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A new method for the electrolysis of sodium chloride using a β-alumina-molten salt system

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This paper is concerned with a new process for NaCl electrolysis. The catholyte is molten sodium hydroxide, containing a small quantity of water. The anolyte is the molten mixture of sodium chloride and zinc chloride. As a diaphragm, sodium ion conducting β-alumina is used. By the electrolysis, chlorine, sodium hydroxide and hydrogen are obtained almost quantitatively from sodium chloride and water. The operating temperature is about 330° C. A terminal voltage of 5 V at 40 A dm^{-2} is estimated from the experimental data and by numerical calculation. This process is very promising on the basis of the current efficiency and estimated voltage balance data.

1. Introduction

The mercury cell for the electrolysis of sodium chloride possesses certain disadvantages, in particular that arising from pollution by mercury. The diaphragm cell recommended in its place also leads, however, to difficulties, such as sodium chloride contamination in the produced sodium hydroxide, oxygen contamination in the evolved chlorine gas and the excess energy which is necessary to concentrate the dilute sodium hydroxide solution obtained from the cell. The sodium chloride contamination in the sodium hydroxide is said to cause severe corrosion and to narrow the market for the sodium hydroxide. For example, there is a severe problem from chloride ion contamination in the synthetic fibre industry. Also the high current density of the mercury cell cannot be achieved and long cell life is not expected due to the deterioration of the diaphragm. A promising ion exchange membrane cell is also under development. In this method, however, the concentration of sodium hydroxide is expected to be no higher than 20% and in addition the ion exchange membrane is rather expensive. We would like to propose a new method, by which such difficulties can be avoided.

2. Principle of this method

The method is shown schematically in Fig. 1. The catholyte is molten sodium hydroxide, containing a small quantity of water. The anolyte is a molten mixture of sodium chloride and zinc chloride. As a diaphragm we employed sodium ion-conducting β-alumina which has recently been used in the sodium-sulphur battery [1, 2]. On electrolysis, water in the melt is reduced at the cathode to produce hydrogen, according to the following equation,

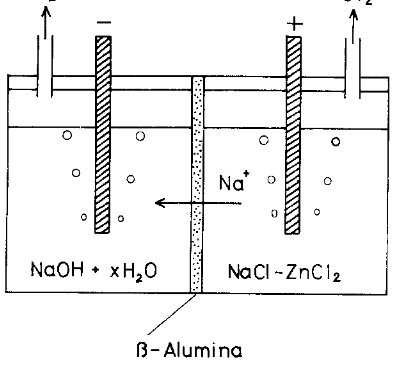

Fig. 1. Scheme of molten NaCl electrolysis using a β-alumina separator.

$$H_2O + e^- \longrightarrow 1/2H_2 + OH^-. \qquad (1)$$

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

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

Sodium ion moves from the anolyte to the catholyte through the β-alumina diaphragm. Thus the overall reaction of this electrolytic cell is as follows,

$$NaCl + H_2O \longrightarrow NaOH + 1/2H_2 + 1/2Cl_2. \qquad (3)$$

By this method, pure molten sodium hydroxide and dry chlorine can be obtained. Also, the overvoltages and ohmic losses can be expected to be lower than in aqueous solution electrolyses because of the higher operating temperature.

3. Outline of experiment

The experimental apparatus is shown in Fig. 2. A β-alumina tube is used as the diaphragm and the sodium hydroxide melt containing a small quantity of water serves as the catholyte inside this tube, which is then immersed in the molten eutectic mixture of sodium chloride and zinc chloride. A nickel rod was used as the cathode and a graphite rod as the anode. The melting point of the pure sodium hydroxide is about 320° C [3] and the eutectic point of sodium chloride-zinc chloride system is 262° C [4]. Therefore all experiments were carried out at about 330° C. All reagents used were of chemically pure grade.

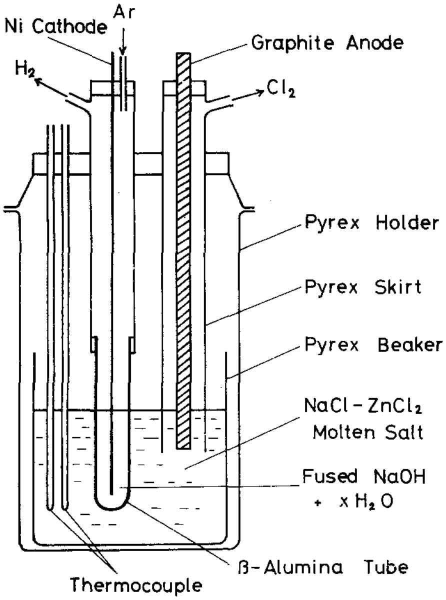

Fig. 2. Experimental cell.

