_d-i)/i$ is linear, in spite of the fact that the plot of E vs. log (i_d-i) does not show a straight line. Similar results have been reported by Delimarskii et al.[3], by Chovnyk[26], and by Hills et al.[7] They reported, as its reason, the diffusion of the reduction product into the internal part of the cathode, into the fissure of cathode metal, and formation of a low-valence intermediate by the reaction with the fused salt, which served as a solvent, or with the substance to be reduced.

The slope of this straight line is 150 mV, which does not agree with the theoretical value at 450°C (71.63 mV at 2.3 RT/nF, with $n=2$), when this electrode reaction is considered to be reversible. The examination of the applied voltage and the deposition curve of the reduced product, using radioactive zinc-65 as a tracer, showed that the deposition of zinc began suddenly at around half-wave potential of the polarogram. The same result was obtained by a similar experiment using radioactive copper-64 as a tracer, and the electrode surface showed reddish brown color at the place where deposition of a large amount of copper appeared. These experimental results seem to suggest that a two-electron reduction has taken place in the case of zinc or copper, although the current-voltage curve of zinc(II) ion does not agree with the theoretical value when its electrode reaction is considered to be reversible. Therefore, this electrode reaction should be considered to be irreversible, and the following equation should be applied instead of the Heyrovsky-Ilkovic equation:

$$E = \text{Constant} + 2.3\,RT/\alpha\, n F \cdot \log\,(i_d - i)/i \qquad (6)$$

In general, it may be considerable that the value of transfer coefficient of electrode process, α, is about 0.5, and that the two-electron reduction mentioned above is reasonable in this electrode reaction.

(2) Polarography of various metal ions

Polarographic behaviors of various metals in this fused salt were examined with metals of different valency state. Thallium was chosen as a univalent metal, cadmium and copper as a bivalent, aluminium as a trivalent, and uranium as a quadrivalent metal. Examinations were made chiefly of the current-voltage curve of their polarographic waves and their half-wave potentials. In addition, the relationship between the concentration of the ion and the limiting current, and the limiting current constant were examined in the case of uranium, the results being as shown in Fig. 8 and Table 3, respectively.

(i) Current-voltage curves and half-wave potentials of thallium(I), cadmium(II) copper(II), aluminium(III) and uranium(IV) ions: Relations of E and log $(i_d-i)/i$ of polarographic waves of thallium(I), cadmium(II), copper(II), aluminium(III)

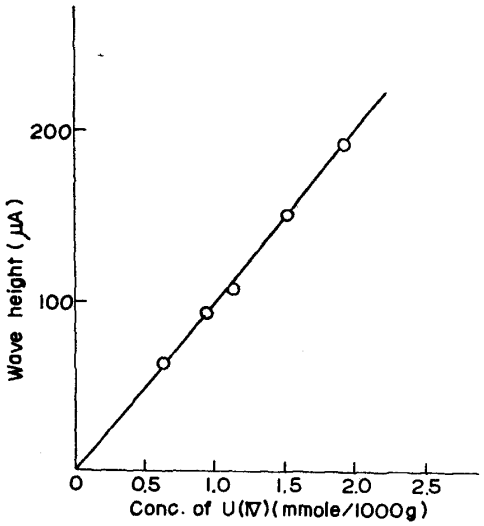

Fig. 8. Relationship between concentration of U(IV) and limiting current.

Table 3. Limiting current constant of U(IV) ion in fused KCl-LiCl eutectic*

Concentration of U(IV) ion (mmole/1000g)	Limiting current (μA)	Limiting current constant (K)
0.640	62.5	12.5
0.894	91.5	13.0
1.087	105.0	12.3
1.450	147.0	12.9
1.836	187.0	13.0

* The cathode surface area was 7.85 mm^2 and the temperature 460±2°C.

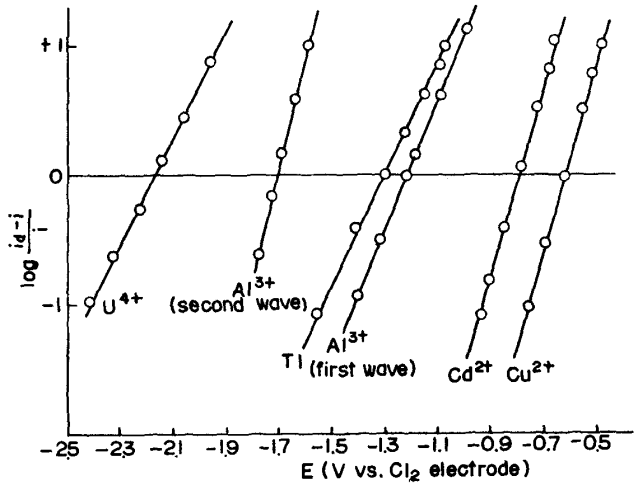

Fig. 9. Relationships between voltage and current of polarographic waves of various metal ions.

