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The recovery of chlorine from by-product hydrogen chloride
Part 2: molten metal cathode method

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A new method of recovering chlorine from by-product hydrogen chloride is proposed and developed. According to the reaction $Me+2HCl = MeCl_2+H_2$ (Me = Metal) hydrogen chloride is reduced to give hydrogen and metal chloride. Gaseous hydrogen was drawn out from the reaction system and the metal chloride dissolved in the electrolyte, where it was electrolysed to give chlorine and metal using molten metal as a cathode. The metal was recovered on the cathode in a molten state and re-used for the former reaction. Bench scale tests were also carried out, where zinc was used as a molten metal cathode and the cell capacity was about 50 A. The cell voltage was 6·5 V at 50 A (working temperature 560°C, distance between anode and cathode 5 mm) and in this case, the ohmic loss was about 70%. The current efficiency was about 90% (anodic current density 200 A/dm^2) when the working temperature was 500°C and electrode distance between anode and cathode was 18 mm.

This method seems very promising on the basis of the above-mentioned data.

Introduction

In Part 1 (p. 245), the direct electrolysis of hydrogen chloride gas using a molten salt as the electrolyte was reported. We would propose another new method, in which two successive reactions occur; i.e. chemical reduction of hydrogen chloride by molten metal followed by electrolysis of the metal chloride formed. This method has not only the advantages described previously but also the following merits.

(1) A diaphragm is not necessary, which is the main cause of ohmic loss.

(2) A gas diffusion-type electrode is not necessary. These need delicate care in order to get a continuous and most effective gas flow rate, to prolong the life-time of the electrode.

Method and apparatus

Hydrogen chloride gas is bubbled into a molten metal which is in the form of a pool on the bottom of the cell under the molten salt of lithium chloride (58 mol%)-potassium chloride (42 mol%), resulting in the reaction,

$$Me+2HCl = MeCl_2+H_2 \qquad (1)$$

where Me = Metal.

Hydrogen is drawn out from the reaction system as a gas, and the metal chloride produced dissolves in the molten salt electrolyte. It is electrolysed there, with the molten metal acting as the cathode.

Metal is recovered on the cathode in a molten state according to the reaction.

$$MeCl_2 = Me+Cl_2 \qquad (2)$$

and re-used as the reactant for the reaction (1).

Compared to other indirect electrolysis methods using aqueous solutions, the reaction rate of the reaction part is very much higher owing to the high temperature and also to the gas-liquid reaction involved, so that much more current can be obtained for the same electrolytic

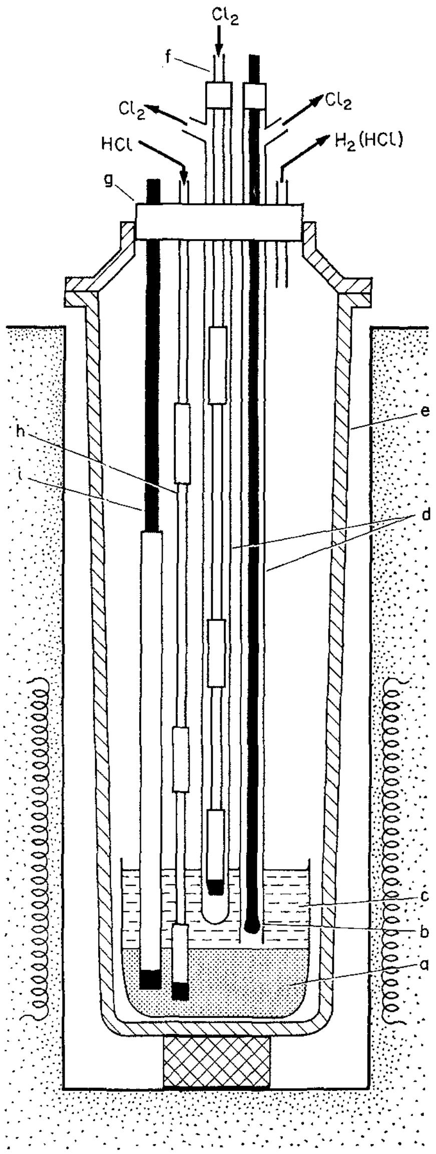

Fig. 1. Electrolytic cell. a: molten zinc metal cathode; b: graphite anode; c: LiCl–KCl eutectic mixture; d: pyrex glass holder; e: pyrex glass cell; f: reference electrode; g: silicon rubber stopper; h: carbon pipe; i: graphite lead (cathode).

cell area.

