

# *A molten salt electrolytic process for recovering chlorine and ammonia from ammonium chloride. II*

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This paper describes the electrolysis in detail and presents the results of bench-scale tests of the molten metal cathode process for recovering chlorine and ammonia from ammonium chloride, reported in the preceding paper (Part I). A zinc chloride electrolyte, 100 A bench-scale electrolytic cell was found to work well. The electrolytic power consumption for 1 kg zinc chloride electrolysis was calculated to be 1120 Wh kg<sup>-1</sup>.

## 1. Introduction

In order to obtain more detailed data for the scaling-up of the molten metal cathode method for recovering chlorine and ammonia from ammonium chloride, a bench-scale electrolytic cell for electrolyzing zinc chloride was first constructed and bench-scale tests of the whole process were carried out in order to identify engineering problems before further scaling-up of this process proceeded.

## 2. Electrolysis of molten zinc chloride

### 2.1. Preliminary studies

Before the macro-electrolyses, several preliminary experiments were carried out in order to obtain semi-quantitative information about the anodic reaction in this system.

### 2.2. Experimental method and apparatus

The experimental cell is shown in Fig. 1. The cathode was a large pool of zinc–tin alloy in the bottom of the cell in order to dissolve deposited alkali metal. The graphite anode was set at an angle to allow effective bubble desorption. The electrolyte was a LiCl–KCl eutectic melt, to which various amounts of zinc chloride were added.

These electrolytes were treated in various ways before use. Measurements were carried out mainly by a current-controlled method.

### 2.3. Results and discussion

**2.3.1. Anode effect.** When the current density is increased, an anode effect occurs. Fig. 2 shows a photograph of the anode effect. A gas film adheres to the electrode surface and glow discharge

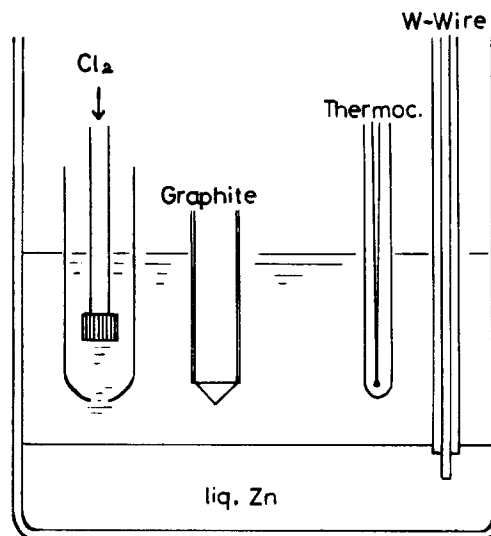


Fig. 1. Experimental cell.

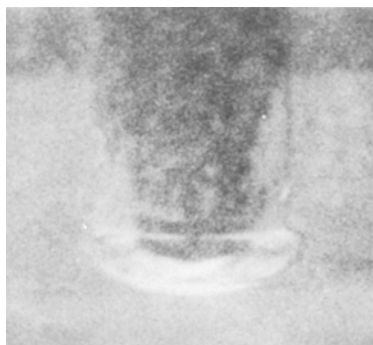


Fig. 2. Photograph of anode effect.

through this gas film can be observed. This anode effect makes the continuation of electrolysis impossible, and hence there exists a maximum current density for stable electrolysis.

**2.3.2. Critical current density.** The critical current density defined here as the electrolysis current where the anode effect suddenly occurs, is reported for various electrolyte pretreatment conditions in Fig. 3.

The data strongly suggests that contamination by  $\text{OH}^-$  ion in the electrolyte plays a role in the anode effect. For experiments 2–6, a longer purge period with chlorine gas at a temperature slightly above the melting point increased the critical current density. This tendency is due to an

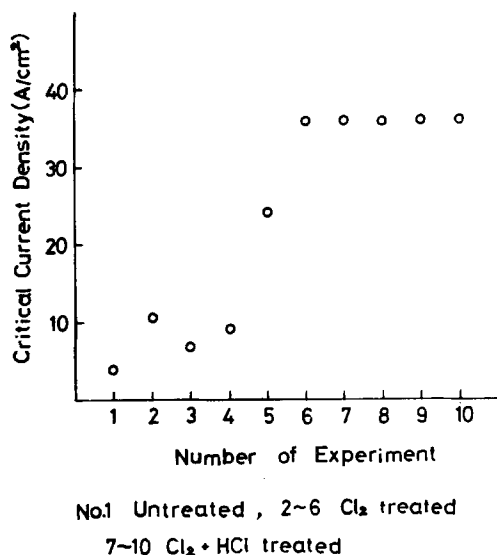
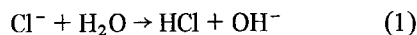
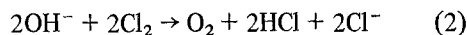


