Preparation, Properties and Application of the Lead Peroxide Electrode Manufactured by a New Method

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This contribution is the abstract of our papers on "Preparation, Properties and Application of the Electrodeposited Lead Peroxide Anode, Part 2-13" already published in Japanese in the *Journal of the Electrochemical Society of Japan*, (Part 2, 3, 7, 10, 11, 12), the *Journal of the Chemical Society of Japan* (Part 6, 7, 8) and the *Journal of the Society of Chemical Industry, Japan* (Part 4, 5, 13).

Our lead peroxide electrode newly prepared consists entirely of pure lead peroxide PbO_2 and has the shape of a rectangular piece or of a hollow cylinder with a bottom. It can be used as an insoluble anode for the electrolysis of aqueous solutions containing such anions as Cl^-, Br^-, I^-, F^-, ClO^-, ClO_3^-, ClO_4^-, SO_4^{--}, NO_3^-, CO_3^{--}, $C_2H_3O_2^-$, etc. It has a high oxygen overvoltage comparable to that of platinum. So it can also be used as an anode for electrolytic oxidation in place of platinum.

Preparation of the Lead Peroxide Electrode

Two different methods were established by the authors.

(a) Method 1.⑴—Compact lead peroxide layer could be deposited electrolytically from neutral lead nitrate solution upon the inner surface of iron or nickel cylinder which acts as anode. An example of the electrolysis was as follows: electrolyte—24.1% lead nitrate solution; anode—iron cylinder with surface polished inside, length 1,000 mm., inside diameter 252 mm., thickness 9 mm., weight 60 kg., available surface area 78.85 dm².; cathode—copper rod (diameter 45 mm.); mean current —549 amp.; anodic current density (D_A)—6.96 amp./dm².; voltage—10.7 v.; temp.—79.7°; flow velocity of electrolyte—12 l./min.; duration of electrolysis—47 hrs.

During the electrolysis, pH of the electrolyte and the concentration of Pb^{++} must be maintained as constant as possible by running the electrolyte at constant velocity and neutralizing the increasing acidity by $Pb(OH)_2$. The apparatus is shown in Fig. 1.

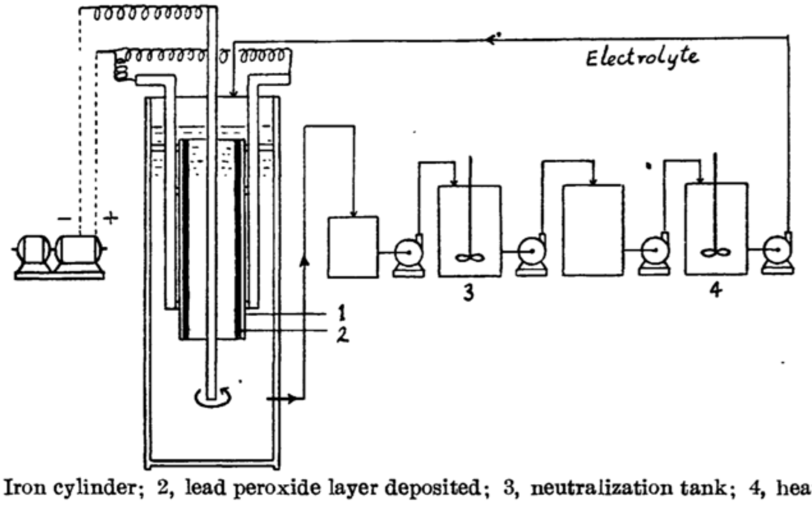

Fig. 1.—1, Iron cylinder; 2, lead peroxide layer deposited; 3, neutralization tank; 4, heating tank.

In an example, the lead peroxide deposited was 8-10 mm. thick. At first, two cylinders of 300 mm. in length were cut from the mother cylinder, then by cutting the iron part of the cylinder lengthwise, a lead peroxide cylinder of suitable strength and compactness as well as of a smooth outer surface was obtained (dia.,

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⑴ K. Sugino, K. Kawamichi, T. Osuga and S. Kitahara, Part 9 of this series (unpublished). A part of this research was reported in Part 2 of this series.

