

1

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LEAD DIOXIDE ELECTRODE

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The present invention relates to a novel electrode for use in electrochemical processes and to the methods of making and using the same; and, more particularly, the invention relates to a novel lead dioxide-containing electrode which is particularly useful in the electrolysis of chlorates in the manufacture of perchlorates, to its method of preparation and to its use in electrochemical processes, especially in the electrolysis of chlorates to perchlorates.

It has long been known that aqueous solutions of chlorate, such as the alkali metal chlorates, can be electrolyzed to form the corresponding perchlorates in solution. For example, in the preparation of potassium perchlorate, common practice is to electrolyze sodium chlorate to form sodium perchlorate, treat the sodium perchlorate with potassium chloride to precipitate potassium perchlorate and return sodium chloride to the chlorate cells. The literature on the electrolytic production of perchlorates indicates a unanimous acceptance of platinum as the only suitable anode material. In spite of the high capital investment involved and the significant replacement costs due to electrochemical attack and mechanical disintegration, platinum is still used as anode in the major perchlorate installations.

However, for reasons apparent from the above, the search for a platinum substitute, both for perchlorate manufacture and for other electrochemical operations requiring highly resistant electrodes, has proceeded for many years. None of the materials investigated, however, have been adopted commercially. Graphite is too strongly attacked to be serviceable as anode material in perchlorate production. Silicon anodes have also been suggested for the electrochemical oxidation of chlorates. Although cold-pressed and sintered silicon anodes have been found to operate without noticeable erosion, during operation the voltage rises rapidly to a very high value due to polarization, and this polarization characteristic renders silicon unusable commercially. Magnetite has been found to be useful only at very low current densities. Although this material shows only slight erosion during operation, the perchlorate is produced at a current efficiency of only about 4-5%.

Lead dioxide has also been suggested for use as anode material in the electrolytic oxidation of chlorates and other materials. In this case, the lead dioxide has been electroplated onto iron, steel, copper or nickel metal bases. Although the lead dioxide, especially in massive form, has a very low rate of erosion itself in the chlorate-perchlorate system, the base metals onto which it is deposited are rapidly eroded since the electrolyte gains access thereto through pinholes in the lead dioxide coating. This leads to breakdown of the anode itself. In addition it also results in the contamination of the perchlorate product which, at least in some applications, is considered highly undesirable.

The metal base onto which the lead dioxide has been deposited, previously, has been in the form of rods, hollow cylinders, sheets, blocks, and the like. It was found

2

that there was a marked tendency for the lead dioxide to crack or break away from the base metal during normal handling or machining operations due to the natural brittleness of the lead dioxide and its poor adhesion to the metal base body and to stresses set up through expansion and contraction differentials during changes in temperature.

It is the principal object of the present invention to provide a novel electrode material possessing properties comparable to those of platinum when employed in electrolytic oxidation systems, such as in the electrolytic oxidation of chlorates to perchlorates.

Another object of the present invention is to provide a novel lead dioxide-containing anode which is markedly less susceptible to breakdown during operation than prior lead dioxide-containing anodes and which imparts less contamination to the chlorate-perchlorate solution than do prior lead dioxide-containing anodes.

Still another object of the present invention is to provide a novel lead dioxide-coated metal base anode which possesses a greater mechanical strength and less tendency to crack or break during handling than do prior lead dioxide-containing anodes.

A further object of the present invention is to provide a novel method for making a lead dioxide-containing electrode having the above-discussed characteristics.

Other objects, including a novel method for conducting electrochemical reactions, especially electrochemical oxidation of chlorates to perchlorates, using the novel electrode of the present invention, will become apparent from a consideration of the following specification and the claims.

The novel electrode of the present invention comprises a fine metal screen having a large surface relative to its volume having a coating of lead dioxide electrodeposited thereon. The electrode is prepared by anodically electrodepositing lead dioxide from an aqueous solution of a lead salt onto a fine metal screen having a large surface area relative to its volume. In one embodiment the metal screen is removed leaving a body consisting essentially of lead dioxide for use as electrode.

