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[54] **ANODE AND METHOD OF PRODUCTION THEREOF**

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[52] **U.S. Cl.**..... **204/286;** 136/120 R; 136/138; 204/83; 204/284

[51] **Int. Cl.²**. **C25B 1/00;** C25B 11/02; C25C 7/02; H01M 1/00

[58] **Field of Search** ..... 204/284, 290 R, 290 F, 204/83, 286; 136/138, 120 R

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

83,339 7/1971 Germany ..... 204/290 F

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[57] **ABSTRACT**

An electrode useful for electrowinning and other processes including evolution of oxygen or chlorine or for plating is formed of titanium particles, compacted cold, and coated and cemented with a first layer of manganese dioxide thermally deposited from Mn $(NO_3)_2$ on the grains to form a coating of a combination of manganese dioxide and titanium oxide having a rutile crystal structure, and a further outer layer of manganese dioxide which is electrodeposited, the two coatings not being limited to the surface of the electrode but extending to all exposed surfaces of the grains including those which are walls of channels between the grains. The compression of the titanium powder is to a density between 30 and 70 percent of the density of solid metal. Solid metal such as metal mesh may be included in the titanium powder prior to compacting, such as expanded titanium metal, to assist in strengthening the form. In an alternate embodiment the metal substrate is lead.

4 Claims, 4 Drawing Figures

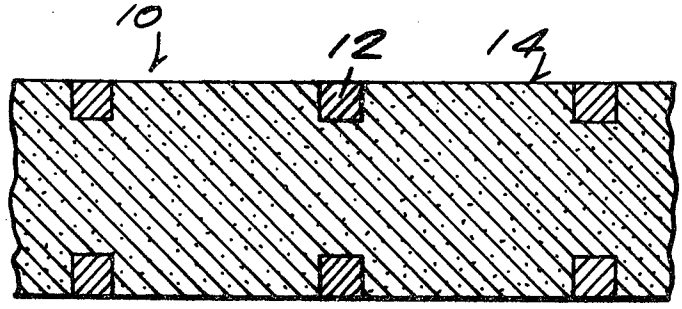


Fig. 1

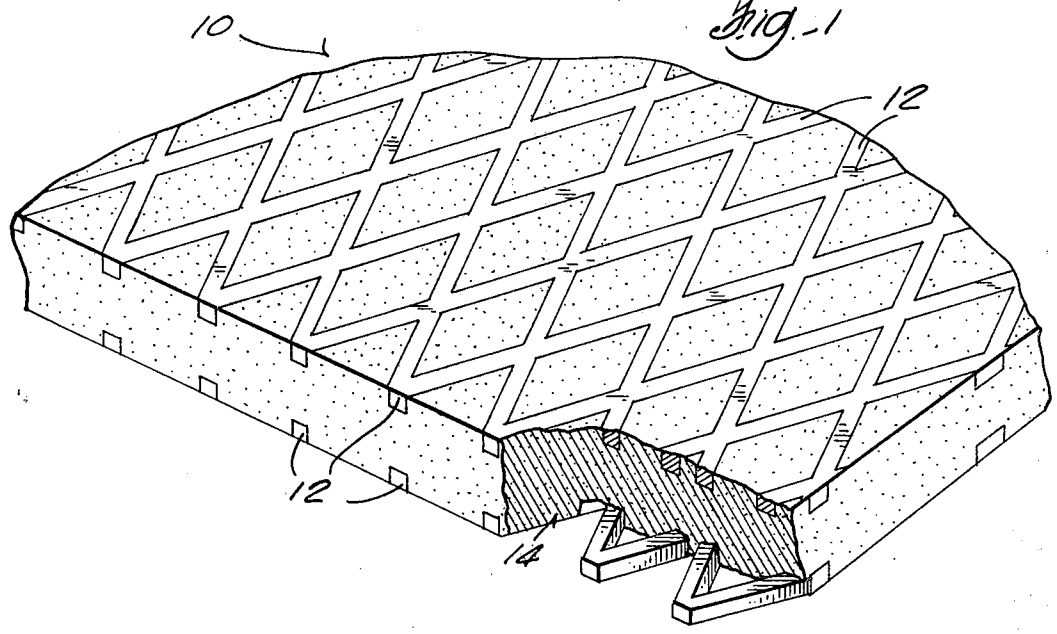
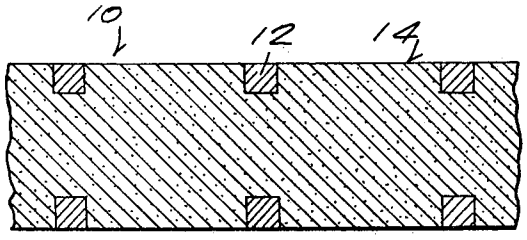


