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Oxygen depolarized electrolysis of sodium chloride by the use of a β-alumina–molten salt system

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This paper is concerned with oxygen depolarized electrolysis of NaCl by the use of β-alumina solid electrolyte and molten salts. In the electrolysis, dry chlorine gas and pure molten sodium hydroxide are produced from sodium chloride, oxygen and water. Because the oxygen reduction proceeds very smoothly in the molten sodium hydroxide, this process is very promising for the future. The theoretical decomposition voltage of this process is estimated to be 1.5 V, which is lower than that of the process without an oxygen cathode by 1.1 V. The model cell study shows that a terminal voltage of 3 V at 50 A dm^{-2} is attainable.

1. Introduction

Since 1974, a new method for electrolysis of sodium chloride by the use of a β-alumina–molten salt system has been studied by the authors. The method is intended to take the place of the mercury cell electrolysis and has been detailed in this Journal previously [1]. The advantages of the process are as follows:

(a) dry chlorine gas and high-purity molten sodium hydroxide are produced
(b) voltage losses caused by ohmic drop and overvoltage can be reduced
(c) no energy is required for concentrating dilute sodium hydroxide solution

Reduction of electrical energy for producing sodium hydroxide is of greater importance in the chlor-alkali industries and many attempts have been made to achieve this objective. If hydrogen is not required, the decomposition voltage can be decreased by using oxygen as a depolarizer at the cathode. Oxygen depolarized electrolysis in the ion exchange membrane process has been investigated by Yeager [2] from such a point of view. However, the oxygen cathode in alkaline solution requires a large amount of noble metal electrocatalyst. Thus, low cost, non-noble metal electrocatalysts must be used in order to exploit the oxygen depolarized process. In molten sodium hydroxide, the oxygen reduction reaction proceeds very smoothly without any noble metal electrocatalyst [3]. This paper describes an investigation into the possible use of the oxygen depolarized electrolysis of NaCl by the use of a β-alumina–molten salt system.

2. Principle of this method

Fig. 1 shows the scheme of this method. As a diaphragm, sodium ion conducting β-alumina is used. The catholyte is molten sodium hydroxide with a small amount of water. The anolyte consists of a molten mixture of NaCl and $ZnCl_2$. On electrolysis, oxygen and water vapour, which are bubbled into the catholyte, are reduced at the cathode to produce hydroxide ions, according to the following equation,

$$1/4\ O_2 + 1/2\ H_2O + e \rightarrow OH^- \qquad (1)$$

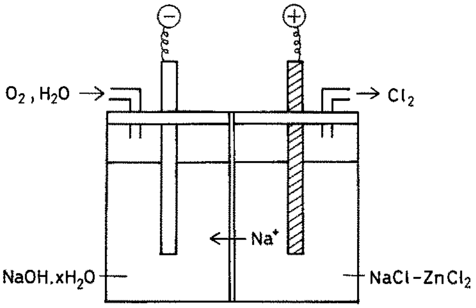

Fig. 1. Scheme of oxygen depolarized electrolysis of molten NaCl by the use of a β-alumina diaphragm.

At the anode, chlorine gas is evolved, according to the following equation,

$$Cl^- \rightarrow 1/2\ Cl_2 + e \qquad (2)$$

Only sodium ions can move from the anolyte to the catholyte through the β-alumina diaphragm, because the transport number of the sodium ion in β-alumina is unity. The overall reaction of the electrolysis is as follows:

$$\begin{aligned}&NaCl\ (\text{in } NaCl\text{–}ZnCl_2) + 1/2\ H_2O_{(g)}\\&\quad + 1/4\ O_{2(g)} \rightarrow NaOH_{(l)} + 1/2\ Cl_{2(g)}\end{aligned} \qquad (3)$$

By this method, molten sodium hydroxide and dry chlorine gas can be obtained. The cell voltage can be expected to be about 1 V lower than that for the process without the oxygen cathode.