The electrode of the present invention overcomes or eliminates many of the above-mentioned limitations and disadvantages of prior lead dioxide-containing electrodes.

In the first place, it has been found that massive layers of lead dioxide can be electrodeposited onto a very fine metal screen which presents a high surface area relative to its volume. The metal screen becomes heavily coated and the interstices completely filled in so that the resulting product consists principally of the lead dioxide, and the removal of the metal, as by dissolution, has little effect upon the mechanical strength of the lead dioxide structure. In other words, during electrodeposition, the lead dioxide fills the interstices of the screen so that the resulting lead dioxide body is in effect a solid body of lead dioxide containing a thin fine network of fine metal members, which, upon dissolution, leaves a thin network of very fine channels which do not affect significantly the mechanical strength of the remaining lead dioxide body.

Of course, prior to dissolution of the metal base or its removal by other means, it may serve to some extent as reinforcement for the assembly during handling, and with certain metals, principally tantalum, the metal base will not become dissolved during use. The removal of the base metal before or during use, and the elimination of contamination will be discussed more in detail hereinafter. Because of the relative fineness of the metal base temperature changes will not set up stresses having an adverse affect upon the structure. Because the product consists substantially entirely of lead dioxide, and the lead dioxide is bonded to itself through the interstices

of the screen, the fact that the lead dioxide bonds poorly to the metal itself is immaterial.

The metal screen employed in accordance with the present invention may be selected from a wide variety of metals including tantalum, steel, nickel, Monel metal, tin, magnesium, aluminum, copper, and the like. Screens may be prepared by weaving individual wires crosswise or by stamping closely spaced holes in a metal sheet in either of which case a reticulated or foraminous network is provided and all of which are referred to herein as "screen." The size of the openings in the screen and of the wires from which they are made, or of the crossing elements in the case of a stamped screen, may vary somewhat. The wire size may range from about 0.08" in diameter down to about 0.003" in diameter, or even finer, preferably 0.03" in diameter or finer. In general, the wire size of the screen may be somewhat finer than when plating on a single wire because of the strengthening effect of the interlacing of the wires in the screen. The number of openings per linear inch, which may in turn depend upon the wire size, may range between about 10 and about 50 mesh. Examples of materials of this type are: 50 mesh surgical tantalum gauze made of 0.003" wire; 14 mesh tantalum screen made of 0.025" wire; 16 mesh nickel screen made of 0.012" wire; 14 mesh steel screen made of 0.020" wire; and the like. The stamped screens employed will be of comparable mesh and crossing element sizes.

As stated, the metal screen onto which the lead dioxide is deposited will have a high surface area relative to its volume. The ratio of surface area (e. g. in square inches) to volume (e. g. in cubic inches) for a 0.08" diameter is 50. This ratio increases as the wire diameter decreases until it reaches 1330 for a 0.003" wire. The metal screen, therefore, will have a ratio of at least 50 square units per cubic unit.

The preparation of lead dioxide-containing anodes using tantalum broadly as a base during the electrochemical deposition is disclosed and claimed in copending application Ser. No. 552,970, filed December 14, 1955. In that application it is pointed out, that although tantalum metal is known to polarize anodically in most electrolytes, it was found quite unexpectedly that, in the conventional lead dioxide plating baths, this polarization does not occur so that lead dioxide of a very high quality and of any desired thickness can readily be anodically deposited on the tantalum. The rapid polarization of tantalum, however, occurs in the chlorate cells, and in this case the rapid polarization of tantalum in the chlorate cells prevents it from becoming attacked chemically. The use of tantalum wire or screen bases in the present invention is particularly preferred.