Fig. 2



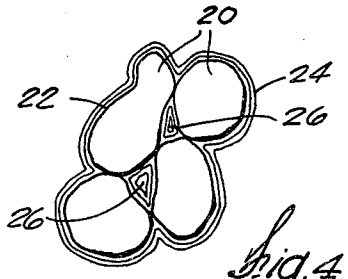


Fig. 4

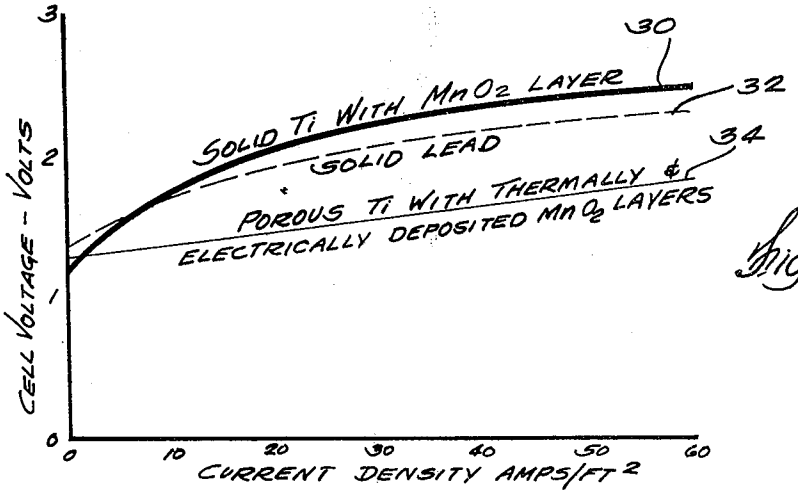


Fig. 3

ANODE AND METHOD OF PRODUCTION THEREOF

This application is a division of application Ser. No. 380,325, filed July 18, 1973, now U.S. Pat. No. 3,855,084.

BACKGROUND OF THE INVENTION

It has long been known that titanium metal has superior properties for use as an electrode in cells, baths or solutions which would corrode and be contaminated by metal from electrodes of other compositions. Nevertheless there are difficulties in the use of a titanium electrode as well. Solid titanium leads to a requirement for high voltage, and gives poor current efficiency. Fox U.S. Pat. Nos. 2,631,115 and 2,608,531 discuss some of the difficulties in connection with specific systems, for instance the passive surface coating on the titanium, and indicate that at least in the production of oxides such as manganese dioxide for use in batteries as a depolarizer, the use of a porous titanium anode made of chips is of assistance. Under certain special conditions described by Fox, the plating of MnO_2 or in a battery, the use of a specific form of titanium chips of about 35 mesh in one case and the use of specific voltage relationships during electrolytic formation of the surface of the electrode prior to use in the other patent, improved results are observed using porous titanium anodes. Fox discloses coating the surfaces of the porous titanium mass with graphite, gold or iron, or with any good conductor which is inert to the electrolyte in which the electrode is to be used. Among other things Fox discloses that his electrodes are useful for the preparation of electrolytic manganese dioxide. His described electrode does not function as an oxygen evolution anode, but passivates under those conditions.

In industry it is most important to select a suitable anode that does not contaminate the electrolyte or contaminate the cathode deposit, that has a long life, and has a low oxygen overvoltage during electrolysis. Platinum is an excellent known anode material which satisifies the above mentioned characteristics.