Fig. 3. Effect of dehydration on the critical current density.

incomplete dehydration procedure for the salt when  $\text{OH}^-$  ion in the electrolyte results.



When this salt is melted under a dry chlorine gas atmosphere, the  $\text{OH}^-$  ion can be removed by the following reaction:



When the temperature is raised to  $450^\circ\text{C}$ , Reaction 2 does not proceed any more and a small amount of  $\text{OH}^-$  ion remains. When, however, dry hydrogen chloride gas is bubbled into the electrolyte at this temperature, Reaction 1 occurs from right to left and  $\text{OH}^-$  ion can be removed almost completely as water vapour. Therefore, the best pre-treatment for obtaining a high critical current density is to raise the temperature under a chlorine gas atmosphere up to the melting point; then the melt temperature should be raised up to the desired electrolysis temperature under a dry hydrogen chloride gas atmosphere. The results of experiments 7–10 show a maximum critical current density due to the minimum amount of  $\text{OH}^-$  ion. In addition, when  $\text{KOH}$  was added to the electrolyte, a drastic decrease of the critical current density was observed as shown in Fig. 4.

The anode effect might be attributed to the C–O bond formation on the graphite electrode surface, which is the intermediate product of the  $\text{OH}^-$  ion discharge on the graphite surface. This C–O bond on the surface might cause an increase of the interfacial tension and hence the strong

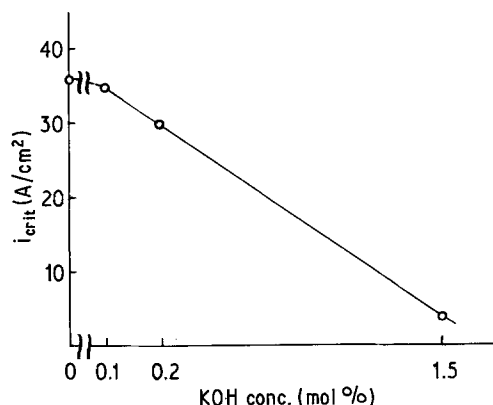


Fig. 4. Effect of  $\text{KOH}$  addition on the critical current density.

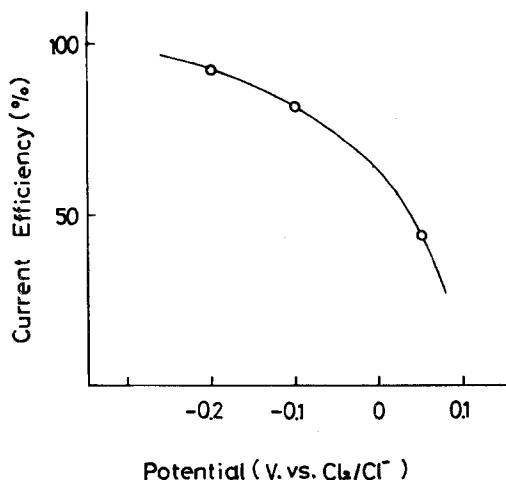


Fig. 5. Current efficiency of CO<sub>2</sub> production (NaCl-KCl-ZnCl<sub>2</sub>, 300° C).

adhesion of the bubble to the electrode surface. In fact, CO<sub>2</sub> evolution at the chlorine evolution potential was observed as shown in Fig. 5, although the melt composition is different in this case and C-O bond formation on the electrode surface might be a reasonable explanation.

**2.3.3. Maximum current density.** The above data allow a qualitative understanding of the conditions required to obtain a high maximum current density. But it should be noted here, that continuous electrolysis with the critical current density is not possible. For example, in the system which shows the critical density of 35 A cm<sup>-2</sup>, the maximum stationary current density is only about 20 A cm<sup>-2</sup>. It is therefore impossible to determine the maximum current density accurately and one should confirm this maximum current density with the use of a practical cell; dehydration of the electrolyte is very necessary not only for preventing side reactions such as CO<sub>2</sub> evolution but also for getting a high maximum current density.

