

Electrolytic Production of Perchlorate by Lead Dioxide Anodes

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ABSTRACT

An outline is given of an electrolytic process for the production of sodium perchlorate using a pure lead dioxide anode. In this process, a saturated solution of sodium chlorate is electrolyzed batchwise at an anodic current density of 25 amp/dm² at 50°C; current efficiency, about 70% with more than 99% conversion of chlorate to perchlorate; cell voltage, 4.5-5.0v. The process has been operated successfully for more than two years without renewal of the anodes. In relation to the above, the results of basic research on anode potential and current efficiency for perchlorate formation from chlorate are also given.

Although we had perfected a new electrolytic process of producing perchlorate using lead dioxide as the anode about two decades ago in both the laboratory and on a semicommercial scale (1), production using the new process was not carried out in Japan

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until 1965, when Sanwa began to produce perchloric acid with this process. The principal reason for the delay was the small demand for perchlorate in Japan after the war. When the Pacific Engineering Company of the United States started to produce perchlorate using a lead dioxide anode, we decided to put our

process in practical use. Because of the small demand for perchlorate, we constructed a small-sized perchlorate plant to produce perchloric acid as the final product. This report mainly describes the outline of the process operated in Sanwa Chemical's plant.

Basic Research on Anode Potential and Current Efficiency for Perchlorate Production from Chlorate

In 1953 one of the authors (K. Sugino) and Dr. S. Aoyagi presented a paper entitled "Mechanism of the Electrolytic Formation of Perchlorate" at the New York Meeting of the Society in which the current *vs.* potential curves for the anodic process of chlorate at platinum were shown. The results were subsequently published (2). The curves were obtained by a kind of polarographical technique at a platinum microanode. In a moderately concentrated solution of chlorate two stages of potential were definitely observed on the curves. In the first or lower stage, the potential was between 1.5-1.7v and in the second or higher stage, it was more positive than 2.1v (*vs.* SCE).

As a result of controlled potential electrolysis, it was clarified that the first stage was the potential of oxygen evolution and the second stage was the potential at which the formation of perchlorate occurred.

From the detailed experiments on the above phenomena, it was proved that the first step of this process is the direct discharge of ClO_3^- at a higher potential than that of oxygen evolution.

Recently, from a practical point of view, the current *vs.* potential curves for perchlorate formation were again measured at the platinum and at the lead dioxide anodes by one of the authors (T. Sekine) and his collaborators by using controlled potential electrolyzer (3). They are shown in Fig. 1 and 2.

At the platinum anode curves similar to those of Sugino and Aoyagi were obtained and two potential stages were clearly observed. On the other hand, at the lead dioxide anode, the curves did not indicate such stages. They showed a steep increase of current at around 1.8-1.9v (*vs.* SCE) and were observed as a simple exponential relationship. However, as shown in Fig. 3, when the chlorate solution of pH 11.4-12.0 was used, curves having two potential stages were obtained and the lower stage was found to be the potential of oxygen evolution. Accordingly the potential at which the current began to flow in Fig. 2

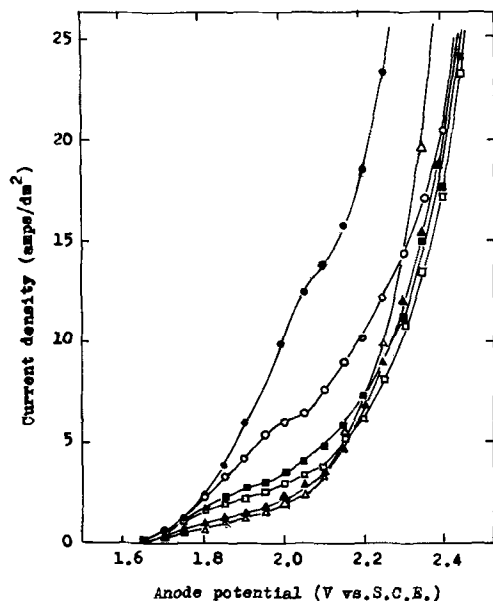


Fig. 1. Current *vs.* potential curves at platinum anode in various concentrations of chlorate solution. ●, NaClO_3 , 1 mole/l; ○, NaClO_3 , 2 mole/l; ■, NaClO_3 , 3 mole/l; □, NaClO_3 , 4 mole/l; ▲, NaClO_3 , 5 mole/l; △, NaClO_3 , 6.4 mole/l (saturated solution).