Recently platinum and other precious metals have been applied to a titanium substrate to retain their attractive electrical characteristics and further reduce manufacturing cost. However such anodes are expensive and are not suitable for some industrial uses. Thus carbon and lead alloy electrodes have generally been used. The carbon anode, however, has the disadvantage that it greatly contaminates the electrolyte, wears fast, and has high electrical resistance which results in an increase in cell voltage. It may also be degraded to CO_2 during oxygen evolution. The disadvantage of the lead alloy anode is that PbO_2 changes to Pb_3O_4 which is poorly conductive. O_2 gets below this layer and flakes off the film. These particles become trapped in the deposited copper at the cathode, degrading it.

In order to overcome these disadvantages it has recently been proposed to plate the surface of a titanium substrate with platinum and to electrodeposit either lead dioxide or manganese dioxide on the plated surface. Such anodes have the disadvantage of comparatively high oxygen overvoltage. In addition both coatings have high internal stress when electrolytically deposited and are liable to be detached from the surface during commerical usage, both contaminating the electrolyte and, in the case of lead, being deposited on the

cathode to reduce its value. Thus current density with such anodes is very limited.

To improve the high oxygen overvoltage it has also been proposed to compact and sinter titanium chips to increase the apparent surface area. Such an anode has somewhat improved characteristics but does not properly receive and retain the electrodeposited manganese dioxide coating.

This invention is based on recognition that deposited manganese dioxide is both insoluble and electrically conductive, and cannot readily be deposited as a reduced product on the cathode. Experiments have shown that my electrode has a low oxygen overvoltage during electrolysis, economizes on electric power necessary for electrolysis, reduces the loss of manganese from the electrode to the bath to a very low figure, and is believed to be the optimum electrode for electrolytic winning of copper, zinc and nickel in sulfate electrolytes. It is also useful for evolving oxygen in sulfate systems and chlorine in chloride systems.

SUMMARY OF THE INVENTION

The preferred electrode of my invention is made of titanium powder cold compacted to the shape of an electrode, the compaction being sufficient to produce a density in the powder between 30 and 70 percent of the density of the solid metal of which the powder is composed. A layer of manganese dioxide is produced on the surface of the grains throughout the mass of the electrode by thermal decomposition of Mn $(NO_3)_2$. That layer is modified by ion exchange with the titanium dioxide surface layer and probably with the titanium metal of the powder grains to contain titanium atoms as well as manganese atoms. These do not significantly modify the crystal structure which is essentially that of rutile. This mixed structure is formed while the material of the coating is in the intermediate manganeous-manganite form during the decomposition from manganeous nitrate to manganese dioxide.

A final coating of manganese dioxide is electrodeposited over the hybrid coating.

Preferably the structure is strengthened by including solid metal in the electrode. A preferred form is an expanded metal lattice of titanium although other shapes may be used. The preferred size range of the titanium powder is +100 mesh to −325 mesh. The preferred thickness of the outer coating of maganese dioxide is 100 microns. The density referred to is calculated on the weight of the powder alone. The upper limit is the loss of connected pores between the particles.

The preparation of an electrode in this manner produces a stronger electrode without the necessity of sintering the powder because the initial thermally deposited layer is extremely effective in cementing the grains of the powder. It has been found that even loose titanium powder may be cemented by this method to produce a coherent shape. Powder which has been cold compacted to between 30 and 70 percent of metallic density and then coated as described produces an extremely durable electrode suitable for use as the anode in an electrowinning process. The anode evolves O_2 in sulfates and Cl_2 in chlorides, and accordingly may also be used for the evolution of chlorine as well.

It has been observed that manganese dioxide coating of prior art electrodes used in electrowinning is lost during periods of shutdown, at which time it goes into solution and becomes a part of the bath, degrading the

electrode. The loss is largely in the form of conversion to manganese cations and permanganate. With the anode of my invention, the ions and permanganate are largely limited to the pores or channels between the grains of titanium powder and a very high percentage is redeposited as manganese dioxide upon application of current for the electrowinning process, in the same manner that the outer layer was originally deposited. Thus degradation of the anode and pollution of the bath are both avoided.