### 3. Macro-electrolysis of molten zinc chloride by the use of 100 A bench-scale cell

Macro-electrolyses were carried out to identify problems for future larger-scale systems.

#### 3.1. Experimental method and apparatus

Fig. 6 shows the experimental cell. When con-

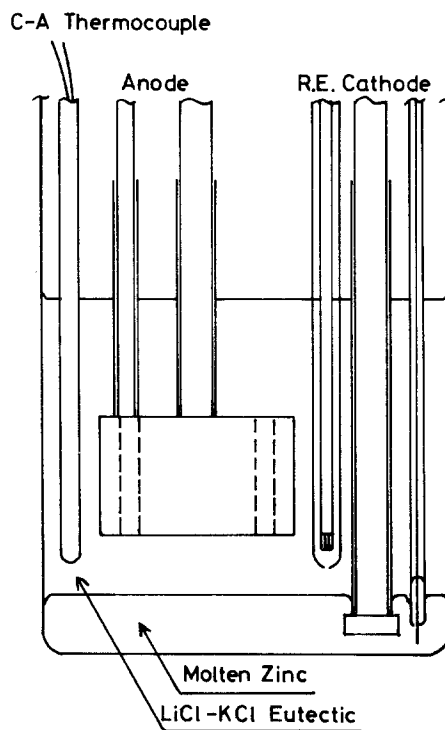


Fig. 6. Electrolytic cell.

structing this cell, the anode effect discussed above was taken into account. For the cathode, 1 kg of molten zinc was used which gave an apparent surface area of 0.86 dm<sup>2</sup>. A graphite cylinder (6 cm diameter × 3 cm height) was used as the anode, 6 holes were drilled in it to accelerate the desorption of the chlorine gas. Two leads were connected to both the anode and the cathode, one for current feed, the other for potential measurements.

A chlorine gas electrode was used as the reference electrode. As the electrolyte, a LiCl-KCl eutectic melt containing a relatively low concentration of ZnCl<sub>2</sub> was used to prevent vaporization of zinc chloride and to minimize the aggressive nature of the zinc chloride against the cell material. The electrolysis temperature was set as 450° C, and the cathode-anode distance was set at 1.5 cm. Photographs were taken when necessary.

#### 3.2. Results and discussion

Anodic polarization characteristics at various zinc chloride concentrations are shown in Fig. 7.

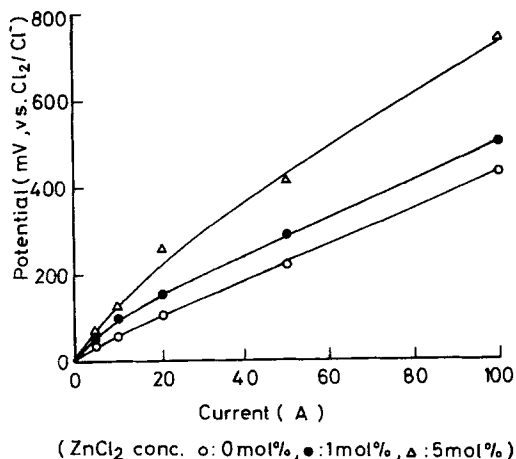


Fig. 7. Anodic polarization curves on graphite anode at several  $\text{ZnCl}_2$  concentrations.

The lower the concentration, the smaller is the polarization observed. This may be due to the lower extent of contamination by water from the zinc chloride addition. The water contamination might cause C-O bonds on the anode surface as discussed above, which might retard the evolved chlorine gas desorption. Cathodic polarization on the other hand, decreases as the zinc chloride concentration increases. The theoretical decomposition voltage is lowest at the lower zinc chloride concentration. Figs. 8 and 9 show the inside of the electrolytic cell. Stable electrolysis can be seen in these figures.