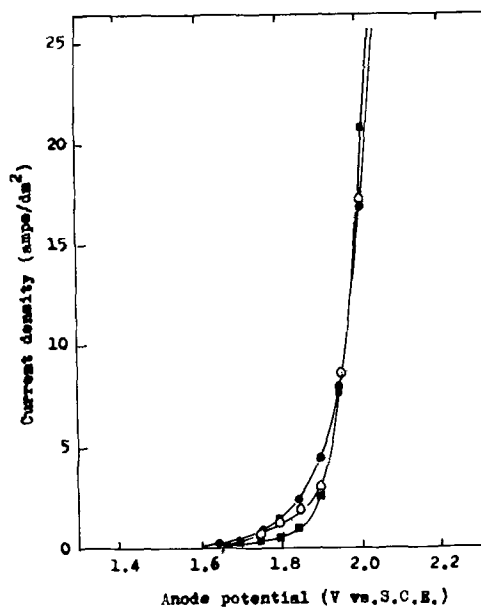


Fig. 2. Current *vs.* potential curves at lead dioxide anode in various concentrations of chlorate solution. ●, NaClO_3 , 1 mole/l; ○, NaClO_3 , 3 mole/l; ■, NaClO_3 , 6.4 mole/l (saturated solution).

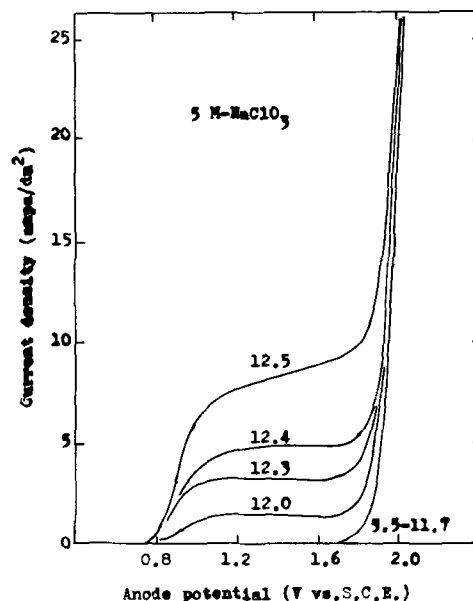


Fig. 3. Current *vs.* potential curves at lead dioxide anode in chlorate solution of different pH.

indicated the potential of perchlorate formation at the lead dioxide anode.

The mechanism of perchlorate formation at the lead dioxide anode may be somewhat different from that at the platinum anode. It is presumed to be due to the simultaneous discharge of ClO_3^- and OH^- , followed by the combination of the radicals formed. This was proposed as a possible route by Sugino and Aoyagi in the paper described above.

It was found that the potential at which the current corresponding to perchlorate formation began to flow was about 0.25v lower than that at the platinum anode in the same concentration. In addition, the increase of anode potential with increasing current density was very small up to high current density such as 30 amp/dm², but at the platinum anode, the potential increased steadily with increasing current density as shown in Fig. 1. This is an interesting characteristic of the lead dioxide anode and it is the main reason for the smaller cell voltage than that at the platinum cell, especially at high current density.

Table I. Bench scale experiment*

Anode	Lead dioxide
Cathode	18-8 stainless steel
Electrolyte	Saturated solution of NaClO_3 containing 2 g/l of NaF
Current	600 amp
Current density, anodic	20 amp/dm ²
Temperature	50°C
Conversion	99.5%
Current efficiency	72%

* Data from ref. (1).