3. Estimation of theoretical decomposition voltage

The theoretical decomposition voltage at 623 K was determined as follows. The free energy change ΔG of the reaction

$$NaCl\ (\text{in } NaCl\text{–}ZnCl_2) = Na_{(l)} + 1/2\ Cl_{2(g)} \qquad (4)$$

is calculated to be 368 kJ mol^{-1} from the decomposition voltage of sodium chloride in the molten mixture of NaCl and ZnCl$_2$ (40–60 mol %) [4]. The standard free energy change of water decomposition

$$H_2O_{(g)} = H_{2(g)} + 1/2\ O_{2(g)} \qquad (5)$$

is given as $\Delta G = 213.8$ kJ mol^{-1} [5]. The standard free energy of formation of the molten sodium hydroxide

$$Na_{(l)} + 1/2\ H_{2(g)} + 1/2\ O_{2(g)} = NaOH_{(l)} \qquad (6)$$

is given as $\Delta G = -330.8$ kJ mol^{-1} [5]. From these three values, the theoretical decomposition voltage E_d of Reaction 3 is calculated to be 1.5 V. This value is 1.1 V lower than that of the process without the oxygen cathode calculated by using the same data*.

4. Experimental details

Fig. 2 shows the experimental apparatus. As the diaphragm, a β-alumina tube (37 mm diameter, 2 mm thickness, 110 mm length, NGK Spark Plug Co. Ltd) was used. Molten sodium hydroxide was used as catholyte and occupied the inside of the β-alumina tube. As the anolyte, a mixture of NaCl and ZnCl$_2$ (40 and 60 mol % respectively), both previously dehydrated, was used. A cylindrical porous gas diffusion electrode, made of sintered porous nickel (Sumitomo Electric Co. Ltd), was employed as the oxygen cathode. Oxygen gas was introduced to the cathode through a nickel pipe, which also served as the lead to the power supply. Water vapour, whose pressure was adjusted before use, was bubbled into the catholyte. Excess water vapour and oxygen were taken out of the catholyte compartment to the condenser. All measurements were galvanostatic. The ohmic drop of the experimental cell was determined by a current–interrupter method. The operating temperature was 623 K, because the melting point of sodium hydroxide is about 592 K and the eutectic point of NaCl–ZnCl is 535 K.

5. Results and discussions

5.1. *Decomposition voltage*

Fig. 3 shows an example of polarization characteristics of this process. (Ohmic drop is excluded.) When the experimental data are extrapolated to the point where current density is equal to zero, the intercept of the cell voltage axis is about 1.6 V. This value is close to the theoretical decomposition voltage.

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* The total reaction of the process without the oxygen cathode is

$$\begin{aligned}&H_2O_{(g)} + NaCl\ (\text{in } NaCl\text{–}ZnCl_2) \rightarrow 1/2\ H_{2(g)}\\&\quad + 1/2\ Cl_{2(g)} + NaOH_{(l)}\end{aligned} \qquad (F1)$$

The theoretical decomposition voltage of the reaction is calculated to be 2.6 V from the data used above.

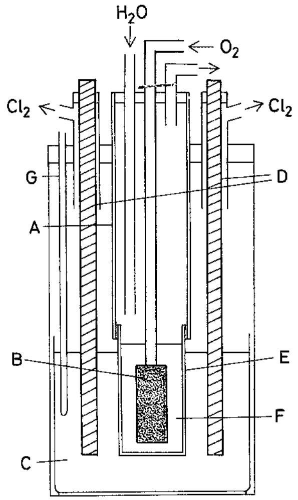

Fig. 2. Experimental apparatus. A: α-alumina tube; B: porous nickel cathode; C: NaCl–$ZnCl_2$ eutectic; D: graphite anode; E: β-alumina tube; F: molten NaOH; G: thermocouple.