250 mm.; length, 300 mm.). The lead peroxide cylinder was then separated into sixteen parts by cutting it again lengthwise. One part of the lead peroxide thus obtained has the shape of a rectangular piece shown in Fig. 2. Its dimensions are as follows: length—300 mm. × 45 mm.; thickness—8∼10 mm.

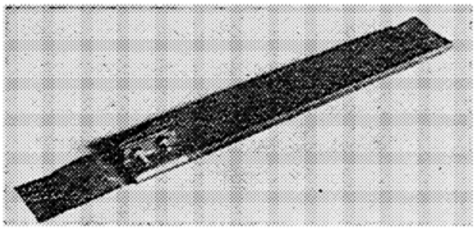

Fig. 2.

(**b**) **Method 2.**(2)—If the outer surface of the metal cylinder was used as anode in the above method, the deposition of lead peroxide was very brittle and easily breakable due to the difference of expansion coefficient between the metal and the oxide. It proved later, however, that a compact and strong layer could be obtained by a similar method to (1) even on the outer surface of cylindrical anode if a soft and non-metallic conducter was used as anode surface of electrodeposition under suitable conditions.

For example, compact lead peroxide layer was deposited from the neutral lead nitrate solution to a considerable thickness on the outer surface of a rotating rod whose surface was consisted of paraffine-graphite mixture. The electrolytic apparatus is shown in Fig. 3.

By taking out the rod by a suitable method, a hollow cylinder of lead peroxide with sufficient strength and compactness was obtained. It has the same shape as the magnetite anode commonly used as is shown in Fig. 4.

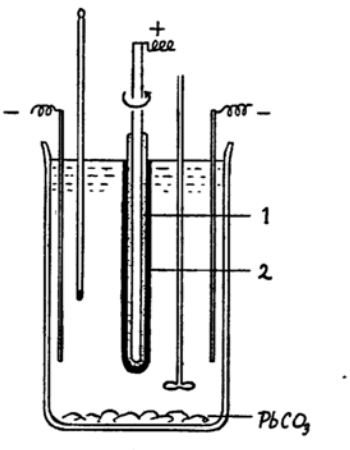

Fig. 3.—1, Paraffine-graphite mixture; 2, lead peroxide deposited.

It can be therefore readily used for the electrolytic bath for chlorate. An example of the electrodeposition was as follows. Conditions of electrodeposition: electrolyte—$Pb(NO_3)_2$ 330∼380g./l., $Cu(NO_3)_2$ 10∼30 g./l., $NaClO_4$ 60∼80g./l.; D_A—7amp./dm^2.; voltage—5∼6 v.; temp.—27∼31°, acidity—0.01∼0.03 N.; neutralization reagent—$PbCO_3$ (electrolyte is not flowed); duration of electrolysis—23 hrs.; lead peroxide electrode obtained: length—550 mm.; thickness—6.5 mm.; diameter (outer)—54 mm.; diameter (inner)—41 mm.; weight—4.8 kg.

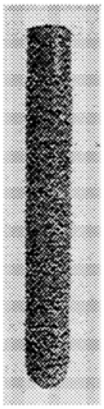

Fig. 4.

Application of the Lead Peroxide Electrode

A. As an Insoluble Anode

Electrolytic Production of Potassium Chlorate.(3)—From the standpoints of conductivity and durability, our lead peroxide electrode appears to be superior to graphite or magnetite as anode material for chlorate production. This electrode is a good conductor carrying the current of above 20 amperes per square decimeter of the surface. In addition, it is almost perfectly insoluble, practically no decrease of weight being perceptible during the course of electrolysis of sodium chloride solution. Our experiments showed that this electrode was a most suitable material as anode for chlorate production. An example of the preparation of potassium chlorate was as follows. Conditions of electrolysis: cathode—Fe; electrolyte—KCl 32 g./100 cc. solution, 0.2 g. $Na_2Cr_2O_7$ added, slightly acidified with HCl during the electrolysis; D_A—20 amp./dm^2.; voltage—3.3∼4.0 v.; temp.—60∼80°. After 33.0 amp. hr. was passed, 20.35 g. of $KClO_3$ (crystal obtained at 15°, 19.02 g.) was formed. Current efficiency, 81 %. $KClO_4$ was not produced at all.