It was thought for a long time that the current efficiency for perchlorate formation from chlorate at the lead dioxide anode was not so high when the electrolysis was continued until almost all the chlorate was converted to perchlorate, although a high value could be expected as an instantaneous current efficiency. Therefore, about 2 g/l of sodium fluoride were added to the cell liquor to maintain the over-all current efficiency above 70%. Thus, one of the authors (K. Sugino) and his collaborators reported about 80% current efficiency in a laboratory cell and 72% current efficiency in a 600 amp cell when more than 99% of chlorate was converted to perchlorate (4) as shown in Table I. These results were later confirmed by Schumacher *et al.* (5).

Recently one of the authors (T. Sekine) carried out a detailed study on the current efficiency for perchlorate formation at the lead dioxide anode. From the results, it seems that a high current efficiency could be obtained at the lead dioxide anode without any additive such as sodium fluoride. A few examples are shown below:

Results of controlled potential electrolysis.—Electrolyses at the lead dioxide anode were carried out in various concentrations of chlorate solution (1-6M NaClO_3) at a certain potential in the range of 1.85-2.10v (*vs.* SCE). The examples with 6M solution are condensed in Table II. In the table about 90% (87-89%) of current efficiency was marked at the potential of 1.90-2.10v (*vs.* SCE), without addition of sodium fluoride in the electrolyte in the initial stage of electrolysis.

Combining the above results with those obtained at the platinum anode, the influence of anode potential on the current efficiency in 5M solution, for instance, is shown in Fig. 4. From the curve, it is also clear that the potential corresponding to the formation of perchlorate at the lead dioxide anode is about 0.25v more negative than that at the platinum.

Results of almost complete conversion of chlorate to perchlorate by constant current electrolysis (6).—The current efficiencies for perchlorate formation are shown in Table III when more than 80% of the chlorate is converted to perchlorate. A decline in current efficiency was observed in the final stage of electrolysis as shown in the table. The results indicate that with lead dioxide a current efficiency of 65-70% was obtained even when about 99% of chlorate was converted to perchlorate.

However, it should be pointed out that commercial chlorate contains a very small amount of bichromate

Table II. Example of controlled potential electrolysis*

Anode potential (v <i>vs.</i> SCE)	Concentration of electrolyte NaClO_3 (mole/l)	Current density (average) (amp/dm ²)	Amount of current (amp · hr)	NaClO_4 (mmole/l)	Current efficiency (%)
1.90	6.39	2.40	1.59	25.7	86.7
1.95	6.39	14.1	2.90	48.5	89.6
2.00	6.39	14.5	2.46	41.2	89.0
2.05	6.39	28.5	2.74	44.5	87.0
2.10	6.23	35.9	2.09	34.8	89.0

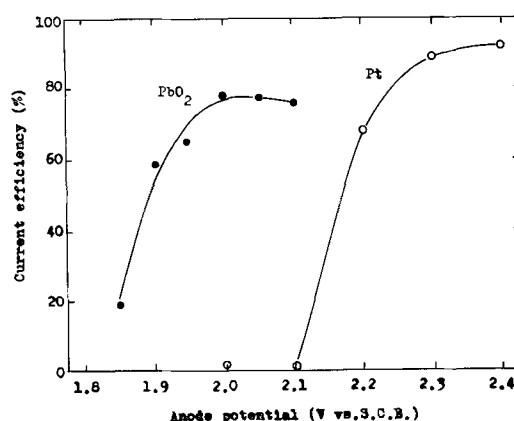
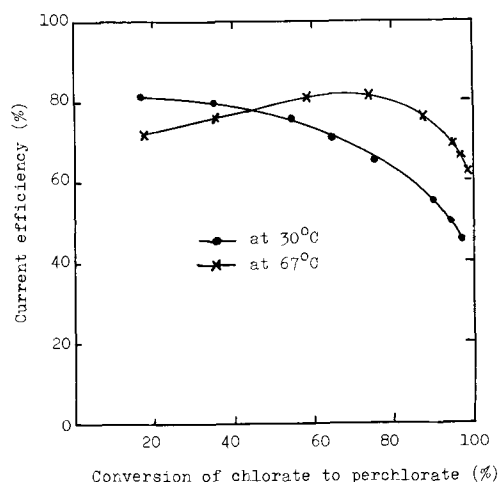
* Anode: PbO_2 , cathode: Pt, temperature: 25°C.Fig. 4. Relation between anode potential and current efficiency with both lead dioxide and platinum anode in 5M NaClO_3 . ●, Lead dioxide, ○, platinum.