Graphite is used as an anode. Fig. 1 shows the experimental cell. Fig. 2 shows the principle of a reaction part.

Zinc as a molten metal cathode

Reaction between zinc and hydrogen chloride

Fig. 3 shows the relationship between hydrogen chloride gas flow rate and hydrogen evolution rate, when the apparatus shown in Fig. 2 is used.

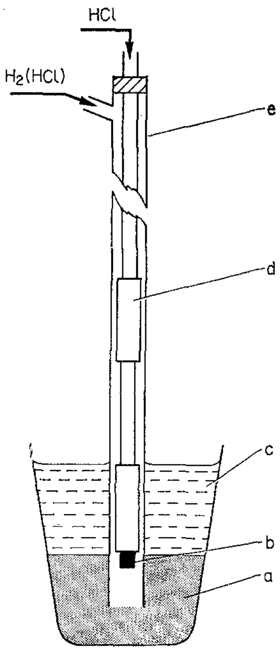

Fig. 2. Reaction cell ($Me+2HCl = H_2+MeCl_2$; Me = Metal).

The conversion efficiency of hydrogen chloride to hydrogen is calculated according to the equation

$$Zn+2HCl = ZnCl_2+H_2 \qquad (3)$$

and summarized in Table 1.

Table 1. Conversion efficiency of hydrogen chloride to hydrogen

HCl gas flow rate (ml/min)	*H_2 evolution rate (ml/min)*	*Efficiency (%)*
33·0	7·7	46·7
65·0	13·3	40·9
125·0	18·7	29·9
185·0	21·8	23·6
240·0	25·0	20·8
325·0	30·7	18·8

Hydrogen evolution rate increases as the supplying rate of the hydrogen chloride gas increases, but conversely the conversion efficiency decreases. In order to increase this efficiency, the method of supplying gas must be improved. In our experiment, the stirring of the solution is also

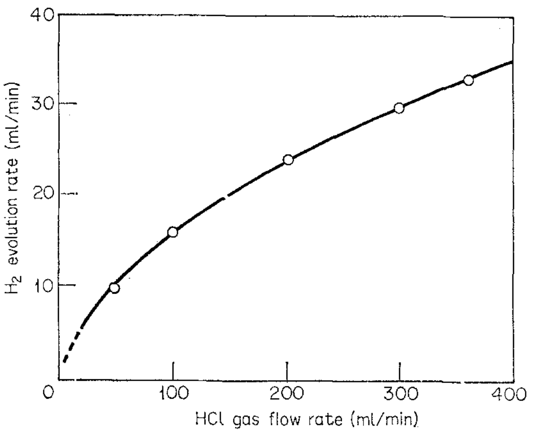

Fig. 3. Relationship between hydrogen chloride gas flow rate and hydrogen evolution rate.

by means of gas bubbling which is somewhat violent, thus this low conversion efficiency is not surprising. The other reason for this low conversion efficiency is the difficulty of getting a dense carbon pipe, which makes it difficult to get an optimum gas flow rate by applying a high pressure inside the pipe.

Current-voltage characteristics at anode and cathode

Figs. 4 and 5 show the current-voltage characteristics at both the anode and the cathode. No anodic overvoltage is observed in the range of our experiment. Cathodic potential shows about the same value at any current density, i.e., $-1 \cdot 8$ V vs. chlorine reference electrode. The theoretical decomposition voltage of zinc chloride is 1·6 V, so it seems that the produced zinc chloride is not electrolysed directly in the form of pure zinc chloride near the electrode but after dissolving in the electrolyte and becoming somewhat diluted.

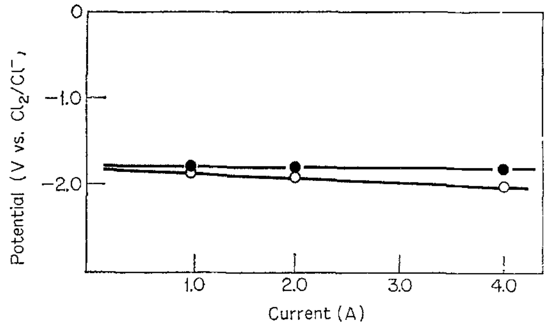

Fig. 4. Current-potential characteristics of the cathode. ○: observed values; ●: values provided there are no ohmic losses. A cross-sectional area of the pyrex glass holder is about 3·0 cm^2.