In preparing the lead dioxide-containing electrode in accordance with the present invention, any lead dioxide plating bath may be employed. The conventional lead dioxide plating baths generally fall within one of three principal systems: (1) alkaline aqueous solutions of lead tartrate; (2) non-alkaline aqueous solutions of lead perchlorate; and (3) acid aqueous solutions of lead nitrate. In preparing the alkaline lead tartrate bath, lead tartrate itself may be added to water along with a suitable base, or lead tartrate may be formed in situ in the bath. This latter embodiment is the preferred method of preparing the lead tartrate bath, and comprises mixing in water a soluble tartrate other than lead tartrate, such as an alkali metal tartrate, like sodium potassium tartrate, a base and lead oxide (PbO). The lead oxide dissolves in the alkaline tartrate solution forming lead tartrate in solution. In this embodiment it is not necessary that stoichiometric amounts of tartrate and lead oxide be employed. For example, with sodium potassium tartrate



between about 1 and about 1.5 parts, by weight, prefer-

ably between about 1.1 and about 1.25 parts, by weight, thereof per part of lead oxide may be used.

The lead tartrate bath, as stated, will be alkaline and hence a soluble base, preferably an alkali metal hydroxide, including ammonium hydroxide, is employed. Sodium hydroxide and potassium hydroxide are preferred with the former being particularly advantageous. The amount of base present in the alkaline lead tartrate bath, that is to say the alkalinity of the bath, may vary somewhat. It has been suggested that as little as 2.7 moles of alkali hydroxide may be present per mole of lead tartrate. In copending application Serial No. 552,967, filed December 14, 1955, however, is disclosed and claimed the anodic electrodeposition of lead dioxide from a lead tartrate bath in which the amount of total alkali hydroxide present in the bath provides a mole ratio thereof to lead tartrate of at least about 4.5 to 1, and the amount of alkali hydroxide may be such as to provide a mole ratio thereof to lead tartrate of as high as about 8 to 1, or higher. In any event, the pH of the alkaline tartrate bath should be relatively high, pH's of above about 12 being particularly satisfactory.

The actual concentration of the main materials of the lead tartrate bath at the beginning of deposition may vary widely, although excessively high concentrations may lead to precipitation and to low quality deposits. For these reasons, the concentration of lead in the bath is generally not in excess of about 8% (about 93 grams per liter). The concentration of lead may be substantially below this, and it may be as low as about 1-2% (about 10 to 20 grams per liter). In preferred practice, the concentration of lead in the bath ranges between about 3 and about 5% (between about 32 and about 55 grams per liter).

The lead perchlorate bath for electrodepositing lead dioxide is essentially an aqueous solution of lead perchlorate having a pH ranging from neutral to acid, preferably acid. The bath may be prepared by adding lead perchlorate itself in water, or the lead perchlorate may be formed in situ in the bath. This latter embodiment is the preferred means of preparing the lead perchlorate bath, and comprises adding lead oxide (PbO) to an aqueous solution of perchloric acid. The amount of perchloric acid employed will be at least that theoretically required to combine with the lead oxide to provide lead perchlorate, and preferably excess perchloric acid is employed so that the pH of the solution is acid. Referring further to the pH, acid pH conditions are preferred, as stated, preferably within the range of about 0.8 to about 5.

The concentration of lead perchlorate in the bath at the beginning of deposition may vary widely, although concentrations at or near the saturation point under the conditions encountered during operation and shutdown are highly desirable. Generally, the concentration of lead perchlorate may range between about 50 and about 500 grams per liter, preferably between about 100 and about 350 grams liter.

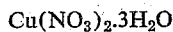
The lead nitrate bath is essentially an aqueous acid solution of lead nitrate. In preparing the bath, lead nitrate itself may be added to water, or the lead nitrate may be formed in situ in the bath, as by mixing lead oxide (PbO) with aqueous nitric acid. In connection with this latter embodiment, slow addition of the lead oxide in finely-divided form to the aqueous nitric acid, with stirring, is advantageous.

