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R. E. CUSHING
METHOD OF PRODUCING INORGANIC COMPOUNDS
OF INCREASED OXIDATION STATE
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Fig. 2

Fig. 1



Fig. 1^a

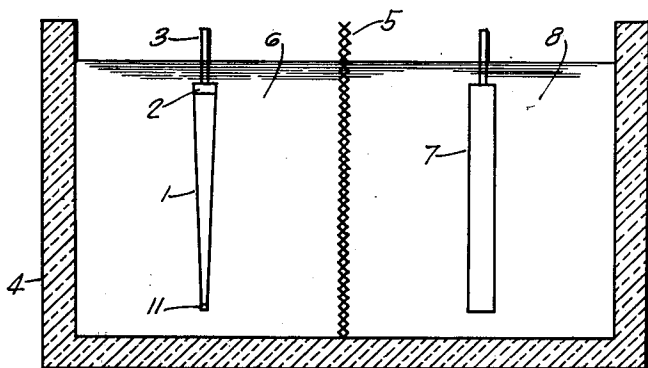
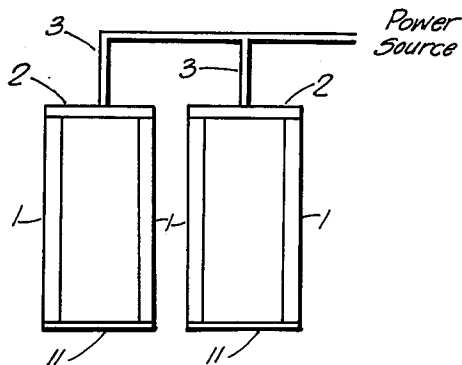
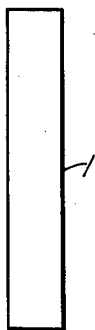
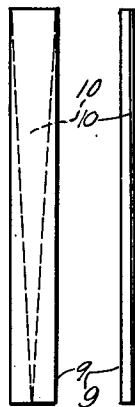


Fig. 3

Fig. 4 Fig. 4^a



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METHOD OF PRODUCING INORGANIC COM-
POUNDS OF INCREASED OXIDATION
STATE

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8 Claims. (Cl. 204—82)

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This invention relates to a new form of electrode for an electrolytic cell in which a desired electrochemical reaction is brought about in the electrolyte.

A large number of chemical reactions are commonly carried out in industry by subjecting solutions containing reactants to electrolytic action. Thus in the production of hydrogen peroxide it is common to subject alkali metal bisulphate, including ammonium bisulphate solutions, or solutions of sulphuric acid, to electrolysis, in order to oxidize the cation to the corresponding persulphate, which is then withdrawn from the electrolytic cell and further treated for the production of hydrogen peroxide. A large number of other well known oxidation and reduction reactions, as well as other chemical reactions, are carried out by electrolytic action in aqueous or non-aqueous solutions. For the economical operation of such electrochemical processes it is usually necessary that certain physical characteristics of the system be carefully controlled. Thus it is usually important that the difference of potential between an electrode and the body of electrolyte, or the current density at the electrode surface or in the body of the electrolyte, be maintained between definite limits; operation under conditions outside such limits will either result in furnishing too little energy to bring about the desired chemical reaction while wasting power in resistance losses, or in furnishing too much energy or providing too high a potential so that some undesirable side reaction is promoted, or overheating the electrode and/or solution so that either lower electrolytic yields or actual decomposition of the desired product results.

In many electrolytic cells the proper electrical conditions can be maintained throughout the electrolyte by merely carefully controlling the overall voltage applied to this cell, but in some electrochemical processes, such as the production of persulphate, or persulphuric acid referred to above, and other processes employing costly material such as precious metals as electrode material, it has been found that despite careful control of cell voltage the electrochemical action occurring in the electrolyte is quite irregular. Under some conditions the reaction is too violent and decomposition and undesirable side reactions occur, while under other conditions the local difference of potential, current density, or over-voltage is apparently insufficient to cause the desired reaction to take place.