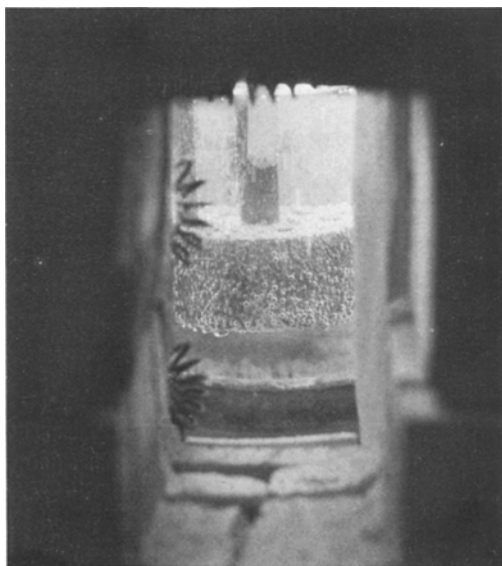


Fig. 8. Photograph of anode (LiCl-KCl, 10 A, 450°C).

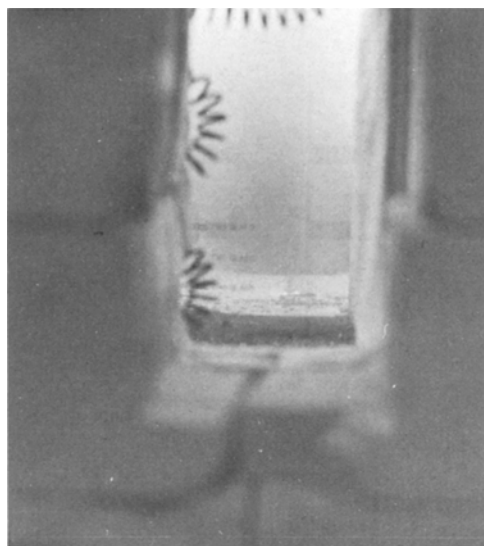


Fig. 9. Photograph of anode ( $\text{ZnCl}_2$  5 mol%, 100 A, 450°C).

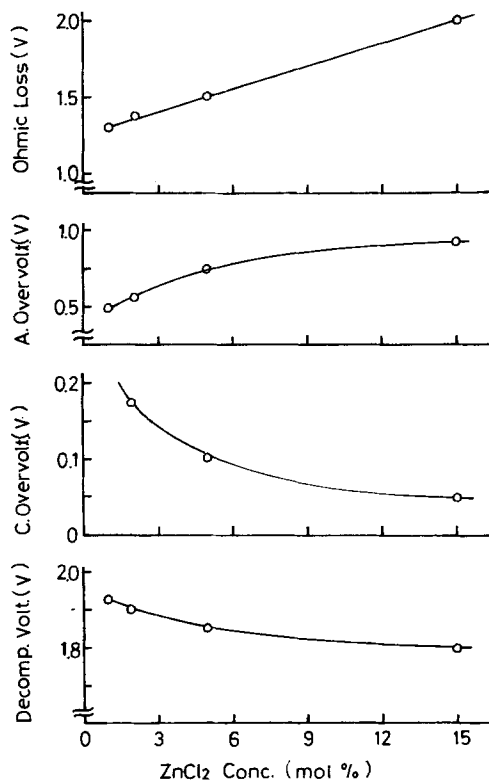


Fig. 10. Zinc chloride concentration dependence of various factors.

Table 1. Dimensions for 100 A cell

Cathode area	0.86 dm <sup>2</sup>
Anode size	60 cm × 30 cm
Electrode distance	15 mm
Optimum ZnCl <sub>2</sub> concentration	2 mol%
Cell voltage	5.7 V
Electric power	0.57 kW
Watt-hour	1.12 kW h kg <sup>-1</sup> of ZnCl <sub>2</sub>

The data and discussions above allow an estimation of the optimum zinc chloride concentration. Fig. 10 shows the zinc chloride concentration dependence of various factors. In this cell, however, the limiting current density is not higher than 100 A dm<sup>-2</sup> at a concentration of 1 mol%. This is not desirable in a practical cell and a concentration of more than 2 mol% is necessary to get an acceptable current density. Thus the most suitable concentration is about 2 mol%. At this concentration, corrosion due to zinc chloride is not rapid.

The dimensions necessary for a 100 A bench-scale cell are summarized in Table 1. In the table, the diameter of the anode graphite is assumed to be 2.5 cm, although the experiments were carried out with a graphite rod of diameter 1 cm. In this type of cell, the electricity power consumption can be calculated as 1120 W h kg<sup>-1</sup>.