In general, the more acid the bath, the better its operation, and pH's as low as about 0.8 may be employed. At acidities appreciably greater than this, acid fuming from the bath becomes excessive, especially at elevated operating temperatures. The exact acidity of the bath may depend on the nature of the metal screen onto which the lead dioxide is to be deposited. For example, tantalum is not attacked at the lower end of the pH range whereas some of the other metals, such as steel, are. With metals that are readily attacked, higher acid pH's may be em-

ployed, such as pH's in the neighborhood of about 4, or even higher. The bath initially made up and at the time operation commences, may have a pH somewhat higher than the above figures, since, once operation has started, the pH drops to the desired level due to depletion of lead and release of nitric acid.

The concentration of lead nitrate in the bath, at least at the start of the deposition operation, may vary widely. In this connection, the concentration of the lead nitrate in the bath may range from as low as about 50 grams per liter to as high as the maximum solubility thereof in the bath at operating temperature, which may be as high as about 700 grams per liter. In general, it is desirable, in order to produce a lead dioxide deposit of optimum homogeneity, strength and surface characteristics, to maintain high concentrations of lead nitrate in the vicinity of the anode. Accordingly, concentrations above the lower end of the range, such as at least about 250 grams per liter and especially at least about 300 grams per liter are preferred. In order to facilitate handling of the bath during shutdown periods and during continuous replenishing procedures, when the bath may be at or near room temperature, it is also preferable that the concentration of the lead nitrate not be substantially in excess of its solubility at these lower temperatures, which may be in the neighborhood of about 400 grams per liter. For optimum commercial operation, the concentration of the lead nitrate will not exceed about 350 grams per liter.

In the lead nitrate bath, a small amount of copper nitrate may be included to prevent deposition of lead on the cathode. The amount of copper nitrate



may vary widely, and may run as high as about 30 grams per liter, although it has been found that amounts as low as about 0.5 gram per liter provide significant results.

In copending application Ser. No. 552,969, filed December 14, 1955, there is disclosed and claimed a novel acid lead nitrate bath for anodically electrodepositing lead dioxide in which is included a non-ionic surface-active agent, stable and soluble therein, such as the alkyl aryl polyether alcohols, the presence of which insures the deposition of hard, dense, fine-grained lead dioxide. The amount of non-ionic surface active agent may range between about 0.5 and about 10 grams per liter, preferably between about 0.75 and about 2 grams per liter. In the bath disclosed in said copending application, it has been found that between about 0.75 and about 2.5 grams of copper nitrate trihydrate per liter are optimum.

As far as the operating temperature of the various bath systems is concerned, in general, any of those baths may be operated at temperatures ranging from about room temperature up to the boiling point of the bath. The exact optimum operating temperature will, of course depend upon the particular bath system selected. In general, however, it has been found that with any of the baths, moderately elevated temperatures, such as between about 60 and about 75° C., are preferred.

In the preparation of the electrode material in accordance with the present invention, the metal screen is immersed as anode, in the desired bath, and is connected to a suitable source of current. Because with very fine screens kinking or bending thereof may be encountered, it may be desirable to weight the metal base so that it will remain straight and perpendicular during the plating operation. In this connection, a weight, such as a small glass bulb filled with mercury, may be attached to the end of a fine screen. Portions of the screen on which it is not desired to plate lead dioxide may be coated with a stop-off lacquer or paint. By appropriate shielding, such as that disclosed and claimed in copending application Serial No. 534,618, filed September 15, 1955, the deposition of lead dioxide at selected portions of the metal base can be controlled.

The metal screen, before being immersed in the lead dioxide plating bath, should be substantially free of oxide film which will hinder the anodic plating of the lead dioxide thereon. Any such oxide film may readily be removed by chemical or mechanical means well known in the art and as dictated by the nature of the metal member.

