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# UNITED STATES PATENT OFFICE.

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## COPPER-OXIDE ELECTRODE AND METHOD OF MAKING THE SAME.

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This invention relates to copper oxide electrodes and methods of making the same; and it comprises as a new electrode for use in the copper oxide type of cells with an alkaline electrolyte, a formed mass of very fine soft copper and coarser copper oxide forced into shape under heavy hydraulic pressure, the pressure being sufficient to flow or smear said copper; the mass usually containing a copper gauze reinforcement; and it further comprises a method of making such electrode, wherein very fine soft copper is produced by a reduction of copper oxide at a relatively low temperature, the copper so formed is mixed with copper oxide and the mixture compressed into the desired form; usually that of a sheet, by heavy hydraulic pressure, the pressure being sufficient to smear or flow the copper; all as more fully hereinafter set forth and as claimed.

The type of cell using copper oxide as a depolarizer is a well known one. In this cell there is an alkaline electrolyte, usually caustic soda solution, although caustic potash is sometimes used, with electrodes of zinc and of copper; the copper electrode being in contact with a body of copper oxide as a depolarizer. This type of battery is very largely used; and particularly for closed circuit work. Electrically it is very efficient. From a practical point of view however there are considerable difficulties in producing a depolarizing body of copper oxide in pervious condition and with good electrical conductivity. Copper oxide, per se, while it conducts the current is not a good conductor; and in any loose or granular form the resistance of a compound pole including a copper oxide depolarizer is apt to be very high. Sometimes the copper oxide is simply suspended around the pole in a bag; usually it is molded into form. Sometimes the copper oxide contains more or less cuprous oxide and sometimes it is treated with a solution of sulfide. Various expedients have been tried for enhancing its conductivity, such as the inclusion of bits of copper; partial reduction, etc. But all the methods of making copper oxide depolarizers leave something to be desired in one respect or another.

It is a purpose of the present invention to provide a simple, cheap and ready method of producing a compound electrode of high efficiency and low resistance and having mechanical strength. To this end I utilize the qualities of soft, fine, pure copper produced by a low temperature reduction of copper oxide. Such copper under hydraulic pressure may be flowed or smeared so as to give a body of considerable mechanical strength; this being possible under pressures which copper oxide granules will withstand without much breaking down. In the present invention this property is utilized to produce what may be termed a copper skeleton; a more or less continuous body of copper firmly holding granulated copper oxide.

In making a composite electrode under the present invention I use for the oxide component the purest commercial form of copper oxide obtainable without excessive cost. Copper oxide suitable for the present purposes may be prepared by roasting copper sulfate, using precaution to avoid any loss of oxygen from the oxide. At high temperatures CuO tends to dissociate with formation of $Cu_2O$. I do not desire the presence of cuprous oxide or lower stages of oxidation than CuO. For the present purposes, the oxide should be in granular form; desirably of a fineness not coarser than 40 mesh and not finer than 100 mesh. With commercial oxides of fine character, it is sometimes desirable to briquet and bake and thereafter crush. Copper scale may be used but should be crushed. Where cuprous oxide is present in scale or other forms of oxide, I roast to get rid of it. With the copper oxide I mix fine soft copper; advantageously made by low temperature reduction. In reduction, it is advantageous to use dilute gases. For example, in using producer gas for reduction of copper oxide I may dilute it with waste products of combustion coming from the operation to such an extent that the mixture of gases used for reduction will just maintain a flame when ignited in a jet. These precautions are advisable since a very soft, fine copper is wanted and over-heated material is not desirable. There is considerable heat evolution in reduction and with rich gas, local high temperatures are apt to occur. Copper suitable for my purposes should not have lumps or portions that cannot be crumbled by pressure between the fingers and should form a bright metallic streak, entirely free from dullness, when rubbed with a knife blade. Soft copper having these characteristics is