4. Results and discussions

4.1. *Current efficiencies*

Hydrogen was obtained from the cathode compartment, according to reaction (1). The current efficiencies of the cathodic reaction are summarized in Table 1. The reproducibility is not very good, owing to experimental error. For example, the loss of molten hydroxide by vaporization or by frothing made it difficult to determine the produced sodium hydroxide quantitatively. The water content in the melt shown in this table was estimated by coulometry as shown in Fig. 3 where the electrolysis current multiplied by the duration of the first stage (a) of this curve corresponds to the total amount of water in the catholyte.

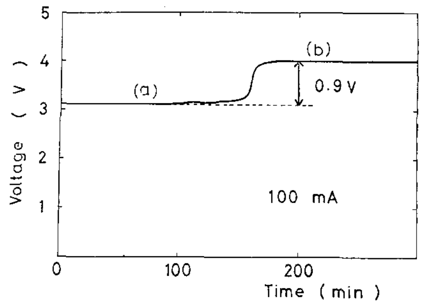

Fig. 3. Voltage-time curve at constant current.

The anodic current efficiencies are shown in Fig. 4. This curve was obtained by determining the evolved chlorine by iodometry. These data provide support for our new process.

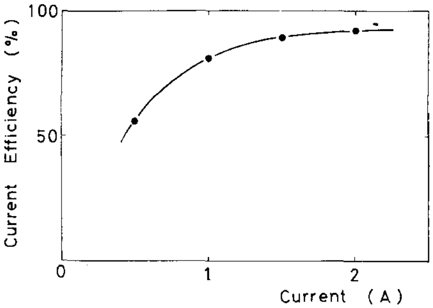

Fig. 4. Anode current efficiency.

Table 1. Cathode current efficiency

Run	*Current* A	*C.D.* A dm^{-2} *β-Al*	*Temp* °C	*H_2O* *wt.%*	*NaOH C.E.* *%*
1	0·1	0·94	330	1·38	–
2	0·2	–	330	1·34	71·7
3	0·3	–	330	1·16	99·6
4	0·3	2·13	380	0·89	89·9
5	0·5	2·70	330	1·65	76·8
6	2·0	10·1	350	0·87	88·5

4.2. *Voltage balance*

4.2.1. Theoretical decomposition voltage. The voltage-time relation during constant current electrolysis is shown in Fig. 3. By eliminating the ohmic loss from this observed value, some information on the decomposition voltage can be obtained. The ohmic loss was measured by the current interruption method. The second stage of this curve (b) after allowing for ohmic loss corresponds to the decomposition voltage of the sodium chloride in a sodium chloride-zinc chloride eutectic. That is, the free energy change ΔG of the reaction

$$\text{NaCl (in NaCl–ZnCl}_2) = \text{Na(l)} + 1/2\text{Cl}_2\text{(g)} \qquad (4)$$

is calculated to be 83 Kcal from the measured decomposition voltage of 3·6 V. The standard free energy change of the water vapour decomposition

$$\text{H}_2\text{O(g)} = \text{H}_2\text{(g)} + 1/2\text{Cl}_2\text{(g)} \qquad (5)$$

is given as $\Delta G° = 51{\cdot}2$ Kcal [5]. The standard free energy of formation of the liquid sodium hydroxide according to the reaction

$$\text{Na(l)} + 1/2\text{H}_2\text{(g)} + 1/2\text{O}_2\text{(g)} = \text{NaOH(l)} \qquad (6)$$

is given as $\Delta G° = -79{\cdot}9$ Kcal [5]. From these three data, the theoretical decomposition voltage E_d of the reaction

$$\text{H}_2\text{O(g)} + \text{NaCl (in NaCl–ZnCl}_2) = 1/2\text{H}_2\text{(g)} + 1/2\text{Cl}_2\text{(g)} + \text{NaOH(l)} \qquad (7)$$

is calculated as $E_d = 2{\cdot}35$ V, corresponding to $\Delta G = 54{\cdot}3$ Kcal for the reaction (7). The observed decomposition voltage obtained by extrapolating the terminal voltage to zero current was 2·7 V, which is not so far from the 2·35 V calculated above.The difference between the two may mainly arise because in our experiment we are not electrolysing water vapour at 1 atm.