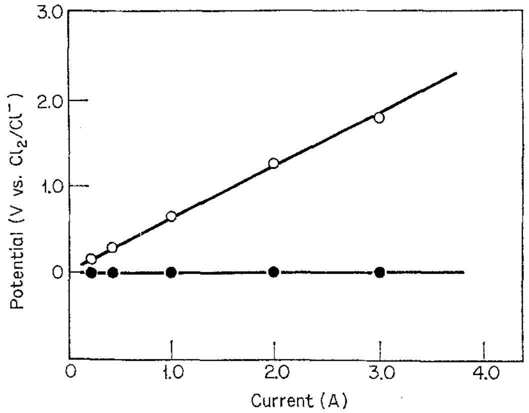

Fig. 5. Current-potential characteristics of the anode. ○: observed values; ●: values provided there are no ohmic losses. A cross-sectional area of the pyrex glass holder is about 3·0 cm^2 and the anode area is about 2·0 cm^2.

Voltage balance

The most important merit of this method is that the diaphragm is not necessary. In principle, the electrode distance can be made as short as that in the case of the mercury-amalgam sodium chloride electrolysis. But in our experiment, no attention was paid to the structure of the graphite anode, and so, in order to prevent mixing of the hydrogen and chlorine produced, more than 4 mm is needed under the electrolysis condition of 4 A(240 A/dm^2). Total ohmic loss is 0·2 Ω, of which the loss in the electrolyte is the most important. By improving the structure of the graphite anode, this kind of loss can be largely decreased. Fig. 6 shows the voltage balance under operations.

Current efficiency

Fig. 7 shows the current efficiency of the anode. Current loss at the anode seems due to the recombination of the evolved chlorine and zinc metal, which must be minimized by improving the cell structure.

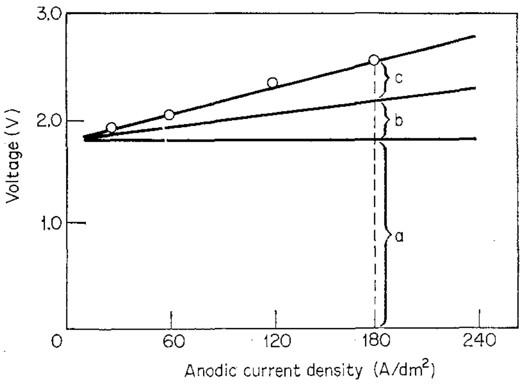

Fig. 6. Voltage balances under operations. (a+b+c): observed cell voltages; a: cell voltages provided there are no ohmic losses; b: ohmic losses caused by the electrolytic parts; c: ohmic losses caused by the leads etc.

Examination with other liquid metals

Zinc metal is not very expensive and the zinc chloride produced is easily soluble in the electrolyte and also not very volatile; therefore it is very suitable for our method. However, other methods may be more suitable. Table 2 shows some characteristic thermodynamic data for various chlorides. From these data, it is evident that there are some other metals which have the ability to produce chloride of which the decomposition voltages are lower than that of zinc chloride and in addition, the ability to react with hydrogen chloride.

Table 2a. Standard free energy change of the reaction $Me+2HCl = MeCl_2+H_2$ (500°C) (Me = Metal)

Me	$-\Delta F^\circ$ *(kcal/mol)*	*Melting point of the metal (°C)*
Sn	9·7	231·8
Pb	11·2	327·4
Cd	17·5	320·9
Zn	26·2	419·5

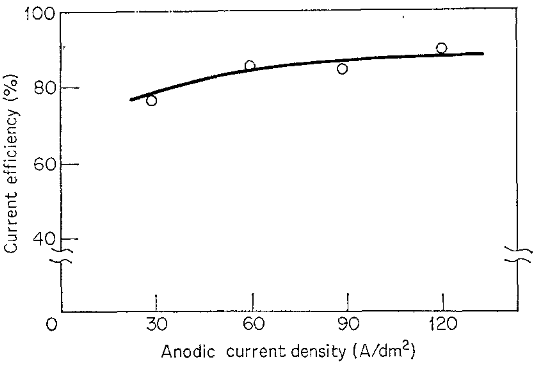

Fig. 7. Relationship between anodic current density and current efficiency.

