Polarography of ZnCl_2 in Molten $\text{Na}_3\text{AlF}_6\text{-CaF}_2$ Bath, with Use of Vertically Vibrating Platinum Micro-cathode*

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Recent advances⁽¹⁾ have been made in the field of molten salt polarography. The authors presented previous reports⁽²⁾ on the cathodic limiting current of zinc chloride in molten fluoride systems with use of platinum micro-cathode.

The present works concern the polarography of ZnCl_2 in molten $\text{Na}_3\text{AlF}_6\text{-CaF}_2$ bath with use of vertically vibrating platinum microcathode.

Apparatus Main apparatus is shown in Fig. 1. A platinum rod of 100 mm. dia and of 15 cm. long was employed as the cathode, and which was connected with the vertical vibration equipment. A platinum crucible of 50 ml. volume was used for the anode, in which salt mixture (eutectic mixture of $\text{Na}_3\text{AlF}_6\text{-CaF}_2$) was fused.

When a sample was fused and the vertical vibration of cathode reached a certain frequency, current was passed between both electrodes and a potential-current diagram during the electrolysis under gradually increasing potential was drawn. Time necessary for one run was about 10 minutes.

- A: Revolve speed counter
- B: D.C. Generator
- C: Motor
- D: Equipment for vertical motion
- E: Platinum micro-cathode
- F: Auxiliary electrode
- G: Platinum crucible (anode)
- H: Pt-Pt-Rh thermo-couple
- I: Alumel-chromel thermocouple
- J: Electric furnace
- K: Molten salt bath

Fig. 1 Main apparatus.

- A: ZnCl_2 (with use of platinum cathode pre-treated)
- B: ZnCl_2 (with use of platinum cathode non-treated)
- C: Cu_2Cl_2
- D: LiCl

Fig. 2 Polarograph.

Prior to the running, the top of platinum cathode should be immersed into molten KNaCO_3 , and then electrolysed in dil. H_2SO_4 solution as anode for 3 minutes (Pre-treatment).

Results Polarographic waves thus obtained are schematically shown in Fig. 2. A-curve was the wave of ZnCl_2 in case of using pre-treated cathode, while B-curve was the one in case of non-treated cathode, C- and D-curves were those of Cu_2Cl_2 and LiCl , respectively.

The result obtained by successive electrolysis in the same bath showed good reproducibility of the

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value of cathodic limiting current by the six trials (Table 1).

Table 1 Effect of Successive Electrolysis (Time for one run=*Ca.* 10 min)
Frequency=140 r.p.m., Temperature=978°C Concentration of $\text{ZnCl}_2=5.52 \times 10^{-2} \text{mol/1000 g}$

No. of succession	Cathodic limiting current (A)	Half-wave potential (V)
1	0.0363	1.08
2	0.0336	1.07
3	0.0354	1.08
4	0.0345	1.06
5	0.0350	0.97
6	0.0341	1.04
7	0.0319	0.98
8	0.0283	0.95
9	0.0230	1.16

Table 2 Effect of Temperature (Frequency=140 r.p.m.)

Concentration of $\text{ZnCl}_2=4.35 \times 10^{-2} \text{mol/1000 g}$			Concentration of $\text{ZnCl}_2=4.00 \times 10^{-2} \text{mol/1000 g}$		
Temp. (°C)	Cathodic limiting current (A)	Half-wave potential (V)	Temp. (°C)	Cathodic limiting current (A)	Half-wave potential (V)
931.6	0.0248	1.03	928.0	0.0230	0.98
945.0	0.0288	0.95	945.0	0.0266	0.97
953.0	0.0297	1.01	958.5	0.0319	0.96
970.0	0.0336	1.06	962.0	0.0292	0.92
990.5	0.0372	1.05	978.0	0.0350	0.14
1,015.0	0.0438	1.16	995.0	0.0381	0.16

The relation between cathodic limiting current and the temperature of bath was obtained as shown in Table 2 and Fig. 3 (curves A and B). The relation between cathodic limiting current and the frequency of vertical vibration of cathode was shown in Table 3 and Fig. 3 (curve C).

A test for the effect of the amplitude of vertical vibration was carried out in the depths of 11 mm. and 13 mm., but an effective result on limiting current was not observed. However, higher wave height was seen in the case of deeper amplitude.

The linear relation between cathodic limiting current and the concentration of ZnCl_2 in molten Na_3AlF_6 bath was obtained under a constant temperature, frequency and amplitude, as shown

Table 3 Effect of Frequency

Temp.=957.5°C, Conc. of $\text{ZnCl}_2=3.75 \times 10^{-2} \text{mol/1000 g}$

Frequency (rpm)	Cathodic limiting current (A)	Half-wave potential (V)
140	0.0275	1.00
120	0.0222	0.96
100	0.0183	0.93
80	0.0175	0.95
60	0.0106	0.97

Effect of temperature:

A: freq.=140 r.p.m.
conc.= $4.35 \times 10^{-2} \text{mol/1000 g}$

B: freq.=140/r.p.m.
conc.= $4.00 \times 10^{-2} \text{mol/1000 g}$

Effect of frequency:

C: temp.=957.5°C
conc.= $3.75 \times 10^{-2} \text{mol/1000 g}$

Fig. 3 Relation among cathodic limiting current, temperature and frequency

in Fig. 4. Linearity was seen in the range of $(2\sim5)\times 10^{-2}$ mole/1000 g. ZnCl_2 .

Decomposition voltage of 10^{-2} mole/1000 g. in fused $\text{Na}_3\text{AlF}_6\text{-CaF}_2$ bath at 1000°C was about 0.7 V, and which was smaller than those obtained in fused ZnCl_2 ⁽⁴⁾ ($408, 489^\circ\text{C}$) and in aquo systems⁽⁵⁾ (Table 4). The diffusion coefficient of zinc ion under a constant condition was calculated about 0.5×10^{-5} cm/sec., applying Drossbach's equation⁽³⁾.

Table 4 Decomposition Voltages of Zinc Chloride under Various Conditions

State of Zinc ion	Solvent	Temp. ($^\circ\text{C}$)	Decomposition voltage (V)	Lit
molten $\text{ZnCl}_2(10^{-2}\text{mol}/1000\text{ g})$	molten $\text{Na}_3\text{AlF}_6\text{-CaF}_2$	1,000	0.7	—
molten ZnCl_2	—	$\begin{cases} 408 \\ 489 \end{cases}$	$\begin{cases} 1.94 \\ 1.83 \end{cases}$	(4)

Conclusion (1) The polarographical wave of ZnCl_2 in molten $\text{Na}_3\text{AlF}_6\text{-CaF}_2$ bath was obtained with use of vertically vibrating platinum micro-cathode. The half-wave potential was about 1 V.

(2) Cathodic limiting current was proportional with the concentration of ZnCl_2 in certain range, and was given as linear functions of the frequency of vertical vibration and of the bath temperature. No effect of the amplitude was seen.

(3) The reproducibility of result was well obtained under the conditions of constant vibration, bath temperature, concentration of ZnCl_2 and the pre-treatment of platinum cathode.

(4) The decomposition voltage of zinc chloride under various conditions was tabulated. The diffusion coefficient of zinc ion in this fused system was calculated about 0.5×10^{-5} cm/sec.

(5) As a conclusion of this work, the concentration of zinc chloride in the fused system could be analysed through the measurement of cathodic limiting current.

Fig. 4 Relation between cathodic limiting current and concentration of ZnCl_2 .

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