Fig. 5. Influence of temperature on current efficiency

as a contaminant. As shown in Table III, in the case of the lead dioxide anode, it was found that this contaminant showed a strong negative effect on the current efficiency. It was also found that the addition of sodium fluoride partly compensates the negative effect of bichromate thus contributing to maintain a high current efficiency. Accordingly we are still using this additive.

In regard to the effects of temperature on current efficiency, a remarkable difference was found between platinum and lead dioxide. In the case of platinum, it has been reported that the current efficiency increases with lower temperature. On the other hand it was found that in the case of lead dioxide the current efficiency increased with higher temperature as shown in Fig. 5. This may be a phenomenon suitable from a practical point of view. However, we had operated at 50°C considering another mechanical factor.

Table III. Example of electrolysis in process of complete conversion*

Concentration of electrolyte NaClO_3 (mole/l)	Current density (amp/dm ²)	Temperature (°C)	Conversion (%)	Current efficiency (%)
5.67	20	50	80.5	80.5
			94.1	76.2
			96.8	73.5
			98.8	69.2
5.98†	42	50	97.9	51.3

* Anode: PbO_2 , cathode: stainless steel.† Electrolyte contains 0.03 g/l of Na_2CrO_4 .

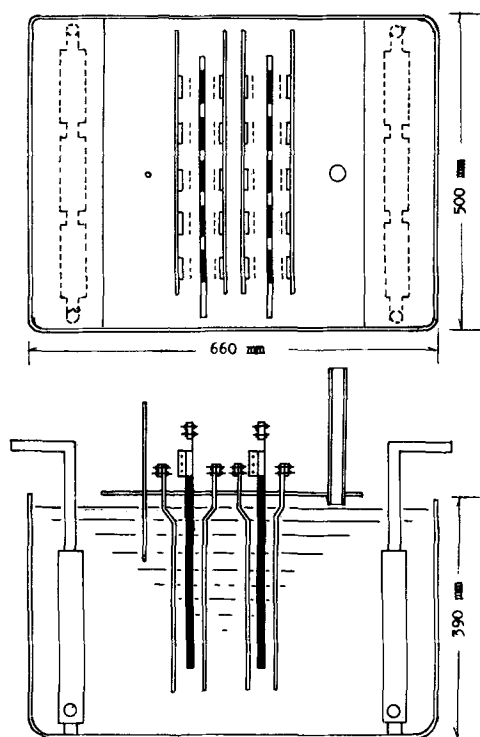


Fig. 6. Cell design

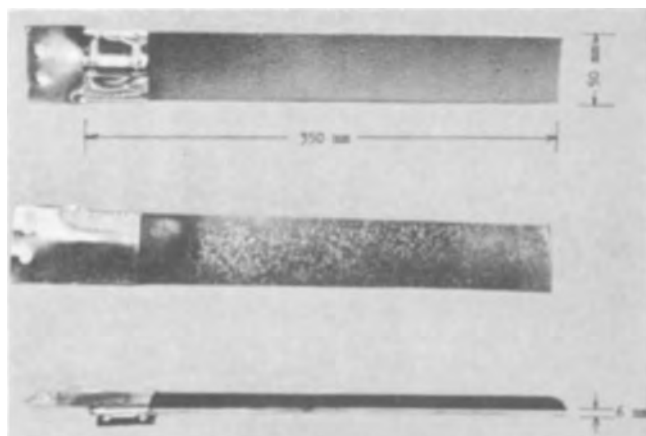


Fig. 7. Lead dioxide anode

Cell Design

The Sanwa perchlorate cell now used is almost the same as that being used in the production of bromate (7). Figure 6 is a diagram of the Sanwa perchlorate cell showing construction and dimensional features.