B. As Anodes for the Electrolytic Oxidation

(a) Electrolytic Production of Sodium

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(2) K. Sugino and Y. Shibazaki, *J. Electrochem. Soc. Japan*, **16**, 9, 10 (1948), (Part 10, 11).

(3) K. Sugino and M. Yamashita, *J. Electrochem. Soc. Japan*, **16**, 123 (1948), (Part 12).

Perchlorate.(4)—Since the oxygen overvoltage of lead peroxide is thought to be comparable to that of platinum, it is easily conceivable that it can be used for the electrolytic oxidation of sodium chlorate. So far, however, the lead peroxide anode formerly used has been a thin film electrolytically formed on the surface of a lead plate and proved to be useless for perchlorate production as the lead dissolves readily. But our lead peroxide electrode was found to be perfectly insoluble when it was used for the same purpose. So the authors have carried out fundamental and semicommercial experiments for the electrolytic preparation of sodium perchlorate with this anode. Main results obtained are shown in Table 1.

Table 1

Expt. No.	Cathode	Cathodic current density, amp./dm².	NaF, g./l.	Current concn., amp./l.	Mean voltage, v.	Temp., °C.	Reaction percentage $NaClO_3 \rightarrow NaClO_4$, %	Current efficiency, %
1	18–8 stainless steel	20	0	80	4.4	29∼30	99.91	40.9
2	〃	〃	2	〃	4.5	〃	99.60	82.9
3	〃	〃	2.5	〃	4.6	35	98.40	81.8
4	〃	26	2	55	5.1	50∼52	99.53	72.2

Electrolyte: Saturated sodium chlorate solution (20°). Anodic current density (D_A): 20 amp./dm².

As is clear from the table, an addition of 2 g./l. of sodium fluoride was found to have a very marked effect in increasing the current efficiency. Thus, in Expts. 2 and 3, the result is about the same as the case of platinum anode. Expt. 4 was a semi-commercial experiment, using 600 ampere cell. With a current efficiency of 72%, the reaction proceeded to 99.5%.

(b) Direct Electrolytic Production of Sodium Perchlorate from Sodium Chloride.(5)—The authors established a new simple and direct process for the electrolytic production of sodium perchlorate. By the use of our lead peroxide anode, it is easily conceivable that the electrolytic preparation of sodium perchlorate is performed by a single electrolysis of sodium chloride solution. The results showed that with a current efficiency of about 60%, almost pure sodium perchlorate (purity being above 99.4–99.9%) was easily obtained directly from sodium chloride. The conditions of electrolysis were as follows: electrolyte—saturated sodium chloride solution; anodic current density (D_A)—15∼20 amp./dm².; temp.—$Cl \rightarrow ClO_3$ 60∼65° (initial stage of electrolysis), $ClO_3 \rightarrow ClO_4$ 30∼35° (final stage of electrolysis). Main results obtained are shown in Table 2.