Table 2b. Some characteristic values of various chlorides

Chlorides	$-\Delta F^\circ$ *(kcal/mol)*	E° *(volts)*	*Melting point (°C)*
$ZnCl_2$	73·9	1·61	290
$CdCl_2$	64·7	1·41	563~568
$PbCl_2$	57·1	1·24	501
$SnCl_2$	58·5	1·27	247
HCl	47·4	1·03	—

Values of $-\Delta F^\circ$ are calculated according to the following equation at 500°C

$$Me+Cl_2 = MeCl_2 \text{ (Me = Metal)}$$

For a metal to be suitable for our method it must have a low melting point and form a chloride of which the melting point is also low. But in the case of the chloride, the low melting point is not absolutely necessary because it is possible for the chloride to form a mixture with the electrolyte immediately and this can melt at a lower temperature. From these viewpoints, cadmium, lead, and tin were selected and examined in addition to zinc.

Fig. 8 shows the relation between the standard free energy change for the reaction (1), and hydrogen evolution rate. The limiting current tends to change in the same manner.

As mentioned above, the smaller the decomposition voltage, the smaller the current obtained. But if the dispersibility of the gas in the molten metal is good and the reaction surface of the liquid and gas is sufficiently high, large currents are obtainable, even when the corresponding metal chloride has a low decomposition voltage. Therefore, the metal to be used depends largely on the scale and purpose of the cell. Thus when only a low current density is needed, tin or lead is recommended, but when a large current density is needed, zinc or cadmium is recommended. The anode shows no overvoltage except for an ohmic loss.

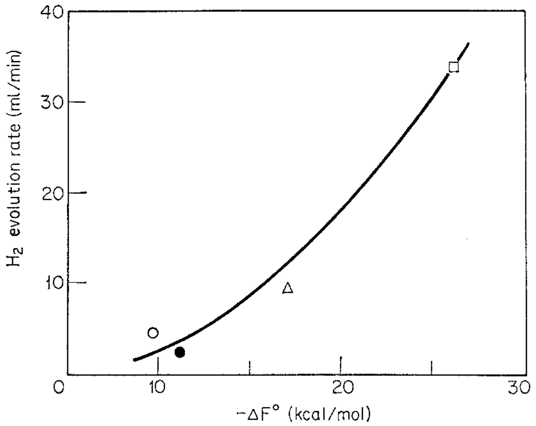

Fig. 8. Relationship between standard free energy change for the reaction $Me+2HCl = MeCl_2+H_2$ (Me = various metals) and hydrogen evolution rate. □: Zn; △: Cd; ●: Pb; ○: Sn; temperature: 500°C; HCl gas flow rate: 400 ml/min.

Bench scale tests

Bench scale tests were also carried out, using the apparatus shown in Fig. 9. The cell capacity is about 50 A. Zinc is used as a molten metal cathode. Fig. 10 shows the details of anode and the hydrogen chloride feeding pipe. A selenium rectifier is used as the power source. Table 3 shows the conversion efficiency of hydrogen chloride to hydrogen gas, which is calculated according to equation (3). Figs. 11 and 12 show the electrolytic current-voltage curves as a function of the electrode distance and the temperature, respectively. Figs. 13 and 14 show the current efficiency as a function of the electrode distance and the anodic current density. Fig. 15 shows the voltage balance under operation. Ohmic loss is large and this is the main engineering problem for the future.

Table 3. HCl conversion efficiency

HCl gas flow rate (ml/min)	*H_2 evolution rate (ml/min)*	*Reduced current (A)*	*Conversion efficiency (%)*
750	400	53	53·3
1000	450	60	45·0