5.2. *Current efficiency*

The current efficiency of the anode reaction has been reported previously [6]. In that report, the impurity level and yield of the envolved gas at the anode were determined by gas chromatography. The relationship between the impurity contents of the melt, such as water or oxide ion, and the concentration of O_2, CO_2 or CO in the gas was derived. It was shown that the current efficiency of the anode reaction (chlorine evolution) is more than 99.8% when the melt is treated by hydrogen chloride gas before electrolysis. Here we are concerned with the cathode current efficiency, i.e. NaOH current efficiency.

After long-term electrolysis at 5–20 A dm^{-2}, the sodium hydroxide produced was taken out of the cell and was weighed. The impurity level of the products was determined as follows. Chloride ion content was determined by volumetric analysis (Mohr's method). The contents of nickel ion and zinc ion were determined by atomic absorptiometry. Table 1 shows the specification of the electrolysis. In this electrolysis, excess amounts of water vapour were continuously supplied to the cathode compartment and so unconsumed water vapour was removed from the cell. A small amount of the sodium hydroxide produced was also removed from the cell, accompanied by water vapour. The value of current efficiency shown in Table 1 is not very good. However, this is based only on products what could be weighed, and the parts lost as described above were not taken into account. Therefore, in order to raise the current efficiency of the process, there are still some improvements to be made, especially in the optimization of the water vapour supply. Table 2 shows the results of impurity level analysis. Since the impurity levels of the nickel and the zinc ions were insignificant, it is expected that the impurities cannot go through the β-alumina diaphragm on electolysis. Therefore, it is considered that much of the chloride ion content comes from the chlorine gas evolved at the anode which might pass through the joint between the β-alumina tube and the α-alumina tube. In order to advance this process, research for construction

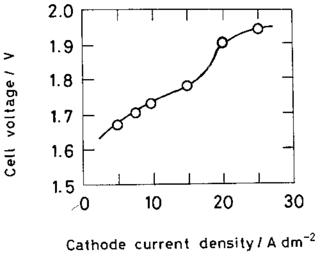

Fig. 3. A typical polarization curve of the process (ohmic drop is excluded).

Table 1. Specification of the electrolysis

Current (A)	*Total quantity of electricity (A h)*	*Yields of NaOH (g)*	*Current efficiency of NaOH production (%)*
1–4	243.3	264.6	72.9

Table 2. The results of impurity level analysis

Number	*Impurities*		
	Cl^- (%)	*Zn^{2+} (ppm)*	*Ni^{2+} (ppm)*
1	1.5	a	a
2	1.0	100	50
3	1.0	a	a
4	0.8	a	a

[a] Not determined.

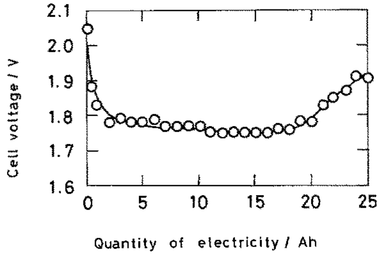

Fig. 4. A typical change of cell voltage during long-term electrolysis at 10 A dm^{-2}.

materials and sealing materials which are compatible both with molten sodium hydroxide and with molten mixtures of NaCl and $ZnCl_2$ is vital.

5.3. *Life of oxygen cathode*

Fig. 4 shows a typical change of cell voltage during long-term electolysis at 10 A dm^{-2}. Just after the start of electolysis the cell voltage indicates a rather high value. However, it then decreases sharply and approaches a constant value, around 1.8 V, which is maintained until the quantity of electricity passed amounts to 20 A h. When the quantity of electricity reaches 20 A h, the cell voltage begins to increase gradually. In this example, the cathode current density was decreased to 5 A dm^{-2} at 25 A h and subsequently the cell voltage was maintained at a constant for more that 10 h. From the potential–pO^{2-} diagram of Ni [3], it is clear that nickel can be oxidized to nickel oxide at the potential where oxygen reduction proceeds. Thus, it is expected that the porous nickel electrode is also oxidized to nickel oxide. Therefore, the reason why the cell voltage began to increase gradually is that the pores of the cathode became choked by nickel oxide during electrolysis, thus reducing the real electrode area.