Table 2

Cathode	Quantity of NaCl used, g.	Voltage. v.	Current, quantity consumed, amp. hr.	After electrolysis NaCl, g.	After electrolysis $NaClO_3$, g.	After electrolysis $NaClO_4$, g.	Reaction percentage, $ClO_3 \rightarrow ClO_4$ %	Current efficiency, %
18–8 stainless steel	40	3.9∼5.5	250.5	0	0.0216	83.77	99.97	58.5
〃	〃	3.9∼5.4	237	0	0.0352	83.75	99.95	61.9
〃	〃	3.9∼5.3	222.5	0	0.3600	83.38	99.51	65.9
Cr plating iron	〃	4.0∼5.5	231	0	0.4610	83.26	99.37	63.4

As the two different electrolytic processes ($Cl \rightarrow ClO_3$, $ClO_3 \rightarrow ClO_4$) seemed to take place successively, a small amount of hydrochloric acid was added from time to time during the primary stage in order to maintain the electrolyte slightly acidic, and when the chlorate formation was almost completed, a small amount (2 g./l.) of sodium fluoride was added at a time for increasing the current efficiency of electrolytic oxidation.

(c) Electrolytic Preparation of Ammonium Persulfate(6) **(Hydrogen Peroxide).—**

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(4) K. Sugino and M. Yamashita, *J. Electrochem. Soc. Japan*, **15**, 61 (1947), (Part 3). S. Kitahara and T. Osuga, *J. Electrochem. Soc. Japan*, **10**, 409 (1942), (Part 2). A part of this research was reported in the earliest paper of this series: Y. Kato, K. Sugino, K. Koizumi and S. Kitahara, *Electrotechnical Journal, Japan*, **5**, 45 (1941), (in English).

(5) Reference (4), (Part 3).

(6) K. Sugino, J. Mizuguchi, M. Yamashita and K. Odo, *J. Soc. Chem. Ind. Japan*, **50**, 34, 36 (1948), (Part 4, 5). K. Sugino, J. Mizuguchi and M. Yamashita, *J. Chem. Soc. Japan*, **67**, 108 (1946), (Part 6). K. Sugino and M. Yamashita, *J. Chem. Soc. Japan*, **67**, 110 (1946); *J. Electrochem. Soc. Japan*, **16**, 120 (1948), (Part 7). K. Odo, *J. Chem. Soc. Japan*, **67**, 129 (1946), (Part 8).

Electrolytic preparation of ammonium persulfate has also only been successfully accomplished by the use of platinum anode. Trials of electrolytic formation of persulfate by the anodes other than platinum (PbO_2, MnO_2, Fe_3O_4, graphite etc.) were already undertaken in vain by a few authors.(7) The authors have therefore tried the application of our new lead peroxide electrode for this purpose.

Preliminary experiments have been conducted in the same conditions as in the case of platinum anode. The conditions of electrolysis were as follows: cathode—Pb; anolyte and catholyte—a mixture of 28% $(NH_4)_2SO_4$ and 30% H_2SO_4; D_A—50 amp./dm².; porcelain diaphragm was used; addition agent—none.

Though the formation of ammonium persulfate was definitely observed in each experiment, its maximum concentration in anolyte never exceed 2–3%, which was followed by a gradual decrease by the prolonged electrolysis, the total current efficiency being also only a few percent as already reported by another author.(8) Upon examining the electrolytic conditions specially suited for lead peroxide anode, the following ones were found as such:

(1) Lowering of the anodic current density to about 10 amp./dm².
(2) Selection of a suitable composition of electrolyte: 10~20% sulfuric acid solution saturated with ammonium sulfate.
(3) Addition of hydrofluoric acid to anolyte: 10~60 g./l.
(4) Increase of current concentration, if desired.

The addition of 50~60 g./l. of hydrofluoric acid to anolyte was of a specially marked effect: about 20% ammonium persulfate solution could be obtained with a current efficiency of about 60% as is seen from Table 3. This result offers a possibility of the use of this anode for the industrial preparation of ammonium persulfate.

Furthermore, the plan of the flow diagram of the new process of the preparation of concentrated hydrogen peroxide by this electrolytic method was established and a semi-commercial experiment has been conducted and completed successfully by Assist. Prof. J. Mizuguchi. But the results are omitted in this paper.

