Lead Dioxide Anode for Commercial Use

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ABSTRACT

Results are presented on one phase of a research carried out under an Office of Naval Research contract for the development of an electrode to replace platinum in the perchlorate cell. Electrodeposition of massive lead dioxide is preferably carried out from a lead nitrate bath. Uniquely, anodic deposition on tantalum is possible without polarization or erosion of the base. In the subsequent anodic process use, this tantalum acts as a polarized, inert filler. Sprayed silver permits the formation of an operable, low resistance current contact to the lead dioxide. Operation of a 100 amp perchlorate cell with a lead dioxide anode is described. Current efficiency of the lead dioxide anode is compared to platinum, and the effect of $K_2S_2O_8$ addition is shown.

The chemical and electrical properties of PbO_2 suggest that it should be an ideal material for anodes in electrolytic processes. With a resistivity as low as 40 to 50 x 10^{-6} ohm-cm, it is a better electrical conductor than many metals, and a much better conductor than carbon or graphite. Chemically, PbO_2 is inert to most oxidizing agents and strong acids. Although it has been suggested as an anode material for several electrolytic processes (1-7), up to the present time no commercially practical anode has been advanced. Electrodes reported to date have been weak; they have been formed in odd shapes difficult to adapt to commercial cells, and methods of making the electrical contact have not been satisfactory.

The purpose of this investigation was to develop a practical PbO_2 anode that could be used in industrial electrolytic processes. It was hoped that a suitable electrode would be developed that would replace Pt in the perchlorate cell.

Experimental

Electrodeposition of Massive PbO_2

Several baths (3, 8, 9) are known for the electrodeposition of PbO_2 on common metals. The compositions of three bath types modified to give improved PbO_2 deposits are shown in Table I. In this work, the $Pb(NO_3)_2$ bath was preferred because it gives the highest quality of deposit. The addition of copper nitrate to this bath serves to suppress Pb deposition on the cathode, which is preferably carbon or graphite. In order to deposit PbO_2 of high strength, density, and surface smoothness, an addition agent is necessary such as Igepal CO-880[1] which is a nonionic surface-active agent of the class of "alkyl phenoxy polyoxyethylene ethanol." Addition to the bath of a natural hydrophilic colloid such as gelatin resulted in the formation of a PbO_2 deposit with a high surface smoothness, but which was very weak

[1] Trade Name of Antara Chemical Division of General Dyestuff Corp.

Table I. Lead dioxide plating baths

1. Alkaline lead tartrate
   100 g potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$
   50 g sodium hydroxide, NaOH
   96 g lead oxide, PbO
   Dissolve in the order listed in distilled water to make 2 liters of solution. Heat to 60°C to complete solution of lead oxide. Cool and filter through sintered glass. Bath pH is about 13.
2. Lead perchlorate
   108 ml of 60% perchloric acid (100 g $HClO_4$)
   167 ml distilled water
   111.0 g lead oxide, PbO
   Dissolve the lead oxide in the diluted perchloric acid. Make up to 2 liters with distilled water. Heat to boiling for 2-3 min to dissolve any white precipitate. Cool and use. Bath pH is about 5.
3. Lead nitrate
   269 ml of 69.9% nitric acid (266.5 g HNO_3)
   1000 ml distilled water
   472 g lead oxide, PbO
   Add the lead oxide slowly to the diluted nitric acid with stirring. Dilute to 2 liters and heat to 75°C with stirring. Cool and filter through sintered glass. To this bath add:
   $Cu(NO_3)_2 \cdot 3H_2O$—0.75 g/l
   Igepal CO-880*—0.75 g/l
   Bath pH is about 3.5.

* Trade Name of Antara Chemical Division of General Dyestuff Corp.

and was laced throughout its cross section with many fine fissures.

Using the acid baths mentioned above, it is difficult to form good deposits on thin attackable base sheets because of the serious anodic dissolution of the metal base. This problem was overcome by using Ta as the base metal. Sound, adherent deposits of PbO_2 2 cm or more in thickness could be formed without any signs of erosion of the base Ta. This plating on Ta was unexpected, since Ta polarizes in most electrolytes when operated as the anode.