Finally the electrical and operating characteristics of my electrode compare favorably with prior art electrodes.

The chief presently known use of my electrode is as an anode for electrolysis. So used, an advantage of the anode is low oxygen overvoltage during electrolysis, thus economizing the electrical power necessary.

A simlar electrode may be made with lead particles, at lower cost. As in the case of the titanium electrode a first coating of MnO_2 is thermally deposited and forms a hybrid with the lead oxide surface layer normally present. A further layer of MnO_2 is electrodeposited. A reinforcement of solid metal, which may be titanium expanded metal mesh, may be used.

DRAWINGS

FIG. **1** is a perspective view of a rectangular electrode made according to my invention with portions broken away to show interior structure.

FIG. **2** is an enlarged cross-sectional view on line **2—2** of FIG. **1.**

FIG. **3** is a graph of cell voltage against current density for an anode according to my invention compared with a lead anode and a solid titanium anode coated with MnO_2.

FIG. **4** is an idealized cross-section of several grains showing the two layers and the pores highly magnified.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Although the disclosure herein is detailed in order to enable those skilled in the art to practice the invention, the embodiments disclosed merely exemplify the invention which may take other forms. The scope of the invention is defined in the claims.

FIG. **1** is a broken away perspective view showing a portion of an electrode **10** formed according to my invention. An expanded metal mesh **12** of titanium metal has been placed with −100 mesh titanium powder in a mold and compacted in a press until the powder has a density of 30 to 70 percent of theoretical density of the metal. The precise shape is not a part of my invention and may conform to specifications for a particular use, so the outline is not shown. FIG. **2** is a cross-sectional view. As shown in FIG. **4,** which is a highly magnified and idealized cross-sectional view through several particles of titanium, each grain **20** is coated with a first layer **22** and a second layer **24,** leaving interconnected pores **26** between the grains.

The first layer **22** is basically MnO_2 which has been deposited by thermal breakdown of Mn $(NO_3)_2$ and which has exchanged ions with the metal and surface layer of titanium oxide normally present on the metal and not separately shown. Thus layer **22** has a modified rutile character. It is strongly adherent and cements the grains **20** and the mesh **12** together.

The second layer **24** is electrodeposited MnO_2. It is not known to interchange ions with the first layer and is believed therefore to be identical with commercially electrodeposited manganese dioxide.

The pores **26** are the spaces between the coated grains. As more fully described elsewhere, they are highly interconnected. This not only creates high available surface area (as opposed to surface in a closed cavity not connected through pores **26** with the exterior of the electrode **10**) thus improving the apparent current density, it also means that a substantial part of the first and second layers **22–24** are in the pores. During inactivity of the immersed electrode MnO_2 can break down to manganese cations and permanganate. In my electrode these are largely trapped in pores **26.** Upon reapplication of current to the anode, MnO_2 is re-formed on the second layer with very little loss.

The method of my invention thus comprises the basic steps of compacting metal particles to a density sufficient to make a coherent final product but not so high as to destroy the high interconnection between the pores, thermally breaking down Mn $(NO_3)_2$ at a temperature between about 120° C. and 475° C. to form a first layer on the particles or grains, and depositing a second layer of MnO_2 over the first layer, to form an electrode. The metal may preferably be titanium but may also be lead.

The density of the compacted titanium powder used in my electrode has both a lower and upper limits for satisfactory performance. The freely poured titanium powder of a typical sieve analysis as follows:

TABLE I

Ti Powder Analysis			
Typical Sieve Analysis			
Size	All powder less than −100 mesh. Typical screen analysis:		
	−100,	+150 mesh	25 percent
	−150,	+200 mesh	21 percent
	−200,	+270 mesh	26 percent
	−270,	+325 mesh	17 percent
	−325 mesh		11 percent
Chemistry (%)	Oxygen		0.30 max.
	Nitrogen		0.04 max.
	Carbon		0.04 max.
	Chlorine		0.20 max.
	Iron		0.50 max.
	Magnesium		0.30 max.
	Total others		0.12 max.
	Titanium		98.50 min.