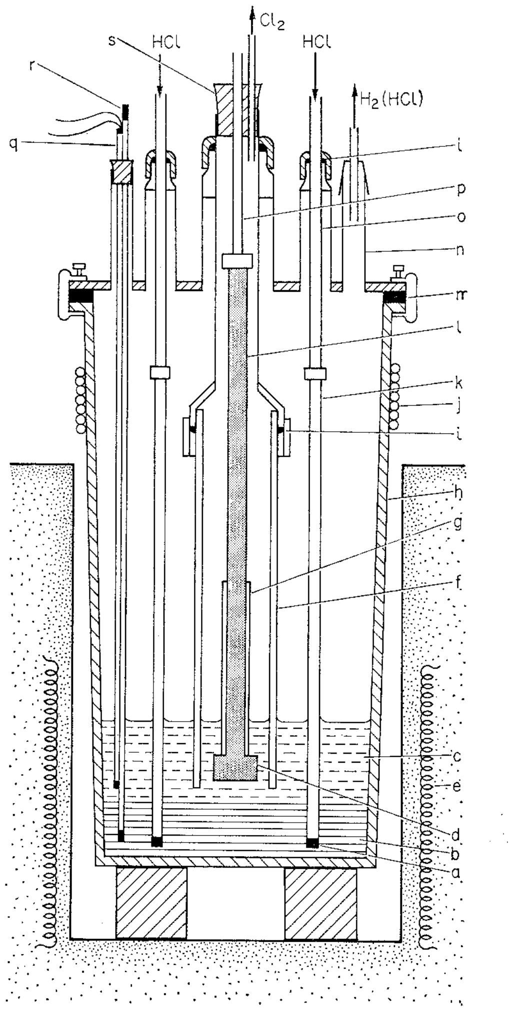

Fig. 9. 50 A-electrolytic cell. a: porous carbon; b: molten zinc metal; c: electrolyte (LiCl–KCl); d: electric furnace; f: skirt; g: anode lead protector; h: cell; i: asbestos packing; j: cooling tube; k: carbon pipe; l: anode lead; m: teflon packing; n: stainless steel cap; o: stainless steel pipe; p: anode lead (stainless steel); q: thermocouple; r: cathode lead (stainless steel); s: silicon rubber.

Conclusion

A new method has been proposed and developed for the recovery of chlorine from hydrogen chloride.

Hydrogen chloride gas was led into a molten metal, where the reaction

$$Me+2HCl = MeCl_2+H_2 \quad \text{(Me = Metal)} \qquad (1)$$

occurred.

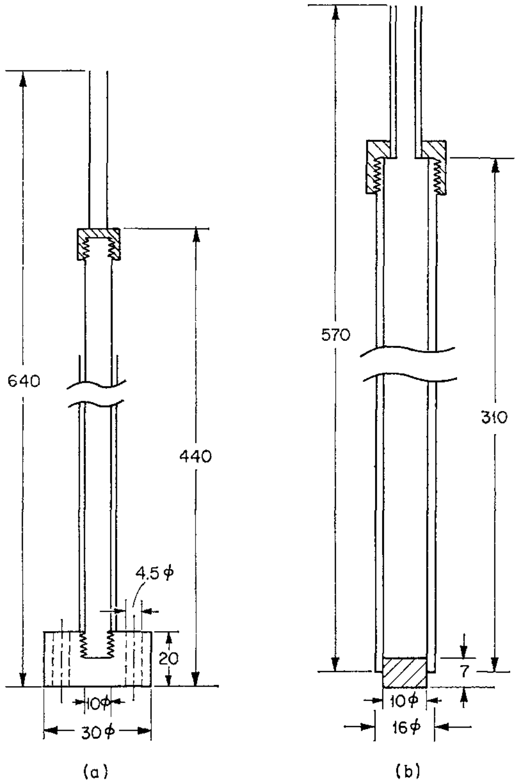

Fig. 10. Details of anode (a) and HCl feeding pipe (b) (unit mm).

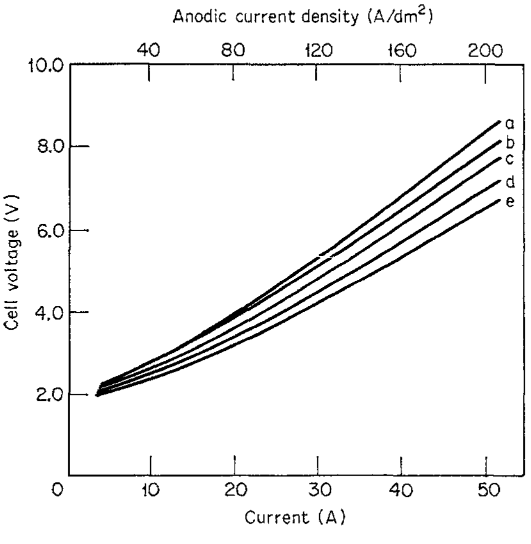

Fig. 11. Current-voltage characteristics with a parameter of the distance between electrodes (560°C). a: 18 mm; b: 15 mm; c: 10 mm; d: 7 mm; e: 5 mm.