I have now discovered that such irregular

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chemical reactions occurring on the surface of the electrode in an electrolytic system employing costly material such as precious metals as electrode material, may be related to the fact that loss of potential throughout the length of the electrode is high, i. e. may be greater than one volt, and that this loss does not occur at a uniform rate over the length of the electrode from one end to the other. I have further found that the irregularity and non-uniformity in the chemical reaction on the surface of the electrode in such a cell, as well as the other disadvantages above mentioned, can be substantially eliminated by providing that the electrode having the substantial resistance referred to be of such construction that the resistance per unit length of successive portions of such electrode be in inverse relation to the magnitude of the current in such successive portions when the electrolytic system is in operation; that is the immersed portion of the electrode may be either of variable size or of variable material of construction, such that the resistance per unit length of electrode has a smaller value in that part of the electrode nearer the point of connection to the source of power, whereas the resistance per unit length of the electrode has a successively greater value in successive parts of the electrode farther from the point of connection to the power source. Thus the platinum anodes generally used in the electrolysis of sulphates or sulfuric acid to form the corresponding persulphate or persulfuric acid may have the cross-section of their immersed portions in tapered form, the thickest part of the electrode being nearest to the connection to the power source. Since a metal such as platinum is costly, a minimum quantity should be employed in electrode construction, but it is a part of my discovery that when the investment cost in such metal is balanced against losses caused by irregularity in the chemical reaction, IR losses in the electrode, and losses due to electrode disintegration caused by the electrochemical action, a surprisingly low total investment and operational cost may be achieved by an electrode construction such as above described.

It must be understood that although in my preferred construction the cross-sectional area of the electrode is continuously varied from one end to the other, this is preferably accomplished without substantial variation in the width of the electrode face presented to the electrolysis zone, in the interest of keeping the electrolytic action as uniform as possible, from one end of the electrode to the other.

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In the accompanying drawing there are illustrated in diagrammatic form two embodiments of the electrode design of my invention as applied to platinum anodes employed in cells for the electrolysis of ammonium bisulphate to produce ammonium persulphate. Figures 1 and 1a are diagrammatic representations of one of the immersed portions of such a platinum anode showing side and face views, respectively, the side view showing the tapered shape. Figure 2 is a diagrammatic representation showing how several such tapered members (face views) are incorporated into a single anode structure in a preferred form of construction. Figure 3 is a diagrammatic representation of a cell showing a side view of the anode, illustrating how the anode structure is placed in the anode compartment. Figures 4 and 4a illustrate another advantageous electrode construction within the scope of my invention.

In the illustrated embodiment, the immersed anode portion 1 is tapered approximately uniformly from its upper end to its lower end as shown. When the anode is immersed in the electrolyte, the lower end of this member is farthest from the source of power, whereas the upper end is closest to the power source. In the preferred construction shown in Figure 2, four members such as those shown in Figure 1 are employed to form a single anode structure. Pairs of these members may be advantageously connected together, top and bottom, by the lateral members 2 and 11 as shown and the two upper lateral members may be connected through leads 3 with the power source. Lateral members 11 are employed for mechanical rigidity only. In the same manner a plurality of single anodes, singly or in groups, may likewise be employed. In use such anode may be immersed in the anode chamber of a cell such as that shown in Figure 3. The cell tank 4 is constructed of a suitable material such as stoneware, porcelain, or glass and is divided into an anode and a cathode chamber by diaphragm 5. In Figure 3 the anode structure 1-2-3 is shown immersed in the anolyte 6 in the anode compartment and the cathode 7 commonly made of lead in this case is shown immersed in cathode compartment 8.

Figure 4 illustrates another construction by which the same result can be achieved. In this case a thin platinum strip 9 of uniform thickness has welded to one surface (namely to the surface that becomes the back of the strip 9 in an electrolytic operation) a second platinum strip 10 of uniform thickness but tapering in width from top to bottom. This method of construction likewise results in an electrode which when used results in a much lower loss of potential throughout its length than is common in the prior art electrode, the potential loss being substantially linear along the length of the electrode, just as in the electrode construction shown in Figure 1.

Representative prior art electrodes of the type under discussion are described, for example, in the section of the War Department's report PB 17331 dealing with operation of the Elchemie G. m. b. H. electrolytic persulfate plant at Shaftebau, Austria; the report states that the working anode surface is provided by platinum strips 400 mm. long, 8 mm. wide and .04 mm. thick, positioned vertically in the cell with the 8 mm. wide surfaces facing the electrolysis zone. Tapered anodes constructed in accordance with my invention, containing approximately the same

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effective anode surface as the above but having all the advantages above enumerated for my new electrode construction, may be exactly the same dimension as the above-described platinum strips except that the thickness increases uniformly from .04 mm. at the bottom to about ten times that value at the top end of the strip.