and uranium (IV) are shown in Fig. 9, and their half-wave potential values in Table 4. As will be seen from Fig. 9, the relation of E and log $(i_d-i)/i$ is linear in all these metal ions, and in Table 4 the values are 245 mV in thallium, in

which one-electron reduction is considered to take place, and 140 mV in cadmium and copper, in which two-electron reduction is considered to take place. The polarogram of aluminium showed a two-step wave, and the slope of the first wave

Table 4. Half-wave potentials of various metal ions.

Metal ion	Half-wave potential (V vs. Cl_2 electrode)	
Thallium (I)		1.31±0.08
Copper (II)		0.65±0.02
Cadmium (III)		0.81±0.02
Zinc (II)		1.10±0.05
Aluminium (III)	first wave	1.25±0.05
Uranium (IV)	second wave	1.70±0.05
		2.16±0.08

was 210 mV and that of the second wave was 120 mV. In the case of uranium(IV) ion it was 110 mV and this is considered to show two- or three-electron reduction, compared with the values of the metal ions. The half-wave potentials of these metal ions remained constant, irrespective of the concentration of reducible species and of the rate of change of the applied voltage, as was found in the experiment with zinc ion. Also, the comparison of the calculated and the experimental slope of logarithmic plot is shown in Table 5. As will be seen from Table 5, the value of α in the present experiment is all about 0.6. It may safely be said that the peculiar characteristics of the polarogram obtained with a solid electrode can be explained clearly only with the above theoretical equation (6).

Table 5. Comparison of the calculated and experimental slopes of logarithmic plot.

Expected electrode reaction	Temperature (°C)	$2.3RT/nF$ calculated (mV)	Slope of log plot measured (mV)	α
$Tl^{+} + e = Tl$	450	143.5	245	0.59
$Cu^{2+} + 2e = Cu$	450	72.0	140	0.52
$Cd^{2+} + 2e = Cd$	450	72.0	140	0.52
$Zn^{2+} + 2e = Zn$	450	72.0	150	0.48
$Al^{3+} + e = Al^{2+}$	450	143.5	210	0.68
$Al^{2+} + 2e = Al$	450	72.0	120	0.60
$U^{4+} + 2e = U^{2+}$	460	72.0	110	0.66
$U^{4+} + 4e = U$	460	36.3		0.33

III. Polarography in fused sodium fluoride, potassium fluoride and lithium fluoride ternary eutectic

1. Experimental apparatus and reagents

So far, it has not been possible to carry out the polarography of metal ions in a medium of fused fluoride salts because of their generally high melting points and because of their strongly corrosive actions. However, a satisfactory polarogram of a metal ion has been obtained by using a eutectic mixture of sodium fluoride,

potassium fluoride and lithium fluoride as the fused salt solvent, as proposed by Bergman et al.[27] The advantages of this solvent are the high thermal stability, the wide range 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 is stable enough to be utilized as a construction material of electrolytic vessels. These properties of the solvent are thus favourable, in principle, for a study of the electrochemistry of a wide variety of solutes without an extensive interference from solvent effects and without a hard experimental difficulty as a high temperature work goes.

(1) Polarographic instrument: The same DC polarograph as described in the first part.

(2) Electrolytic cell: In fluoride bath, quartz cannot be used but highly pure alumina is comparatively stable at high temperatures. Therefore, a highly pure alumina cell, 48 mm in diameter and 300 mm in length, as shown in Fig. 10 (A), was used as the outer cell, and the inner cell, in which the melt was placed, was made of the same alumina, 25 mm in diameter and 150 mm in length, and was inserted in the outer cell. A molybdenum microelectrode of dipping type was placed in the melt with the movable shaft seal. The temperature of the cell was controlled