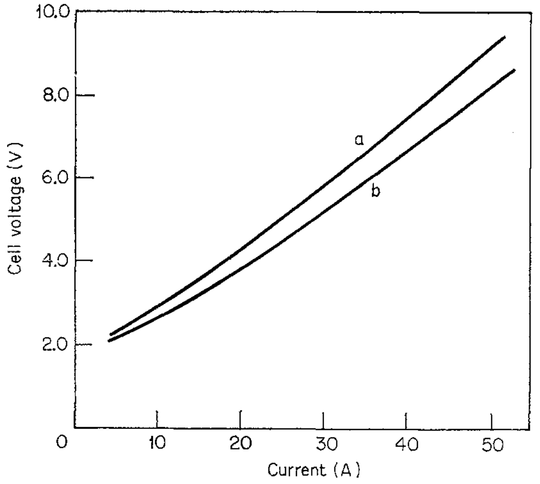

Fig. 12. Current-voltage characteristics with a parameter of temperature (electrode distance 18 mm). a: 500°C; b: 560°C.

Gaseous hydrogen was drawn out from the reaction system. The metal chloride dissolved into the electrolyte, where it was electrolysed using molten metal as a cathode. The metal was recovered at the cathode in the molten state and recycled. Graphite was used as the anode.

As an electrolyte, the molten salt of lithium chloride (58 mol%)–potassium chloride (42 mol%) was used. As a cathode molten metal, zinc, tin, lead and cadmium can be used.

Bench scale tests were also carried out using zinc as the cathode molten metal and the capacity of the cell was about 50A. The cell voltage was 6·5 V at 50 A (working temperature 560°C, distance between anode and cathode 5 mm), and in this case the ohmic loss was about

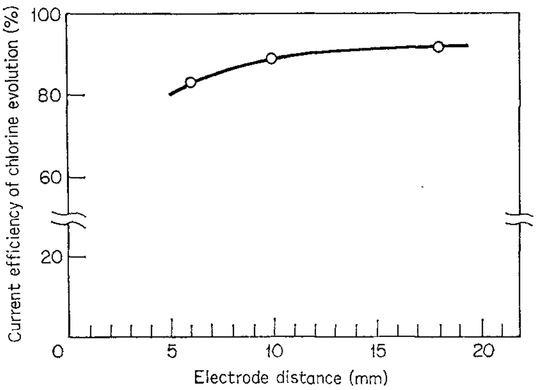

Fig. 13. Relationship between electrode distance and current efficiency (anodic current density 200 A/dm², 500°C).

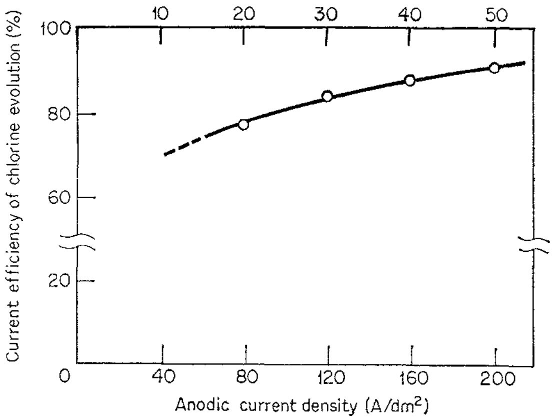

Fig. 14. Relationship between current densities and current efficiency (electrode distance 18 mm, 500°C).

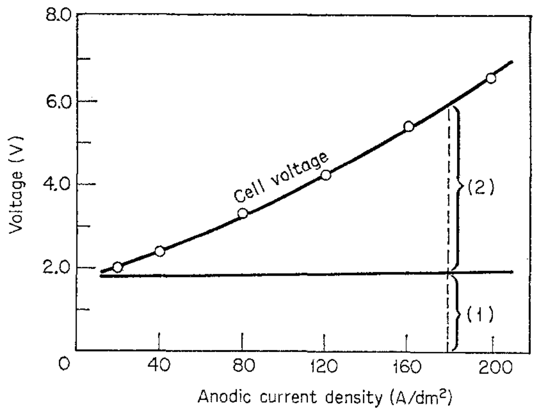

Fig. 15. Voltage balances under operations (electrode distance 5 mm, 560°C). (1) theoretical decomposition voltage + overvoltage; (2) ohmic loss.

70%. The current efficiency was about 90% at 50 A (anodic current density 200 A/dm²), when the working temperature was 500°C and the electrode distance between anode and cathode was 18 mm. The conversion efficiency of hydrogen chloride to hydrogen was 50% and this value was independent of the electrolytic current densities.

From the data mentioned above, it can be concluded that this method is also very promising.

Acknowledgments

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