Electrodeposits of PbO_2 were made readily on Ta wire, rod, and sheet without any nodular growth, using the $Pb(NO_3)_2$ bath at an anode current density

of 0.016-0.032 amp/cm² (15-30 amp/ft²) and a temperature of 70°C. Figure 1 shows a rod of massive PbO_2 formed on a single wire. The wire core was withdrawn by a sharp pull with pliers. In plating flat base-free deposits by blanking off one side of the starting sheet and stripping away this base after a thick deposit had formed, it was difficult to secure unbroken specimens. Therefore, this approach was discontinued in favor of plating on permanent base sheets.

Flat, massive PbO_2 deposits of surprising strength were made by plating on both sides of rectangular sections of Ta screen in the mesh range of 10-50. The use of baffles around the edges of flat, rectangular anodes permitted the formation of nodular free deposits to within rather close tolerances, as shown in Fig. 2. Using a 14 mesh (0.064 cm wire) Ta screen, a PbO_2 electrode measuring 36.8 x 8.9 x 1.6 cm and weighing 4500 g was plated in 142½ hr from the $Pb(NO_3)_2$ bath. Current was maintained at 0.016 amp/cm² on the anode and the bath temperature at 70°C throughout the electrolysis.

If the pH of the nitrate plating bath is not carefully controlled, the bath drifts strongly acid during electrolysis and is very corrosive to all of the common metals. However, by very careful maintenance of the pH in the range of about 2-4 during electrolysis by the frequent addition of lead oxide, and by protecting the base metal at the surface of the electrolyte, it is possible to plate PbO_2 on such metals as Ni and Fe. Even with these precautions, the base is slowly eroded away and by the time a thick plate has formed most of the base metal (in contrast to Ta) will have been eroded away, leaving voids (which are not always objectionable) in the center of the PbO_2 deposit.

Current Contacts to PbO_2 Anode

Whenever PbO_2 with a conventional Cu current contact is used as anode in electrolytic cells, severe
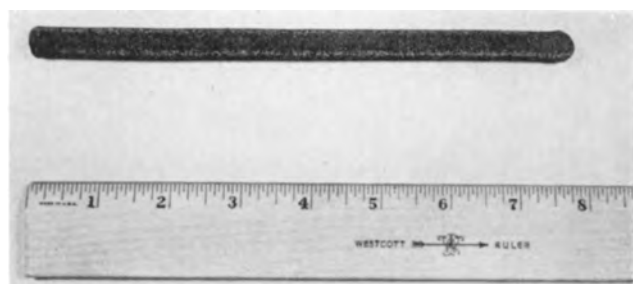

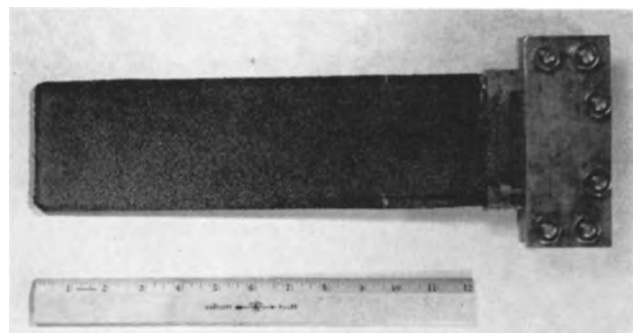Fig. 1. Lead dioxide rod formed on a wire (#20 B&S); wire core withdrawn.

Fig. 2. Massive PbO_2 plated on a Ta screen base, and having a sprayed Cu over Ag current contact.

Table II. Contact resistance of electrodeposited PbO_2 to various metals sprayed thereon

Metal	Contact potential at 1 amp Volts
Tin	0.65
Lead	0.52
Copper	0.04
18-8 Stainless steel	0.69
Zinc	0.5
Aluminum	0.19
Silver	0.0002
Copper over silver	0.0002
Tin over silver	0.0002
Aluminum over silver	0.0002

heating is observed in the contact area. If Ag current contacts are used, no heating occurs. The contact resistance between a number of the common metals and lead dioxide was measured[2] and it was found that all metals tested with the exception of Ag show high contact resistance to PbO_2 as seen in Table II. It is suggested that the resistance is caused by an oxide layer forming between the contact metal and the PbO_2. Most metal oxides being poor electrical conductors show high resistance. Silver, on the other hand, forms a conducting oxide and therefore has a low contact resistance.