#### 4. Bench-scale tests for the whole process

Based on the experimental results above and in the previous paper [1], a bench-scale cell of 100 A capacity for the whole process was constructed and examined in order to determine its performance.

##### 4.1. Experimental methods and apparatus

Fig. 11 shows the experimental cell with a diameter of about 20 cm. 100 kg zinc metal was placed in the bottom of this cell; the height of zinc was about 6.5 cm. The electrolyte was LiCl (667 g)-KCl (831 g), and these salts were melted under a dry argon atmosphere. The height of the melt was about 4.0 cm. The anode graphite was perforated with 6 holes of 7 mm diameter. The cathode lead was a stainless steel rod. To measure the lead resistance, two leads were attached to the cathode and the anode, one for current feed, the other for potential measurements. To protect the silicon rubber stopper from thermal attack from the cell bulk, a stainless steel flange was used to ensure air cooling. Fig. 12 shows the NH<sub>4</sub>Cl feeding capsule. Four such capsules were put into the electrolyte, each one of which stayed 10 min in the electrolyte. Capsule exchange was carried out every 2.5 min to keep the NH<sub>4</sub>Cl feed constant.

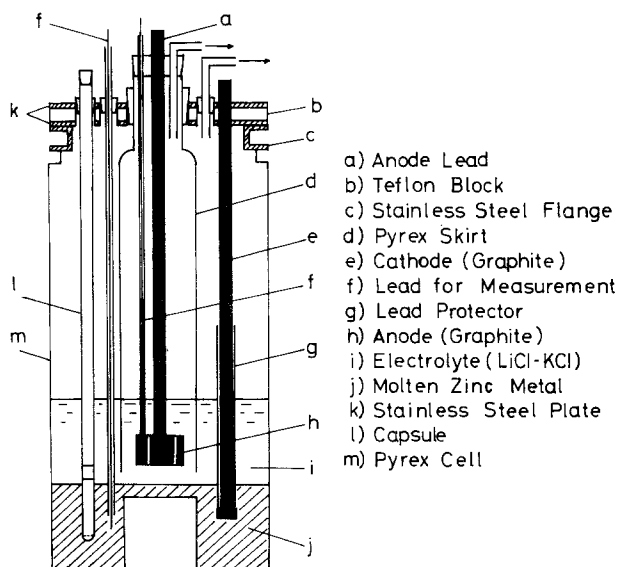


Fig. 11. Bench-scale cell.

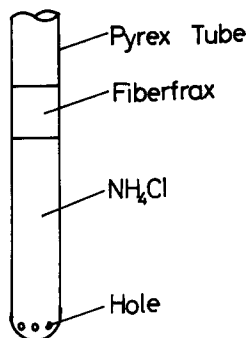


Fig. 12.  $\text{NH}_4\text{Cl}$  feeding capsule.

Each capsule contains 5 g of  $\text{NH}_4\text{Cl}$  and more than 90% has sublimed in ten minutes. The electrode distance was set visually to be about 1.5 cm, because  $\text{NH}_4\text{Cl}$  gas hold-up in the liquid metal caused changes in the cathode level, and it was very difficult to set the electrode distance before electrolysis.

#### 4.2. Results and discussion

The conversion efficiency of  $\text{NH}_4\text{Cl}$  was found to be 74% by chemical analysis. This is not high enough and more detailed study of the reaction between  $\text{NH}_4\text{Cl}$  and liquid metal is planned. Unreacted  $\text{NH}_4\text{Cl}$  dissolved in the electrolyte and moved towards the anode where it was oxidized.

This caused a decrease in the chlorine evolution current efficiency. For example, only 54.0% was obtained at 40 A. The current efficiency of the zinc chloride electrolysis itself was, on the other hand, almost 100%, as shown in [1].

#### 5. Conclusions

Bench-scale tests showed the efficiency to be too low although the bench-scale electrolytic cell worked well. The low efficiency is attributed to the insufficient reaction rate between  $\text{NH}_4\text{Cl}$  and liquid metal. To improve this reaction efficiency, separation of the chemical reaction and the electrolysis might be recommended. Using such separate systems, a 100% reaction efficiency should be possible.

#### Acknowledgement

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#### References

- [1] Y. Ito, T. Ohmori, S. Nakamatsu and S. Yoshizawa, *J. Appl. Electrochem.* **10** (1980) 000.