In the lead dioxide electrodepositing bath, a cathode is also provided. The cathode material may be selected from a wide variety of conducting materials, including lead itself, carbon, and the like. Preferably the cathode is a material non-reactive with the bath during shutdown, such as carbon.

Upon completion of the circuit, lead dioxide begins to deposit at the anode, and the flow of current may be continued until the desired deposit has been built up. Preferably, the lead dioxide is deposited in a relatively massive layer, that is, in layers of at least $\frac{1}{16}$ " thick and upwards of 1" thick or more. In the resulting product the lead dioxide will make up the preponderant portion in terms of volume and weight, and the interstices of the screen are completely filled in and the lead dioxide has the appearance of being a solid, continuous plate or block.

If desired the metal base may be removed before using the electrode in the contemplated electrochemical procedure to provide an electrode material consisting entirely of lead dioxide. Chemical dissolving means may be employed. For example the metal base may be dissolved out in a pre-electrolysis using a sodium chlorate or other suitable electrolyte.

Operation of any of the various baths, of course, removes lead therefrom. Before the concentration of lead in the bath falls to a point where the bath no longer operates efficiently, it may be necessary, for further deposition, to replenish the bath. The bath may be replenished periodically or continuously. In replenishing any of the baths more lead dioxide (PbO) may be added. In the case of the lead nitrate bath, some nitric acid is also lost during operation of the bath so that it may be also necessary to add further nitric acid as the bath is replenished in order to maintain the desired pH.

The resulting product may thus be used as electrode in electrochemical procedures in accordance with technique conventional therein. One of the principal uses of the present electrode is as anode in the electrolytic oxidation of chlorate to perchlorate. The product may also be used as anode in the electrolytic oxidation of chromic sulfate to chromic acid and of sulfate to persulfate and in the electrolysis of sodium chloride to sodium perchlorate. When the metal base is of a type which will become dissolved during the contemplated electrochemical reaction and it is not removed before use, means may be provided to eliminate the possible contamination of the electrolyte by the dissolved metal where such contamination would be undesirable. For example a chlorate cell may be operated under slightly alkaline or neutral conditions when the metal body is nickel or iron. As the metal dissolves it in part precipitates as the hydroxide and in part plates at the cathode. The precipitate can be removed leaving the final solution free of contamination by the metal. In some cases, however, it may be desirable to operate the electrochemical process under acid conditions where the dissolved metal remains in solution. In this case the final electrolyte can be treated, as by making it alkaline, to precipitate the metal which can then be removed.

The present invention will be more readily understood from a consideration of the following specific examples which are given for the purpose of illustration only and are not intended to limit the scope of the invention in any way.

Example I

An acid lead nitrate bath is prepared by dissolving lead oxide (PbO) in sufficient aqueous nitric acid to provide a concentration of lead nitrate of 350 grams per liter and a pH of 1-2.2. One and one-half grams

per liter of copper nitrate trihydrate and 1.5 grams per liter of alkyl phenoxy polyoxyethylene ethanol (Igepal CO-880), are added to the solution.

A 14 mesh tantalum screen of 0.025" wire and having dimensions of 3" x 18" is immersed in the bath to a depth of 14 $\frac{1}{8}$ ". The screen is attached as anode to a suitable source of current.

A carbon rod is also immersed in the bath and attached as cathode to the same source of current.

Plastic shields are immersed in the bath at the edges of the screen and at the bottom thereof to prevent serious treeing of lead dioxide at these points. Suitable shielding means form the subject matter of copending application Serial No. 534,618, filed September 15, 1955.

The bath is heated to 70° C., and the circuit is completed. The anode current density is 15 amperes per square foot.

Smooth, hard coating of lead dioxide forms on the tantalum screen. After 143 hours of plating, the lead dioxide deposit has a thickness of $\frac{5}{8}$ ", and weighs 4,900 grams.