has a theoretical density of 25 percent, that is, its weight is 25 percent of the weight of an equal volume of solid titanium metal having the same analysis. Using great care it is possible to compact such powder to only 30 percent density in the shape of an anode and cement the grains of the powder together by thermal decomposition of Mn $(NO_3)_2$ as described elsewhere in this specification. Thus 30 percent density is believed to be a practical lower limit of density. With greater compacting force the density of the powder may be increased to about 70 percent while retaining highly interconnected passageways between the grains of metal of sufficient size for the application of the coatings of my electrode. Above 70 percent theoretical density the pores lose interconnection and surface area is lost to the extent that following the process described in this specification does not result in deposition of sufficient MnO_2 either in the layer produced by thermal decom-

position or in the electrodeposited layer. Above 70 percent density the oxygen overvoltage rises unduly as shown in table 2 below:

TABLE 2

The Relationship Between Theoretical Density And Anode Performance

% Den.	Anode Thickness	% MnO_2	Back EMF	Cell Voltage at 24 amps/ft²	at 120 amps/ft²
72%	1.0cm	2%	1.15 volts	1.55	1.95
63%	1.1cm	3%	1.20 volts	1.54	1.90
49%	1.0cm	15%	1.06 volts	1.43	1.87
46%	1.6cm	6%	1.20 volts	1.48	1.84
38%	2.1cm	14%	1.11 volts	1.35	1.69
37%	1.2cm	17%	1.08 volts	1.30	1.71

Another method of defining the upper limit is by blowing air through the compacted mass. Substantial resistance to the passage of air indicates that few passages are interconnected, showing that compaction is too great. The upper limit may vary with particle size and shape but includes only a degree of compaction which leaves the pores highly interconnected.

In my electrode, the grains of titanium powder are cemented together by the first coating of MnO_2 which is produced by thermal decomposition of Mn $(NO_3)_2$ between 120° C. and 475° C. During the thermal decomposition there is an extensive reaction with the surface titanium oxide layer which is normally present on titanium metal by ion exchange, during the phase when the coating is black liquid manganeous-manganite. The result is an adherent coating bonding the grains of titanium powder with a highly conductive oxide film. Subsequently a further layer of MnO_2 is electrolytically deposited, resulting in an electrode having extensively interconnected passages between the grains, the surface of each grain both on the surface of the electrode and in the passages being coated with a first layer of modified rutile containing titanium, and then with MnO_2.

Electrodeposited manganese dioxide is brittle, and has large internal stresses. It is readily detached from a substrate when deposited to an appropriate thickness for electrode use, making it difficult to form an effective and long lived electrode from such manganese dioxide alone. My invention permits the application of heavy deposits in excess of 100 microns thick of manganese dioxide within the pores between the grains of titanium powder, thus taking advantage of the large internal stresses of the coating to improve its adherence rather than to cause failure as in the case of a flat sheet electrode.

Finally, by depositing much of the coating internally it is protected both from mechanical dislodgement and from loss into the solution when the electrode is inactive.

Although under anodic potential as applied during electrolysis, manganese dioxide is insoluble, under an open circuit permanganate is observed in solution. As the potential is again applied to the anode the permanganate is redeposited on the anode as manganese dioxide. By coating the porous substrate internally the dissolution of manganese dioxide is reduced and the concentration of permanganate is sufficiently high in the pores for redeposition to reduce significantly the loss of manganese from the anode and the pollution of the bath.

EXAMPLE 1

An example showing the comparison between my electrode and a similar electrode made with solid titanium plate is as follows:

Two sheets of expanded titanium mesh, each 1.5 millimeters thick, were placed in a mold 500 centimeters by 7.50 centimeters by 3 millimeters thick with 82 grams of titanium powder having the sieve analysis and chemical analysis shown in Table **1.** These were subjected to a pressure of 5,400 kilograms, resulting in a composite structure in which the powder component had a theoretical density of 52 percent of the density of solid titanium. The electrode was impregnated with an aqueous solution of Mn $(NO_3)_2$ and was baked at 176° Centigrade. The electrode developed a gray adherent coating. The electrode was then placed in a bath of $MnSO_4$ and H_2SO_4 at 90° Centigrade and current was applied to electrolytically deposit a coating of manganese dioxide following accepted techniques. It was found that during this step current density could be varied from 0.1 ampere to 6.7 amperes per square foot, which was the observed oxygen evolution value for the anode. A black layer of MnO_2 developed over the first layer.