4.2.2. Specific resistance of the β-alumina. The specific resistance of the β alumina was measured in the following way using the cell shown in Fig. 2. At first, both sides of the β-alumina tube were filled with molten sodium chloride-zinc chloride eutectic and the resistance of the whole cell was measured both by the current interruption method and the alternating current impedance method. Both data are in good agreement. After that, the β-alumina tube was removed from this cell and the resistance remeasured. The difference of the two measured values can be considered as the resistance of the tube itself. The specific resistance of this β-alumina is then calculated to be 97 Ωcm in a conventional manner. Next, the measurement was repeated, with molten sodium hydroxide in place of the sodium chloride-zinc chloride eutectic melt. The specific resistance measured in this way was 60 Ωcm, rather than 97 Ωcm. This can be attributed to the fact that the wettability of the β-alumina depends on the contacting melt. In our case, the mean value of these two values is taken as the specific resistance of the β-alumina because one side of the tube is in contact with the sodium chloride-zinc chloride eutectic melt and the other with molten sodium hydroxide.

4.2.3. Overvoltage. Both anodic and cathodic overvoltages were negligibly small in the current density range studied here.

4.2.4. Voltage balance. From the above mentioned data and conductivity data [6, 7], the voltage balance of this process can be estimated as shown in Fig. 6, assuming a rectangular unit cell as shown in Fig. 5.

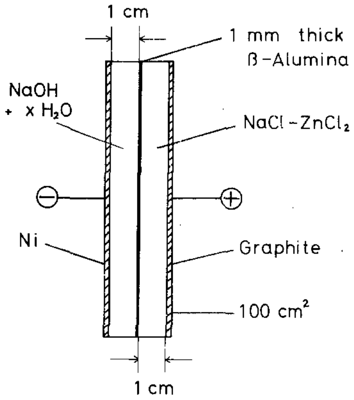

Fig. 5. Model cell for voltage balance calculation.

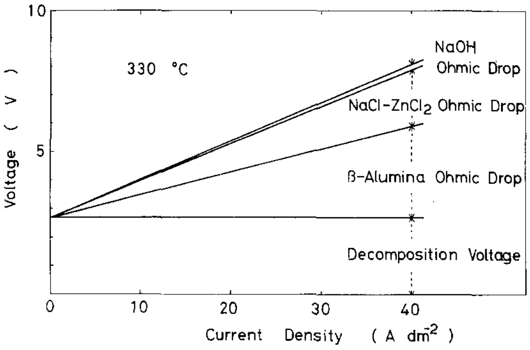

Fig. 6. Voltage balance.

5. Life of the β-alumina

The life of the β-alumina mainly depends on the following two factors;

(a) The aggressive nature of molten caustic soda;
(b) The affect of stress caused by the passage of the current.

The aggressive nature of the molten chloride was observed to be negligible. An immersion test in the molten caustic soda was carried out and a corrosion rate of 0·002 mm per year at 330° C was observed. This is an acceptable low rate of corrosion.

Concerning the effect of stress caused by the passage of current, no deterioration was observed after a 3 h electrolysis of 20 A dm^{-2}. Further experiments should be carried out to assess the effects of prolonged electrolysis, but recent work of Lazennec on the Na/S battery [8] suggests a life of $1{\cdot}7 \times 10^5$ Ah dm^{-2}, which is quite hopeful.

6. Conclusion

From the above mentioned data and considerations, this process seems very promising. For example, if we electrolyze vapour at 1 atm with the most well-developed β-alumina, whose specific resistance is said to be 6 Ωcm, even electrolysis at 5 V and 40 A dm^{-2} may be possible by the use of the cell shown in Fig. 5. If hydrogen is not required, it may also be possible to decrease the decomposition voltage by using oxygen as a depolarizer at the cathode. Of course, there are still problems to be solved, such as the materials problem caused by the high temperature operation and above all, the development of β-alumina with high conductance and long lifetime (*1) might assure a promising future for this process.

Acknowledgement

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