The following example is illustrative of the advantages of my electrode construction, as demonstrated for platinum anodes employed in a conventional electrolytic operation, namely persulfate production, operated in the manner fully described in the art.

In a number of illustrative runs the operation of an ammonium persulfate cell equipped with tapered platinum anodes as above described was compared with the operation of a cell equipped with the prior art type of anode, containing approximately the same effective anode surface area but so constructed that the immersed portion of the anode had substantially the same cross-sectional area throughout its length. The following tabulation shows the cell voltage required for the two types of anodes, namely the prior art type (identified as "old type anode") and the type of the present invention (referred to as "new type anode").

	Cell Voltage; Old Type Anode	Cell Voltage; New Type Anode
A. Operation at 1.0 amp./cm. ² -----	4.9	4.4
B. Operation at 1.5 amp./cm. ² -----	5.7	4.8 to 5.0
C. Operation at 1.8 amp./cm. ² -----	6.1	5.2

On a commercial scale the current efficiency of the old type anode has been found to be 66.7%. Under the same conditions the new type anode resulted in a current efficiency of 77.8%.

In addition to the increased efficiency of operation and the reduction in power requirement as shown by the above tabulation, other important advantages were noted in the use of the tapered electrode, as compared to the old type anode. In the formation of ammonium persulfate the maintenance of relatively low temperatures in the anode chamber results in improved current efficiency. Temperatures are usually kept low by providing cooling coils or tubes by means of which the heat developed as a result of the electrolytic oxidation and electrical power losses through the cell is removed. Because of the decreased power waste resulting from the use of the new type anode, the cooling load on the electrolyte refrigeration system was reduced substantially. Moreover with the old type of electrode it was noted that there was a tendency for violent activity to take place near the upper part of the immersed portion of the anode and this activity resulted in the attack of the platinum of which the anode was constructed which made periodic repair and replacement of the anode structure necessary. No such attack was noted with the tapered anodes of the above example. Other electrolytic processes to which the electrode construction of my invention is applicable include:

(a) Electrolysis of chlorides such as sodium chloride to form chlorine and caustic soda employing an aqueous solution of chlorides, the anodes being made of platinum and cathodes made of iron.

(b) Electrolysis of aqueous chloride solutions to form chlorates, using electrodes as in A.

(c) The electrolytic preparation of perphosphates employing platinum anodes.

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(d) The electrolytic formation of percarbonates employing platinum anodes.

(e) Electrolytic oxidation of chlorates to perchlorates, using platinum anodes.

(f) The electrolytic production of hypochlorites, using bipolar electrodes of platinum-iridium.

(g) The electrolytic production of iodoform from alcohol and iodide, using platinum anodes.

(h) Electrolytic reduction of p-aminophenol to nitrobenzene, using platinum cathodes.

As above stated, the new electrode construction of my invention is important for electrodes made of costly material such as the precious metals. Examples of such materials include: platinum, gold, tantalum, iridium, palladium, related metals, and the various chemically resistant costly alloys, e. g. an alloy containing a precious metal. Such electrodes are employed in electrolytic operations in which the desired electrochemical reaction does not consume the material of the electrode under discussion.

Although, as above made clear, a uniformly decreasing cross-section in the immersed portion of the electrode of my invention is preferred in order that the small potential loss that still exists in my electrode construction be substantially linear, in relation to the electrode length, it is also within the purview of my invention that the decrease in cross-sectional area (or the equivalent variation in construction employed to obtain decreasing current-carrying capacity) may be step-wise, in two or more steps, resulting in three or more electrode sections of successively decreasing current-carrying capacity. Various contours of constructions of the immersed part of the electrode may be feasible so long as it is a general characteristic of the greater part of the immersed electrode member that the current-carrying capacity of successive portions thereof decreases either continuously or step-wise as the length of the electrical path to each such portion increases. Such terms as "generally decreasing" and "generally increases" are used in the claims to mean that the decrease or increase (as the case may be) may be either uniform or step-wise, and that small irregularities in electrode contour or construction are disregarded.

Since many modifications to the apparatus of my invention as described above are possible without departure from the scope of the invention, it is intended that the above description of my invention should be interpreted as illustrative, and the invention is not to be limited except as set forth in the claims which follow.