In the same manner a titanium plate 500 centimeters by 750 centimeters by 3 millimeters thick having a sandblasted surface was coated with two layers as described above.

The two electrodes thus produced are compared in FIG. **3** along with an electrode of solid lead. The bath was a copper plating bath containing $CuSO_4$ and H_2SO_4 at 60° Centigrade and a gap of ½ inch. The anode made from titanium plate was less durable and required higher cell voltage, despite the use of both thermal and electrolytic deposition of MnO_2 in accordance with a portion of my invention. Line **34** is the curve for the porous anode with two layers made according to my invention. Line **32** is the curve for lead. Line **30** is the curve for the solid titanium anode with two MnO_2 layers.

A porous anode as described in this example was used for electrolytic winning of copper, zinc and nickel in the respective commercial sulfate-sulfuric acid electrolytes. The anode performed satisfactorily and exhibited a substantial improvement in cell voltage in the system as compared to lead anodes in each electrolyte.

The porous electrode described has also been tested as an anode for evolution of oxygen, and as an anode for evolution of chlorine, both with good efficiencies and service life. The anode is useful for chlorination of water, for instance.

EXAMPLE 2

The effect of changes in the density of the powder component of my electrode may be seen in table 2 below. Anodes prepared according to the first paragraph of Example 1, with the exception that the compaction and amount of MnO_2 varied, are compared.

TABLE 2

The Relationship Between Theoretical Density And Anode Performance

% Den.	Anode Thick-ness	% MnO_2	Back EMF	Cell Voltage at 24 amps/ft²	at 120 amps/ft²
72%	1.0cm	2%	1.15 volts	1.55	1.95
63%	1.1cm	3%	1.20 volts	1.54	1.90
49%	1.0cm	15%	1.06 volts	1.43	1.87
46%	1.6cm	6%	1.20 volts	1.48	1.84
38%	2.1cm	14%	1.11 volts	1.35	1.69
37%	1.2cm	17%	1.08 volts	1.30	1.71

EXAMPLE 3

In a manner like that of Example 1, lead electrodes were prepared using lead shot particles and titanium expanded metal mesh but using lower pressure. In respective trials lead particles ranging from no. 6 shot (0.110 in.) to no. 11 shot (0.065 in.) were used. After the two layers of MnO_2 are deposited as in Example 1, the electrode was tested as an anode in a copper sulphate and sulfuric acid conventional electrolyte. The graph of cell voltage vs. amperes/sq. ft. for this electrode was intermediate between such a graph for a solid lead anode and that for the anode of Example 1 for the particle sizes tested.

It will be understood that the invention is not limited to the examples described and that many modifications may be introduced therein. The scope of the invention is intended to be limited only by the scope of the appended claims.

I claim:

1. An electrode formed from compacted metal particles comprising titanium, the grains being covered with a first layer of MnO_2 deposited by thermal decomposition of $Mn(NO_3)_2$ the particles being further covered with an outer layer of manganese dioxide, an extensively interconnected pore system being left between the compacted particles, the particles being compacted along with at least one solid metal reinforcement to increase the mechanical strength of the electrode.

2. The electrode of claim 1 in which the particles are cemented together by the first layer.

3. The electrode of claim 1 in which the particles are titanium having sizes predominantly between 100 mesh and 325 mesh, the particles being compacted to between 30 and 70 percent of the density of the solid metal of which the particles are composed.

4. The electrode of claim 1 in which the particles are titanium with a titanium oxide surface film and in which the first layer contains atoms from the surface film and thereby comprises a mixture of titanium oxide and manganese dioxide.

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