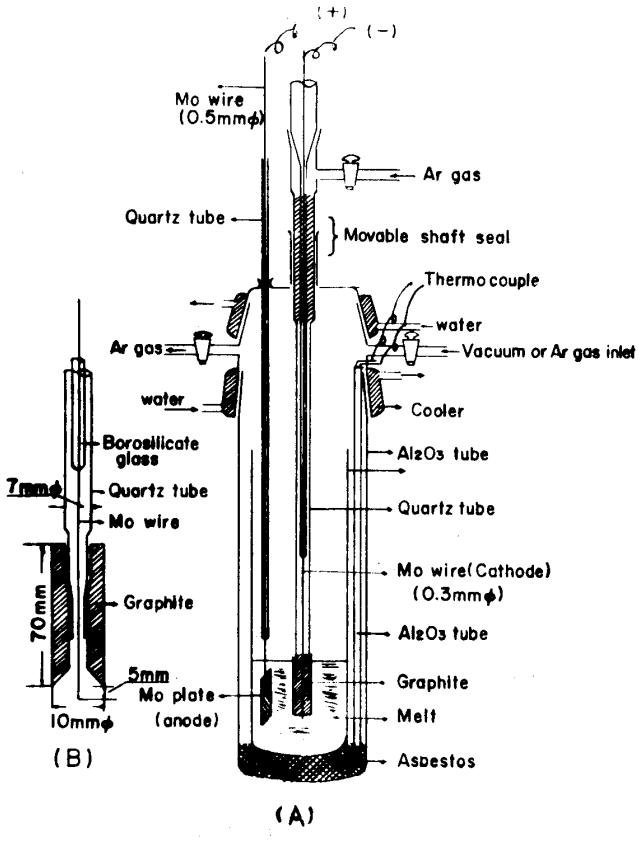

Fig. 10. Cell assembly used in fused fluoride salt polarography.

(27) A.G. Bergman and E.P. Dergnnov, Compt. rend. acad. sci. U.S.S.R., **31** (1941), 754.

by the same method as described in the first part.

(3) Molybdenum microelectrode of dipping type: As shown in Fig. 10(B), a high purity graphite ring, which is stable in fluoride melts and easily preparable, was sealed at the tip of the electrode.

(4) Anode: Metallic molybdenum plate of $15\times50\times0.1$ mm^3.

(5) Reagents: All the grade of analytical use.

(6) Preparation of the eutectic salt of ternary system of potassium fluoride, sodium fluoride and lithium fluoride: The composition of this ternary system[27], which has the lowest eutectic point of 454°C, is sodium fluoride 11.5, potassium fluoride 42 and lithium fluoride 46.5 mole per cent, or 11.7, 59.2 and 29.1 per cent by weight, respectively. In the present study, this composition was used as the fluoride bath and it was prepared as follows: 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 mole per cent sodium fluoride, 42 mole per cent potassium fluoride and 46.5 mole per cent 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 850~900°C to fuse the salts and maintained for 1.5~3.0 hours. The furnace temperature was then adjusted to 650°±2°C required for the polarographic operations. Residual current curve obtained with the mixture thus prepared is shown in Fig. 11. The terminal voltage rise occurred at about –2.1 V vs. the molybdenum anode.

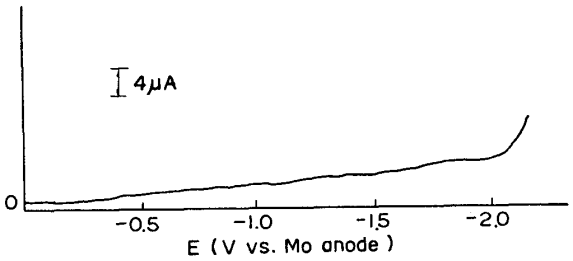

Fig. 11. Residual current in fused NaF-KF-LiF eutectic.

2. Experimental method

(1) Preparation of sample solution: A definite amount of lead(II) oxide was added directly to the purified fused salt at the experimental temperature.

(2) Measurement: Polarographic analyses were made 5~6 times for each sample at the constant temperature of 650°±2°C.

3. Experimental results and considerations

(1) Relationship between the concentration of lead(II) ion and the limiting current: Lead(II) ion in the concentration range of 1.95 to 4.60 mmoles per 1000g fused salt was used and the results are shown in Fig. 12. As will be seen from Fig. 12, the limiting current is directly proportional to the concentration in the above range.

(2) Current-voltage curve and half-wave potential of lead(II) ion: A typical polarogram of lead(II) ion in this fused salt is shown in Fig. 13. The wave form is similar to that stated in the first part.

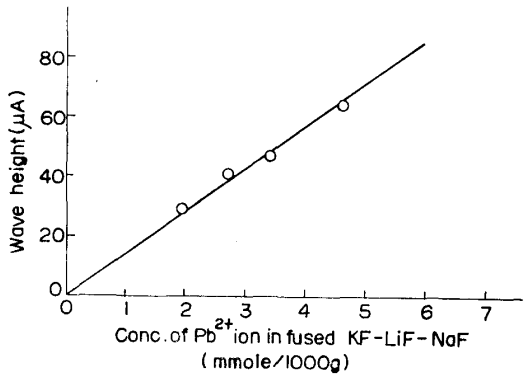

Fig. 12.