A coating of Ag only 0.002 cm or less in thickness applied by a metal spray technique was sufficient to produce low resistance and to overcome completely the heating previously observed in these electrode connections. In order to protect the Ag and to provide a rugged electrical contact to the PbO_2, the Ag-coated area is sprayed with a heavy layer of Cu, 0.16 cm or more in thickness. Preferably, the Ag and Cu are sprayed to form a jacket over the top end of the PbO_2 electrode, as in Fig. 2. The combination is sufficiently adherent to the base oxide so that it can be machined to fit in a mechanical current contact or it can be soldered directly to the power bus without injury to the PbO_2.

Testing the PbO_2 Anodes

Electrodes formed by plating a thin coat of PbO_2, 0.04 cm or less, on a base metal proved unsatisfactory when used as anode in a perchlorate cell. With such a thin coating on Ta there was poor electrical contact and poor adhesion. The PbO_2 coating on Ni and other base metals proved to be extremely porous and did not protect the base metal from rapid anodic erosion when used in the perchlorate cell.

Thick PbO_2 deposits, 0.16 cm or more, on Ta proved to be efficient anodes in the perchlorate cells. The Ta base polarizes rapidly and then acts as an inert filler. Thick deposits on Fe and Ni also proved satisfactory after they had operated sufficiently long to leach out all traces of the base metal that were left after the original plating operation. It is, therefore, desirable when electrodepositing PbO_2 on metals such as Fe and Ni, to keep the weight of the base to a minimum.

Table III. Current efficiencies in electrolysis of NaClO₃ with PbO₂ and Pt anodes (no additives)

Anode	Test No.	NaClO₃ conc. range over which eff. is calculated Initial g/l	Final g/l	Current efficiency, %
Pt	1	602	100	85.2
		293	39.8	82.4
	2	602	100	87.4
		197.6	3.9	65.4
PbO₂	1	606	100	75.0
		198	1.8	27.1
	2	612	100	61.2
		186	49.1	33.9

Anode current density = 0.3 amp/cm²; cell temperature = 25°-35°C; cell potential = 5-6.5 v.

Table IV. Effect of K₂S₂O₈ additive on current efficiency in electrolysis of NaClO₈ with PbO₂ anode

g K₂S₂O₈ per liter of electrolyte	Test No.	NaClO₃ conc. range over which eff. is calculated Initial g/l	Final g/l	Current efficiency, %
2.08	1	606	7.1	73.3
		204	7.1	52.0
2.08	2	606	30.3	68.2
		200	44.9	49.2
None	1	606	28.9	46.5
		200	28.9	27.1
		126	28.9	20.3
None	2	606	31.0	43.4
		200	31.0	30.5
		128.4	31.0	22.9

Anode current density = 0.3 amp/cm²; cell temperature = 25°-35°C; cell potential = 5-6.5 v.

The large PbO₂ electrode formed on the Ta screen, and described above, was used with a sprayed Cu over Ag contact in a 100 amp perchlorate cell at a current density of 0.28 amp/cm² and a temperature of 30°-50°C. The cathodes were type 430 stainless steel and the electrolyte was 5 liters of NaClO₃ solution having an initial concentration of 600 g/l. This cell was operated for 24 batches for a total running time of 860 hr without noticeable erosion of the anode, and with less than 0.25 ppm of Pb in the recovered NaClO₄.

The current efficiency of PbO₂ anodes in the conversion of chlorate to perchlorate, although less than that of Pt, is reasonably high when the concentration of NaClO₃ in the electrolyte is above 100 g/l. Below this concentration of chlorate, the current efficiency drops sharply. In Table III, the current efficiencies of PbO₂ and Pt anodes are compared for various chlorate concentration ranges when operated in 10-amp cells.

In order to obtain higher current efficiencies with the PbO₂ anode, especially in the lower chlorate concentration range, the use of additives becomes necessary. Sugino (10) has reported using NaF additive at a concentration of 2 g/l. In the present work, K₂S₂O₈ was found (11) to be even more effective, and the increase in current efficiency due to this additive is shown in Table IV.

Acknowledgments

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