I claim:

1. The method of producing an inorganic compound of an increased oxidation state comprising inserting in an electrolyte formed of a water solution of a corresponding compound of lower state of oxidation a pair of electrodes with electric leads connected thereto, said electrodes comprising an anode and a cathode, said anode being formed of material of the group consisting of platinum, gold, tantalum, iridium, and palladium and having an active surface of substantially uniform width and a body of progressively decreasing cross-sectional area from one end to the other, the conductivity being greatest at its end of greatest cross-sectional area and progressively decreasing with decrease in cross-sectional area toward its end of smallest cross-sectional area, maintaining substantially equal the potential between all facing areas of said electrodes by passing substantially all of the current through said anode portion of greatest conductivity and passing sub-

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stantially equal increments of current from said anode to said electrolyte at various portions of said anode spaced from said portion of greatest conductivity, and thereby progressively decreasing the flow of current through said anode at successive portions with decrease of conductivity in said anode.

2. The method of claim 1 in which the anode is made of platinum.

3. The method of producing inorganic compounds of high oxidation state comprising inserting in a water solution of a corresponding compound of lower state oxidation a pair of electrodes with electric leads connected thereto, said electrodes comprising an anode and a cathode, said anode being formed of at least one material of the group consisting of platinum, gold, iridium, and palladium and formed with a rectangular face and a progressive cross-sectional taper, the conductivity being greatest at its thickest portion and progressively decreasing with the taper towards its thinnest portion, maintaining a substantially equal potential between all facing areas of said electrodes by connecting said lead to said anode at its portion of greatest conductivity and passing substantially equal increments of current from said anode to said electrolyte at various portions of said anode spaced from said portion of greatest conductivity, and thereby progressively decreasing the flow of current through said anode at successive portions with decrease of conductivity in said anode.

4. The method of claim 3 in which the anode is made of platinum.

5. The method of producing persulfates comprising inserting in an electrolyte formed of a water solution of a compound in lower state of oxidation containing the sulfate radical, a pair of electrodes with electric leads connected thereto, said electrodes comprising an anode and a cathode, said anode being formed of material of the group consisting of platinum, gold, tantalum, iridium, and palladium and having an active surface of substantially uniform width and a body of progressively decreasing cross-sectional area from one end to the other, the conductivity being greatest at its end of greatest cross-sectional area and progressively decreasing with decrease in cross-sectional area toward its end of smallest cross-sectional area, maintaining substantially equal the potential between all facing areas of said electrodes by passing substantially all of the current through said anode portion of greatest conductivity and passing substantially equal increments of current from said anode to said electrolyte at various portions of said anode spaced from said portion of greatest conductivity, and thereby progressively decreasing the flow of current through said anode at successive portions, with decrease of conductivity therein.

6. The method of claim 5 in which the anode is made of platinum.

7. The method of producing persulfates comprising inserting in an electrolyte formed of a water solution of a compound in lower state of oxidation containing the sulfate radical a pair of electrodes with electric leads connected thereto, said electrodes comprising an anode and a cathode, said anode being formed of platinum, and formed with a rectangular face and a progressive cross-sectional taper, the conductivity being greatest at its thickest portion and progressively decreasing with the taper toward its thinnest portion, maintaining a substantially equal potential between all facing areas of said

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electrodes by connecting said lead to said anode at its portion of greatest conductivity and passing substantially equal increments of current from said anode to said electrolyte at various portions of said anode spaced from said portion of greatest conductivity, and thereby decreasing the flow of current through said anode at successive portions with decrease of conductivity in said anode.

8. The method of producing inorganic per compounds comprising inserting in an electrolyte formed of a water solution of a corresponding compound of lower state oxidation a pair of electrodes with electric leads connected thereto, said electrodes comprising an anode and a cathode, said anode being formed of material of the group consisting of platinum, gold, tantalum, iridium, and palladium, and formed of two substantially flat strips securely bonded together and in electrical contact with each other throughout their immersed length the first of said strips facing said cathode and being substantially rectangular in shape, whereas the second of said strips decreases successively in width throughout a substantial portion of its length, the conductivity of said anode being greatest at the portion at which the second of said strips is widest and progressively decreasing with decrease in width of said strip, maintaining a substantially equal

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potential between said electrodes by passing substantially all of the current through said anode portion of greatest conductivity and passing substantially equal increments of current from said anode to said electrolyte at various portions of said anode spaced from said portion of greatest conductivity, and thereby decreasing the flow of current through said anode at successive portions, with decrease of conductivity in said anode.

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