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(54) METHOD OF PRODUCING SELF-SUPPORTING AND FULLY ACTIVATED IRON ELECTRODES

(71) We, WESTINGHOUSE ELECTRIC CORPORATION of Westinghouse Building Gateway Center, Pittsburgh, Pennsylvania, United States of America, a corporation organized and existing under the laws of the State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of producing self-supporting and fully activated iron electrodes.

Iron electrodes for batteries are well known. U.S. Patent Specification No. 3,525,640 (McCormick), teaches double sintering of essentially pure, 3 to 5 micron diameter, iron particles, at 760°C to 930°C, in a hydrogen atmosphere, onto a nickel mesh support. This iron electrode, however, must then be electrochemically activated by cycling in a sulfur-containing alkaline solution.

U.S. Patent Specification No, 2,871,281 (Moulton) discloses activation moist Fe_2O_3, by spraying with $FeSO_4$, $(NH_4)_2SO_4$, Na_2SO_4 or K_2SO_4 solution. This composition is dried and then reduced in a hydrogen atmosphere, at 500°C to 820°C, to form an active battery material containing Fe and FeS, which can be loaded into a support, to provide an iron electrode. U.S. Patent Specification No. 3,066,178 (Winkler) teaches superactivation of an active iron battery material containing FeS by soaking with $CuSO_4$ solution. This composition is then dried and loaded into a support to provide an iron electrode. All of these active materials must be pasted into a supporting plaque, which provides a thick, heavy electrode. Generally, these active materials must be charged-discharge cycled before they are useful.

What is needed is a low cost battery material which in activation processing can be made into a thin, light weight, porous and structurally rigid electrode in a fully charged state and capable of immediate discharge without charge-discharge cycling. All references to "parts" given herein in respect if proportions of constituents, should be understood as meaning parts by weight.

According to the present invention a method of making a self-supporting and fully activated electrode structure consisting of iron active material particles consisting of essentially pure Fe, which comprises the steps of: (A) mixing 100 parts of metallic iron particles with from 0.5 part to 5.0 parts of a water soluble metal sulfate additive effective to activate the iron and consisting of at least one of $MgSO_4$, $CdSO_4$, $MnSO_4$, $ZnSO_4$, $BaSO_4$, $Cr_2(SO_4)_3$, $CuSO_4$, $CaSO_4$, Li_2SO_4 and a hydrate thereof, and an amount of water effective to form a thin coating of the metal sulfate on the surface of the metallic iron particles; (B) drying the mixture and sizing the mixture to provide particles having an average particle size of from 10 microns to 275 microns diameter; (C) pressing the coated metallic iron particles to provide a plaque; and then (D) reducing and sintering the plaque consisting of the coated metallic iron particles at from 700°C to 1,000°C, in a reducing atmosphere, to provide an interconnected, self-supporting metallic electrode structure consisting solely of fully charged metallic iron particles consisting of essentially pure Fe, coated with the activator metal of the additive, said electrode being capable of immediate discharge.

It has been found that the above need can be met by producing substantially pure metallic iron particles preferably by thermally reducing Fe_2O_3 powder at from 400°C to 1,000°C in a reducing atmosphere. The particles are then ground, preferably to an average particle size of from 10 microns to 275 microns. The particles are then mixed with from 0.5 part to 5.0 parts, per 100 parts of iron particles, of a water-soluble metal sulfate selected from $MgSO_4$, $CdSO_4$, $MnSO_4$, $ZnSO_4$,

$BaSO_4$, $Cr_2(SO_4)_3$, $CuSO_4$, $CaSO_4$, Li_2SO_4, their hydrates, or their mixtures. Sufficient water is added to form a thin film of metal sulfate on the surface of the metallic iron particles.

The iron-sulfate mixture is dried, sized to from 10 microns to 275 microns average particle size, pressed, and then thermally reduced and sintered, at from 700°C to 1,000°C, in a reducing atmosphere, preferably H_2 gas, for from, say, 15 minutes to 600 minutes, to activate and consolidate the electrodes. This process can provide a 50 mil to 150 mil electrode of about 2.5 g./cm. cm to 3.5 g./cu. cm, density, and 70% to 95% porosity, having a high structural integrity. The sintered electrode needs no support and is capable of immediate discharge, providing an output of about 0.30 Ah/g. to about 0.70 Ah/g.

In the iron-air electrochemical cell, the iron electrode provides fuel for the electrochemical couple. In order to achieve maximum capacity per unit weight in a cell, it is necessary to provide the iron electrode with the best active material in terms of utilization, and simultaneously to reduce the weight of the inactive components, such as the supporting structure and electrode current collector. The ultimate objective would be to provide an iron electrode containing 100 per cent active material.

In the method of this invention, an activated, sintered, metallic iron itself constitutes the entire electrode structure. The starting material is substantially pure iron particles. This material can be easily produced from ferric oxide (Fe_2O_3), which is an inexpensive, commercially available material. The Fe_2O_3 can be thermally reduced to metallic iron, Fe, at from 400°C to 1,000°C, in a reducing atmosphere, preferably H_2, for from, say, 15 minutes to 600 minutes. It can then be ground or otherwise pulverised to a powder having an average particle size of from 10 microns to 275 microns. These particles, consisting of essentially pure Fe are then mixed with a water soluble metal sulfate, used as an electrochemical activator.