The cell body is constructed of a sheet iron rectangular tank 660 mm long x 500 mm wide x 390 mm high. The inside surface of the body are all lined with hard polyvinylchloride sheet. A plate of the same hard polyvinylchloride is placed on top of the cell and supports 10 anodes and 20 cathodes. These are arranged in 6 rows running the length of the cover. Down the middle are two rows of 5 anodes and on either side of the rows is a row of 5 cathodes.

The lead dioxide anodes,¹ which are shown in Fig. 7, are 50 mm wide, 6-7 mm thick, and 350 mm long and extend about 65 mm above the cover. The stainless steel cathodes (18-8) are 35 mm wide, 3 mm thick, and 300 mm long. The distance from an anode to the nearest cathode is about 10 mm. Six stainless steel cooling boxes are placed in both ends of the cell and act somewhat as a cathode.

¹ The method used in making the lead dioxide anode was reported in the previous paper (7).

Hydrogen discharged at the cathodes caused sufficient circulation of the cell liquor. It was vented through the roof from each cell.

Although the present cell is operated in a 500 amp capacity, it is possible to bring it up to a 1000 amp cell by doubling the electrode assembly in the container.

A 5000 amp cell can be constructed by combining five unit cells lengthwise. Cells of larger capacities, some 10,000 amp, can also be constructed with lead dioxide anodes of the same size.

The Process

Each cell was filled with 85 liters of a solution of sodium chlorate nearly saturated. Its concentration was 736 g/l NaClO_3 . To increase the current efficiency, 2 g/l of sodium fluoride was added to the cell liquor. The cells were operated batchwise and each portion of cell liquor was electrolyzed to a final chlorate content of 5-6 g/l before being discharged.

Cell temperature was kept as constant as possible ranging from 47° to 52°C. A current of 500 amp was carried by each cell.

The anodic and cathodic current densities were 25 amp/dm² and 35 amp/dm², respectively. Current efficiency averaged 70% or a little less based on the analysis of unconverted chlorate. The potential drop across each cell ranged from 4.5 to 5.0v (average 4.7v). Accordingly, energy consumption is estimated to be 3 kw-hr (d.c.) or a little more for each kilogram of sodium perchlorate.

The operation characteristics are listed in Table IV.

The process has been operated successfully for more than two years without renewal of the anodes. It indicated that the loss, if any, may be very small. However, an experiment was made to determine the loss of the anode by using a practical cell. The results are shown in Table V. Conditions of electrolysis are the same as in Table IV.

The data showed that practically no loss resulted after the anode had been used for about three months. A few anodes sustained a very small loss which averaged 8.1 mg/1000 amp-hr.

After electrolysis, the cell liquor was treated with a small amount of calcium chloride to remove fluoride. The resulting solution was then evaporated to a desired concentration. By cooling the concentrated solution at 20°C, about 75-80% sodium per-

Table IV. Operation characteristics

Capacity	85 l/cell
Cell feed	NaClO_3 736 g/l
	NaF 2 g/l
Cell effluent	NaClO_3 5-6 g/l
	NaClO_4 892 g/l
	NaF 2 g/l
Current, amperage	500
Current density, anodic	25 amp/dm ²
	35 amp/dm ²
Temperature	47°-52°C
Cell voltage	4.5-5.0v (average 4.7v)
Current efficiency (average)	70%
Power consumption	3 kw-hr (d.c.)/kg NaClO_4

Table V. Weight loss of lead dioxide anode

Anode No.	Duration of electrolysis: 81 days		Loss (g)
	Before test (g)	After test (g)	
1	1133	1133	0
2	1098	1096	2
3	1118	1116	2
4	990	990	0
5	957	957	0
6	899	899	0
7	885	884	1
8	960	959	1
9	849	847	2
10	958	958	0
Total	9847	9839	8

Average
0.081% by weight for 982.1 kamp-hr
8.1 mg/kamp-hr

chlorate crystallized out as monohydrate. The mother liquor was subsequently returned to the evaporator. In Sanwa Chemical Company, 60% perchloric acid is being produced by treating sodium perchlorate thus obtained with hydrochloric acid.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1969 JOURNAL.

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