Oxygen Overvoltage of Lead Peroxide Anode in Sulfuric Acid and its Variation in the Presence of HF (9)

Oxygen overvoltage of lead peroxide anode in sulfuric acid solution (1 N and 30%) was measured at various current densities by the direct method and the values obtained were compared with that of the smooth platinum anode.(10),(11) The oxygen overvoltage of lead peroxide was found to be somewhat lower than that of platinum at a definite current density (for example, 0.16 v. lower at 1 amp./dm².). The overvoltage (π^+_V) is shown in Fig. 5 against the logarithm of the anodic current density (D_A).

The variation of overvoltage with current density could also be expressed by the usual equation,

$$\pi = a + b \log I$$
(from 10 milliamp./dm². to 1 amp./dm².),

and the value of b of lead peroxide and platinum was found to be 0.13 and 0.18 respectively at ordinary temperatures. The inferiority

Table 3

Expt. No.	Quantity of anolyte, cc.	Mean current, amp.	Current concn., amp./l.	Anodic current density, amp./dm².	Mean voltage, v.	Temp., °C.	Current quantity consumed, amp. hr.	$(NH_4)_2S_2O_8$ formed, g.	Concn. of $(NH_4)_2S_2O_8$ in anolyte, g./100cc.	Current efficiency, %	Variation of acidity of anolyte, N
1	100	4	40	10	5.0–5.4	30	6	15.92	16.58	62.3	4.76 → 4.53
2	150	3	20	11	4.6–4.8	28–29	9	23.76	17.60	62.0	4.81 → 4.60
3	300	3	10	11	4.7–4.9	30–32	18	48.62	17.06	63.5	4.61 → 4.72

Cathode—Pb; anolyte—98% H_2SO_4 10 g./100 cc., $(NH_4)_2SO_4$ 58 g./100 cc., HF 5~6 g./100 cc.; catholyte—saturated ammonium sulfate solution. Porcelain diaphragm was used.

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(7) Skirrow and Stein, *Trans. Am. Electrochem. Soc.*, **38**, 209 (1920).

(8) R. Matsuda, This Bulletin, **12**, 331 (1937).

(9) K. Sugino, T. Tomonari and M. Takahashi, *J. Soc. Chem. Ind. Japan*, **52**, 75 (1949), (Part 13).

(10) Oxygen overvoltage at platinum anode has been found to be higher than that at lead peroxide anode by several investigators, (for example, E. Müller, *Z. Elektrochem.*, **10** 61 (1904)).

(11) A few authors recorded a higher value of overvoltage of lead peroxide than that of platinum (E. Müller, *Z. Elektrochem.*, **11**, 865 (1905); Tsutusi, *Bull. Electrotech. Lab. Japan*, **6**, 91 (1942)).

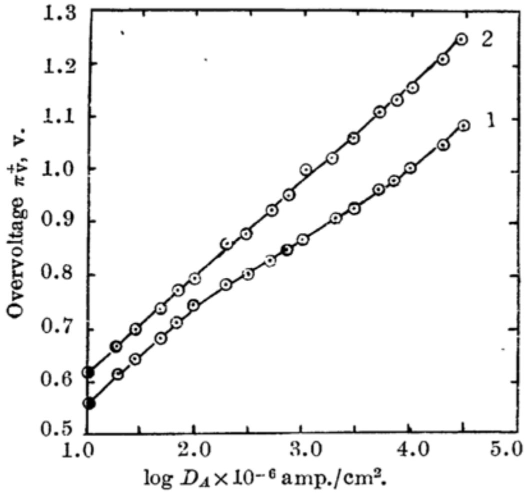


Fig. 5.—Overvoltage of lead peroxide and platinum in H_2SO_4 (1 N) at 30°C.: Curve 1, PbO_2, Curve 2, Pt.: at $D_A=1$ milliamp./cm². PbO_2 0.86 v., Pt 0.99 v.; at $D_A=10$ milliamp./cm². PbO_2 1.00 v., pt 1.16 v.

of the current efficiency of electorolytic oxidation process at lead peroxide anode may be due mostly to the above difference of overvoltage at definite current density.

