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[54] REACTIVE MIXTURE FOR FABRICATING AMALGAMALED CHLORIDE FREE ZINC ANODE

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[51] **Int. Cl.** **H01m 43/02**

[58] **Field of Search** .... 136/30–31, 136/125–126, 95–98, 102–106, 20, 75, 120 R; 75/169; 423/99, 169; 75/201, 178 R, 211, 214, 222

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[57] ABSTRACT

A porous zinc anode produced and adapted for use in alkaline solution, said anode in said solution constituting means for obviating gassing characteristics as contrasted to a porous zinc anode produced in other ways. The essential step in the invention is free acid leaching with an acid other than hydrochloric acid in order to form a water soluble salt of the free acid.

2 Claims, No Drawings

REACTIVE MIXTURE FOR FABRICATING AMALGAMALED CHLORIDE FREE ZINC ANODE

This is a divisional application of U.S. Ser. No. 114,349, filed Feb. 10, 1971, now matured into U.S. Pat. No. 3,713,891, granted Jan. 30, 1973.

This invention relates to batteries and more particularly to improved structures and systems therefore, and specifically to the electrodes used therein.

The efficiency of a battery depends to great extent on the surface area of the anode structure used therein. The present invention provides an anode of greatly improved characteristics comprising compacted porous zinc amalgam, and utilizing an aqueous solution leachant of a chloride free acid in combination with the salt of this chloride free acid as a filler in contact with this acid. A zinc mercury amalgam is created by an electrochemical reaction cementation process, and a water soluble salt of the chloride free acid is formed simultaneously.

The reactive cementation process utilizes the electrochemical reaction of zinc powder with mercury oxide to produce an alloying of amalgam bond between the zinc particles. In order to facilitate the process of amalgamation of the zinc powder, a free acid other that hydrochloric acid is used as a fluxing agent for the zinc particles to facilitate their intimate contact with each other, along with the use of a chloride free filler that is a soluble salt of the chloride free acid. Examples of chloride free acids and of their corresponding chloride free fillers include acetic acid and sodium acetate, or boric acid and sodium borate, or oxalic acid and sodium oxalate.

In the past zinc electrodes were produced by preparing a compacted porous mixture of zinc powder, mercurous chloride, and ammonium chloride; and adding water thereto so as to utilize the ammonium chloride to dissolve and to clean away the zinc oxide on the surface of the zinc particles. The newly cleaned zinc particles would then react with mercurous chloride to liberate the metal mercury from its salt and to form an amalgam bond with the newly liberated mercury.

It was found that gassing may occur from zinc anodes produced by the ammonium chloride process, with this instability toward gassing being due to the presence of unremoved zinc oxide and/or zinc chloride impurity sites on the zinc anode that had not been displaced by mercury metal during the electrochemical displacement reaction.

Furthermore in the past it was thought that a way to avoid gassing would be to have zinc mercury amalgam spread over substantially the entire anode surface. Nevertheless anode gassing still may result even with a complete amalgam coating. It has been found here that if a chloride free acid leaching agent is used in combination with a chloride free filler material to dissolve zinc oxide on the surface of zinc particles to facilitate their intimate metal-to-metal contact with one another and with metallic mercury, and also to deposit trace amounts of chloride free inert ions integrally united to the zinc at specific lattice sites; then it is possible to prevent or to substantially reduce gassing at those sites caused by the zinc oxide or the zinc chloride that would otherwise be present therein. These ions are inert because they do not directly or indirectly cause anode gassing to occur.

It is therefore a prime object of the present invention to provide, in a battery, an amalgamated zinc anode of great porosity and uniform density fabricated by reactive cementation and characterized by substantially reduced gassing in the finished anode.

It is another object of the present invention to provide finished anodes showing much lower gassing rates in alkaline solutions than do anodes produced by a process using chloride ions; having much cleaner surfaces with an appearance of a sparkling crystalline structure completely free of zinc oxide; and generating much higher short circuit discharge rates due to a much larger active clean surface area present in the porous anode structure.

It is another object of the present invention to provide an anode structure for an electrochemical cell, said structure formed by mixing specific portions of the zinc powder, mercuric oxide, and a chloride free filler selected from the group consisting of sodium acetate, sodium borate and sodium oxalate, and by leaching out said chloride free filler with an aqueous solution of the corresponding chloride free acid selected from the group consisting of acetic acid, boric acid and oxalic acid.

It is a further object of the present invention to produce a porous anode structure of specific shape in the form of a selfsupporting open three dimensional zinc mercury metal network consisting essentially of chloride free zinc and mercury amalgam metal particles which are pressure welded one to another having communicating voids therebetween and further consisting of trace amounts of inert nonchloride ions selected from the group consisting of acetate ions, borate ions, oxalate ions present therein up to 1% by weight of said structure integrally united at specific lattice sites to reduce anode gassing.

Still another object of the present invention is to provide a primary cell including a zinc amalgam porous anode for a battery.

Other objects of the invention will become apparent from the following description.

Generally speaking, the present invention provides a new battery system in which the problem of anode gassing is substantially reduced. This substantial reduction is the direct result of the presence, in the battery, or a novel anode consisting of porous zinc amalgam containing trace amounts of an inert nonchloride ion selected from the group consisting of acetate ions, borate ions, and oxalate ions present up to 1% by weight of the anode. The anode is formed as a uniformly porous pellet by means of reactive cementation of admixed materials such as zinc powder, mercuric oxide, and a chloride free filler selected from the group consisting of sodium acetate, sodium borate, and sodium oxalate, and by leaching out the chloride free filler with an aqueous solution of the corresponding chloride free acid selected from the group consisting of acetic acid, boric acid and oxalic acid.