substantially free from cuprous oxide. I do not desire a copper containing any substantial amount of iron. The reduced copper is broken down into an impalpable powder and this powder is admixed with granular copper oxide. In comminuting the copper, there may be used a disk mill with hard wood disks in conjunction with an air separator. As the best proportions in making electrode material I regard 2 parts by weight of granular copper oxide with 1 part by weight of soft fine copper. Mixing should be extremely thorough. A blending liquid, (alcohol, water, etc.) may or may not be used. The mixture may be directly compressed into units of the size and shape wanted; but for most purposes I regard it as desirable to use a reinforcement; this reinforcement being copper gauze or netting. In making a reinforced electrode, the mixture is spread on and through copper gauze, and compressed. A single electrode may be so made; or a sheet from which a plurality of electrodes can be cut. With material made under the present invention this cutting is readily practicable. Part of the cutting or configuration may be done in the compression step. A sheet of copper gauze 10 x 9.75 inches will produce a compound sheet from which 16 electrodes of the size used in B-batteries can be cut. The pressure used should be sufficient to flow or "smear" the copper without substantially displacing the copper oxide, that is to say, without further "mixing" the copper and copper oxide. With too much pressure, the plate will become impervious. A good plate made under the present invention has a specific gravity of 3.8 to 4.1, and a porosity, (as determined by the increase of weight upon soaking in water, wiping quickly and weighing) of from 25 per cent to 35 per cent. The final plate has a bright, coppery luster, is strong and is easy to handle without loss of material. It has an extremely high initial conductivity; the resistance of an electrode being of the order of tenths of ohms. In service, full voltage is given as soon as the circuit is closed.

Other metals may be used in place of copper. Where the plate can be salvaged, or in cases where extreme excellence is of greater importance than first cost, sponge silver may be used in lieu of copper. A cell using a copper oxide plate with a sponge silver bond gives an open circuit voltage of 1.09 to 1.10 volts. Silver is of course usually too expensive. Sponge nickel and sponge cobalt may be used in lieu of either copper or silver. Sponge iron is less desirable. The metals used should be, like those mentioned, inert as regards the caustic alkali which is ordinarily employed as an electrolyte in cells using copper oxide as a depolarizer.

Sometimes I give my compound plate a flash metallic coating, by electroplating, using copper, nickel or silver for this purpose. Care must be taken to prevent excessive reduction of copper oxide during plating; a very slight coating of electro-deposited metal is sufficient. My plates as so electroplated give high open circuit voltages over long periods;—from 1.07 to 1.1 volts.

The discharge characteristics of cells using my plates are most extraordinary. Thus an average cell with plated CuO plate reads initially 1.1 volts on open circuit. After eleven days' service four hours per day, with five milliamperes current draft the open circuit voltage is 1.06, the initial closed circuit voltage 1.04, and the closed circuit voltage at the end of the daily four hour load period, 1.00. After twenty-one days the open circuit voltage is still 1.05, and at the end of the daily load period, 0.83.

Certain cells using my plate give 1.09 volts initial open circuit. After twenty-one days at the above described load, the open circuit voltage is 1.06 and at the end of the load period, 1.00.

What I claim is:—

1. An electrode composed of granular copper oxide and fine soft copper as a bonding means therefor, said copper being flowed into coherent form by heavy pressure.

2. An electrode composed of copper gauze carrying a mixture of granular copper oxide and soft fine metallic copper compressed together under a pressure sufficient to flow the copper.

3. An electrode composed of copper gauze carrying a mixture of granular copper oxide and soft fine metallic copper compressed together under a pressure sufficient to flow the copper but not sufficient to decrease the porosity of the plate below 20 per cent.

4. A compressed electrode comprising a metallic current collector, granular copper oxide, and a continuous bonding body of soft fine copper flowed into metallic union under pressure, said electrode having a porosity between 20 and 40 per cent.

5. A copper oxide electrode containing granular copper oxide bonded with soft fine copper flowed into continuous metallic union under pressure there being about 2 to 6 parts of copper by weight to 10 parts of copper oxide.

6. An electrode composed of granular copper oxide continuously bonded by compression of a soft fine metal inert to caustic alkali.

7. A copper oxide electrode bonded by compression of a soft fine metal inert to caustic alkali, and lightly coated with such a metal.

8. A compound electrode composed of a skeleton of copper gauze and a body of a mixture of fine copper oxide and fine soft copper, the whole being bonded together by compression of said fine soft copper.

In testimony whereof, I have hereunto affixed my signature.

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