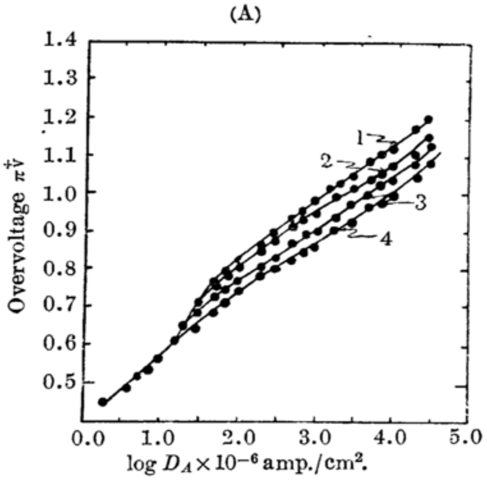
The variation of overvoltage of lead peroxide due to the addition of various amount of hydrofluoric acid was also measured.(12) The result obtained is shown in Fig. 6.

It was found that the overvoltage increased in a linear manner with the logarithm of the concentration of hydrofluoric acid added. This relation may be expressed by the following equation.

$$\pi = 1.10 + 0.04 \log C_{HF} \text{ (mol./l.) at } 1 \text{ amp./dm}^2. \ (C_{HF}=0.05\sim5 \text{ mol./l.})$$

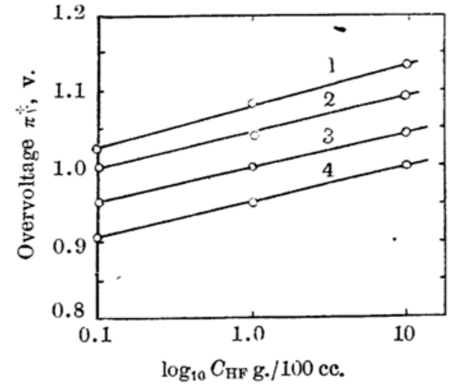
The study of the rate at which the potential of the anode falls after the polarising current being switched off has been also made by the authors using a modified Bearth circuit, and it was found that the plot of the potential against the logarithm of the time was a straight line and the discontinuity could not be found in that curve on the contrary of Isgarischew's observation.(12)

(A)



Curve 1, 10 g. HF; Curve 2, 1 g. HF.
Curve 3, 0.1 g. HF; Curve 4, without HF.

(B)



Curve 1, 10×10^{-3} amp./cm².; Curve 2, 5×10^{-3} amp./cm².; Curve 3, 2×10^{-3} amp./cm².; Curve 4, 1×10^{-3} amp./cm².

Fig. 6.—The variation of overvoltage of lead oxide anode in H_2SO_3 (1 N) due to the addition of various amount of HF.

In conclusion, the author wishes to express his sincere thanks to Dr. Y. Kato, a professor emeritus of Tokyo Institute of Technology, for his kind advice and encouragement in the initial stage of this research. The author also extends his thanks to the Nippon Carbide Industries Company Inc. and Mr. Okumura, President of the said company, for the conveniences and funds furnished to this research, and to Mr. K. Kawamichi, Director of the same company, for his kindness and collaboration for the industrial production of this electrode. Thanks are also due to his collaborators, specially to Mr. T. Osuga of the same company, Assist. Prof. J. Mizuguchi and Mr. M. Yamashita of Tokyo Institute of Technology, Prof. Dr. T. Tomonari and Assist. Prof. Y. Shibazaki of the Yokohama Institute of Technology who gave earnest and valuable assistance and collaboration in the investigations. A part of the cost of this study was defrayed from the Scientific Research

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(12) It has already been noted that the presence of fluoride ion in the electrolyte increases anodic overvoltage (E. Müller, *Z. anorg. Chem.*, **48**, 112 (1906); *Z. Elektrochem.*, **13**, 257 (1907); N. Isgarischew, *Z. Elektrochem.*, **30**, 138 (1924)).

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