EXAMPLE 1

The following reactive mixture was utilized to produce the anode of the invention.

5000 grams zinc powder, sifted through 60 mesh onto and through 100 mesh; 2100 grams anhydrous sodium acetate sifted through 60 mesh; 780 grams HgO fine dust, battery grade; 30 ml. kerosene which is inert and utilized to hold these types of particles together. The blending was carried out for 10–12 minutes at speed of 15–30 r.p.m. About 1.68 to 1.70 grams of the above mixture was pressed into a green anode 77–80 mils thick. The pressure required was about 12,000 psi.

The leaching of the anodes was carried out with acetic acid diluted in the ratio of 1 part by weight acid to 3 parts by weight water. The amount of acid should be in a controlled relation to the weight and number of anodes, at least during the first 15 minutes of leaching. About 2 ml. of the above solution is the maximum allowed for the above anodes; in other words approximately 1 ml. of the above solution per each gram of the green anode of any size and shape. The excess of the above leaching solution can be added for faster leaching but only after the initial 15 minute period.

The acetate leaching process is generally faster than the chloride leaching process. It is completed in 5–6 hours at room temperature when the above size anodes are processed. The leached anodes were washed in distilled water, until the effluent showed a pH value of 6 or higher. The anodes were then washed with alcohol, dried in air, and had a dry weight of 1.14 grams ± 0.05 grams and had a porosity of 70 percent and contained 12% mercury.

EXAMPLE 2

Anodes of various porosities can be produced using the same procedure except for the mix composition. The following is another variation of the above mix, used for the production of large anodes: 5000 grams of zinc powder, 1300 grams of sodium acetate, 780 grams HgO, and 30 ml. kerosene.

48.5 grams of the above mix were pressed into a rectangular anode 3.2 inches by 1.6 inches with a force of 30 tons (5.86 tons per square inch). The resulting anode produced by the chloride free acetic acid leaching process weighed 36.5 grams and contained 12% mercury; it was 4.2 mm. thick and 64% porous. The same type of anode was pressed with a copper screen in the middle as a current collector for the rechargeable cell application. The copper screen was amalgamated during the leaching process and provided a good contact to the porous anode body over the entire anode cross-section.

EXAMPLE 3

Other combinations of acids as leachants and their salts as fillers were also utilized. The following mixture of 5000 grams of zinc powder, 2100 grams sodium metaborate, 780 grams HgO was prepared and the pressed anodes were leached in correspondingly diluted boric acid in the ratio of 1 ml. per gram of green anode as in Example 1 and produced a zinc anode of about the same weight, porosity, and mercury content of Example 1.

EXAMPLE 4

The following mixture of 5000 grams zinc powder, 1300 grams sodium metaborate, 780 grams HgO, and 30 ml. kerosene was treated with the same quantity of boric acid as in Example 3 and produced a zinc anode of about the same weight porosity, and mercury content of Example 2.

EXAMPLE 5

The following mixture of 5000 grams zinc powder, 2100 grams sodium oxalate, 780 grams HgO, and 30 ml. kerosene was treated with correspondingly diluted oxalic acid in the ratio of 1 ml. per gram of green anode as in Example 1 and produced a zinc anode of about the same weight porosity, and mercury content of Example 1.

EXAMPLE 6

The following mixture of 5000 grams zinc powder, 1300 grams sodium oxalate, 780 grams HgO, and 30 ml. kerosene was treated with the same quantity of oxalic acid as in Example 5 and produced a zinc anode of about the same weight, porosity, and mercury content of Example 2.

Zinc particles in anodes produced by the above 6 examples measured between 25 to 40 microns.

A zinc anode prepared according to each of the above six examples was tested as follows. The anode, wherever necessary, was reshaped into the form of a disc pellet having a diameter of 0.5 inches and a thickness of 0.1 inches. The pellet was then inserted as an anode into an alkaline cell of flat cylindrical construction in contact with an absorbent spacer impregnated with an alkaline electrolyte, such as 35–40% KOH, 3.5–6.5% ZnO, and the balance water. In contact with the opposite surface of said spacer was a suitable depolarizer such as the metal oxide HgO, M_nO_2, or Ag_2O containing from 5–25% graphite. This sealed cell was subjected to 180°F for 24 hours with the result that about 0.05–0.07 cu. cm. of gas were produced.

When zinc pellets of about the same size weight, porosity, and mercury content were produced by the use of ammonium chloride, the gassing rate was determined to be 0.20 cu. cm. to 0.25 cu. cm. for a 24 hour period at 180°F.

Thus the gassing rates for the chloride free leaching are very satisfactory relative to the gassing rate for the chloride process and indicate the superiority of the present invention over conventional anode structures.

Although the present invention has been disclosed in connection with a few preferred embodiments thereof, variations and modifications may be resorted to by those skilled in the art without departing from the principles of the new invention. All of these variations and modifications are considered to be within the true spirit and scope of the present invention as disclosed in the foregoing description and defined by the appended claims.

What is claimed is:

1. A reactive mixture for fabricating a highly porous amalgamated chloride free zinc anode for a current producing device, said mixture consisting essentially of zinc powder, mercuric oxide, and a chloride free filler material which is selected from the group consisting of sodium acetate, sodium borate and sodium oxalate.

2. The reactive mixture of claim 1 further comprising an aqueous solution of a chloride free acid corresponding to the respective filler material.

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