A sprayed copper over silver current contact is formed on the top 3" of the electrode prepared as described above. This copper over silver current contact is disclosed and claimed in copending application Serial No. 534,617, filed September 15, 1955, now U. S. Patent No. 2,824,027. The electrode is then operated as anode in the electrolysis of a 600 gram per liter sodium chlorate solution.

Typical data obtained in electrolyzing sodium chlorate with this anode are as follows:

Anode current density—28 amperes per square decimeter.

Anode current—100 amperes.

Cell voltage—6.3.

Cell temperature—33° C.

Cathodes—type 430, stainless steel.

Current efficiency on electrolyzing sodium chlorate solution from 602 to 55.6 grams per liter—52.6%.

Current efficiency on electrolyzing sodium chlorate solution from 602 to 100 grams per liter—60.4%.

The cell operated for 860 hours at 100 amperes without any noticeable erosion of the lead dioxide anode.

Example II

In this example the bath employed in Example I is also used. A 16 mesh nickel screen of 0.012" wire and a width of 3" and a length of 20" is immersed in the bath to a depth of 15". The screen is attached as anode to a suitable source of current. Carbon cathodes are also employed, and attached to the same source of current. The anode current density is 20 amperes per square foot.

A hard, dense lead dioxide deposit is plated on the nickel screen. After 138 hours of plating the lead dioxide has a thickness of $\frac{7}{8}$ " and weighs 6,900 grams.

Example III

In this example the bath of Example I is used. A 50 mesh surgical tantalum gauze of 0.003" wire and a width of 1" and a length of 12" is immersed in the bath to a depth of 7". The gauze is attached as anode to a suitable source of current. Carbon cathodes are also employed, and attached to the same source of current. The anode current density is 20 amperes per square foot.

A dense deposit of lead dioxide is formed on the tantalum gauze. After 117 hours of plating, the lead dioxide deposit is $\frac{1}{4}$ " thick and weighs 788 grams.

A current contact is formed on the top 2" of this electrode by casting a block of Wood's metal alloy about this portion of the electrode.

Typical data obtained in electrolyzing sodium chlorate with this electrode are as follows:

Anode current density—10 amperes per square decimeter.

Anode current—10 amperes.

Cell voltage—7.1.

Cell temperature—10° C.

Cathodes—type 430 stainless steel.

Current efficiency on electrolyzing sodium chlorate solution from 605 to 100 grams per liter—71.8%.

Example IV

In this example the bath employed in Example I is used. A 14 mesh steel screen of 0.020" wire and a width of 3" and a length of 18" is immersed in the bath to a depth of 14". The screen is attached as anode to a suitable source of current. Carbon cathodes are also employed, and attached to the same source of current. The anode current density is 20 amperes per square foot.

Plastic shield of the type disclosed and claimed in said copending application Serial No. 534,618 are immersed in the bath at the edges of the screen and at the bottom to prevent serious treeing of lead dioxide at these points.

A hard, dense deposit of lead dioxide is formed on the steel screen. After 113 hours of plating, the lead dioxide deposit is $\frac{3}{8}$ " thick and weighs 4,715 grams.

Considerable modification is possible in the selection of the base metal members, the constituents of the bath and the conditions under which the bath is operated, and in the use of the novel electrode material without departing from the scope of the invention.

We claim:

1. An electrode for electrochemical processes comprising a metal screen presenting a large surface area relative to its volume having a coating of lead dioxide electrodeposited thereon, said electrodeposited lead dioxide completely filling the interstices of said screen.

2. The electrode of claim 1 wherein the screen is a tantalum screen.

3. The electrode of claim 1 wherein the screen is a nickel screen.

4. The electrode of claim 1 wherein the metal screen has a surface area to volume ratio of at least about 50 square units per cubic unit.

5. An electrode for electrochemical processes comprising a metal screen presenting a large surface area relative to its mass having a coating of at least $\frac{1}{16}$ " thick of lead dioxide electrodeposited thereon, said electrodeposited lead dioxide completely filling the interstices of said screen.

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