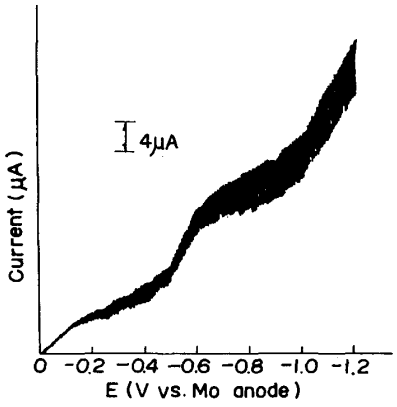

Fig. 13.

Fig. 12. Relationship between concentration of lead(II) ion and limiting current.
Fig. 13. Polarographic wave of lead(II) ion in fused NaF-KF-LiF eutectic.

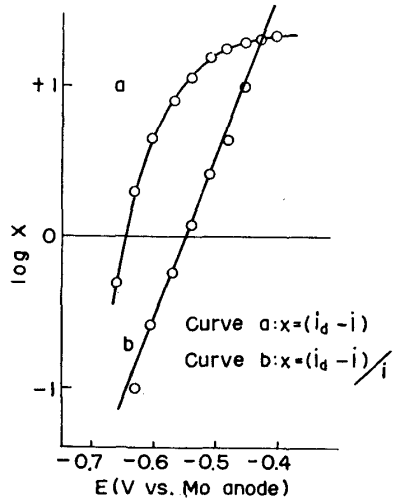

Fig. 14. The log plot of the current-voltage curve of lead(II) ion in fused NaF-KF-LiF eutectic.

The logarithmic plot of the current-voltage curve of the polarogram of lead(II) ion is shown in Fig. 14. The wave form is similar to that stated in the first part. It was found that the relationship between the applied voltage and $\log(i_d-i)/i$ is linear in spite of the fact that the plot of the applied voltage against log (i_d-i) did not show a straight line. The half-wave potential was -0.55 ± 0.01 V vs. the molybdenum anode. These characteristics can be clarified on the basis of a totally irreversible reduction process, as discussed in the first part.

Summary

(1) Fundamental examinations were made of the polarographic behaviors of metal ions in fused salt of potassium chloride and lithium chloride eutectic, by using

an improved molybdenum microelectrode of dipping type.

(2) The flow rate of argon gas over the cathode surface hardly affected the wave height in the range of 0.5~3.5 sec/bubble and the wave height was directly proportional to the cathode surface area and to the concentration of reducible species.

(3) Based on these facts an empirical formula was proposed for the limiting current constant independent of the cathode surface area: $i_d=K\cdot A\cdot C$. Limiting current constants for zinc(II) and uranium(IV) ions in the fused salt at 450°C and 460°C were calculated as 3.46±0.04 and 12.7±0.3μA/mmole·mm^2, respectively. From the effect of temperature on the wave height of the polarogram of zinc(II) ion, the activation energy of diffusion process at the voltage showing limiting current was calculated as 4.6 kcal.

(4) The current-voltage curve was of an S-shaped form, the slope of which was less steep than the theoretical one when the electrode reaction was assumed to be reversible; but the plot of E vs. log $(i_d-i)/i$ gave a linear relationship and the value of the half-wave potential remained nearly constant, irrespective of the changes in the concentration of reducible species and in the rate of change of the applied voltage. From these results, the equations proposed by previous workers were criticised and it was concluded that this electrode reaction should be completely irreversible.

(5) The dipping type microelectrode for the polarography in the fluoride bath was improved and satisfactory polarograms of lead(II) ion in fused salt of potassium fluoride, sodium fluoride and lithium fluoride eutectic were obtained.

(6) The polarogram obtained showed an S-shaped form without a bend and resembled that in the fused chloride. The logarithmic plot of the current-voltage curve, i.e., the relation between the applied voltage and $\log(i_d-i)/i$ was linear, in spite of the fact that the plot of the applied voltage against $\log(i_d-i)$ did not show a straight line.

(7) The half-wave potential was –0.55 ± 0.01 V vs. the molybdenum anode. The limiting current was proportional to the concentration of lead(II) ion ranging from 1.95 to 4.60 mmoles per 1000g fused salt.

(8) The improved microelectrode of dipping type will be used in polarography as well as in the electrochemical studies in fused salts.