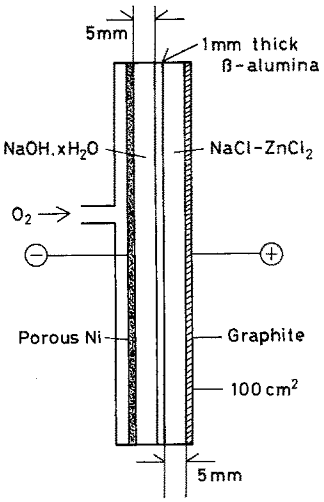

Fig. 5. Model cell for voltage balance calculation.

5.4. *Voltage balance*

The voltage balance of this process was estimated on the basis of the above results and conductivity data. In this case, a rectangular unit cell as shown in Fig. 5 was assumed. The area of cathode, anode and β-alumina diaphragm is 100 cm^2 each. The distances between the cathode and β-alumina, and between the β-alumina and anode are each of 5 mm. The thickness of the β-alumina diaphragm is 1 mm. The cathode is made of porous nickel to the rear side of which oxygen gas is supplied. Water is dissolved in the molten sodium hydroxide before being introduced into the catholyte compartment. The calculated voltage balance for this cell at 623 K is shown in Fig. 6. The conductivities of molten sodium hydroxide, the molten mixture $NaCl–ZnCl_2$ and β-alumina were chosen from the literatures as follows: NaOH – 2.5 S cm^{-1} [7], $NaCl–ZnCl_2$ – 0.34 S cm^{-1} [8], β-alumina – 0.1 S cm^{-1} [9]. The cathode overvoltage was estimated from the polarization characteristics of the porous oxygen cathode in the molten sodium hydroxide [3]. The anode overvoltage was negligible. Fig. 7 shows the voltage balance of the cell used in this experiment. Ohmic drop, besides that of β-alumina, is expected to be the sum of the resistance of the electrolyte, that of the leads and the interfacial resistance between anolyte and β-alumina. By decreasing voltage losses from such

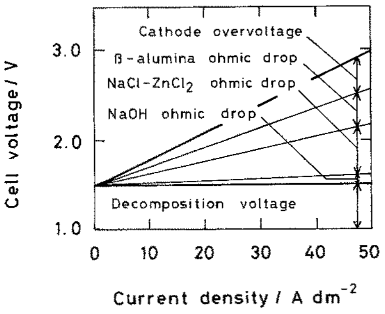

Fig. 6. Calculated voltage balance.

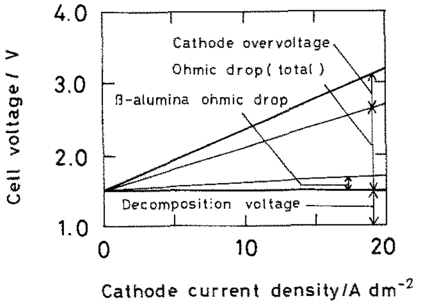

Fig. 7. Voltage balance of the cell used in the experiment.

resistance sources, the voltage balance of the real cell may approach that of the model cell.

6. Conclusion

From the experimental results it was shown that the oxygen depolarized electrolysis of sodium chloride by the use of the β-alumina–molten salt system is very promising. The conclusions are summarized as follows:

1. The theoretical decomposition voltage of this process was 1.5 V and was 1.1 V lower than that of the process without the oxygen cathode. This value was confirmed by the experiments.
2. The terminal voltage of 3 V at 50 A dm^{-2} is attainable when the electrolysis process is optimized.
3. By the long-term electrolysis, it was certified that impurity levels were insignificant.
4. The current efficiency was not good for these experiments. There is still room for improvement, especially in the optimization of water vapour supply.

Though there are still many problems to be solved, such as extending the life time of the cathode, etc., this process shows promise for future industrial application.

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