Useful water soluble metal sulfates effective to activate the iron are $MgSO_4$, $CdSO_4$, $MnSO_4$, $ZnSO_4$, $BaSO_4$, $Cr_2(SO_4)_3$, $CuSO_4$, $CaSO_4$, $LiSO_4$, their hydrates, as well as mixtures thereof. Preferred activators are $MgSO_4$, $3CdSO_4 \cdot 8H_2O$, $MnSO_4$, $ZnSO_4$, $BaSO_4$, $Cr_2(SO_4)_3 \cdot H_2O$. $CuSO_4 \cdot 5H_2O$, $CaSO_4 \cdot 2H_2O$, $Li_2SO_4 \cdot H_2O$ and their mixtures. An especially useful activator is a mixture of $MgSO_4$ and $3CdSO_4 \cdot 8H_2O$. The Fe particles are mixed with the metal sulfate in a ratio of from 0.5 part to 5.0 parts, preferebly from 0.8 part to 3.0 parts of metal sulfate per 100 parts of Fe particles. Use of sulfates or sulfides would present solubility problems, and would not provide a uniform adhesive coating on the iron particles. Under about 0.5 part of selected metal sulfate and little increased performance is noted. Over about 50 parts and the improved electrochemical performance tapers off.

The Fe-metal sulfate mixture is blended with an amount of water effective to substantially completely coat the Fe particles with a thin film of the metal sulfate additive. Usually from 30 parts to 200 parts (about 30 ml to 200 ml) of water per 100 parts of Fe particles will form a slurry and coat the Fe particles. The slurry is then generally poured onto or into a container and dried, by any suitable means, for a time and at a temperature effective to evaporate or remove most of the water, generally from 30 minutes to 120 minutes, at 25°C to 75°C. The dried material is broken up, reground or otherwise powdered, and then sized, by pouring it through a Tyler or other suitable screen system, to an average particle size of from 10 microns to 275 microns diameter. Over about 275 microns and problems may be encountered in later reduction and sintering steps.

The dried, sized, Fe-metal sulfate mixture is then pressed by a suitable pressing means to provide a plaque structure that can be handled. The structure is then thermally reduced, activated, and sintered at from 700°C to 1,000°C in a reducing atmosphere, preferably H_2, for, say, 15 minutes to 600 minutes. The particles fuse at their contact points to provide an interconnected metallic structure comprising Fe, substantially completely coated with a thin film of the metal of the additive used, and trace amounts, generally from 0.05 weight percent to 0.75 weight percent of sulfur, generally as free sulfur. The rest of the sulfur goes off as H_2S, sulfate radicals and free sulfur through a hood, along with some steam.

It is believed that during the activation-sintering step, the metal fo the additive sulfate used, for example Mg, undergoes a solid state interdiffusion of atoms with the metallic iron particle surface, to form a type of alloy, or solid state mixture of the metals, as a thin film, at the metal interface which somehow contributes to improved electrochemical properties and provides improved resistance.

This electrode structure can advantageously be made very thin, i.e., from 50 mil to 150 mil. It will have a density of from 2.5g./cu. cm. to 3.5g./cu. cm, a porosity of from 70% to 95% and high structural integrity. The porous, bonded particle structure contains 100 percent active material with no inactive support structure. This method eliminates the use of weighty supports and the need of intricate and time consuming plaque pasting or other plaque loading techniques.

This method also provides an electrode that is capable of immediate discharge, providing an output of up to 0.70 Ah/g. of active material-structure. This method eliminates the need for charge-discharge cycling prior to use and further eliminates the need for any activation dipping or spraying steps. This method provides a very simple, inexpensive, commercially feasible method making high output iron electrodes.

In order that the invention can be more clearly understood, convenient embodiments thereof will now be described, by way of example, with reference to the accompanying drawings in which:—

Figure 1 shows a schematic diagram of a hydrogen reduction sintering furnace used to make the iron electrodes of this invention;

Figure 2 shows a magnified view of the electrode structure of this invention; and

Figure 3 shows a three dimensional view of the iron electrode test apparatus used in the Example.

Referring now to the drawings, Figure 1 shows a schematic diagram of the furnace that can be used to reduce Fe_2O_3 to metallic iron and to sinter-activate the electrode. Figure 2 shows a magnified view of the support fiber free electrode structure 20, with sintered, bonded, interconnected, relatively smooth metallic Fe active material particles 21 joined at fusion points 22 without melting, which could cause melt globules and loss of volume. The iron particles are discontinuously coated with a thin film of metal activator 23. At the interface of the metal activator and Fe particles, there may be an alloy or solid state metal mixed film (not shown). The structure is porous, as shown by the voids 24 between the joined particles. The fused metal powder structure is free of clefts and protuberances and melt globules and requires no exterior or interior support fibers of sheets, the electrode being rigid and self-supporting. Figure 3 is an illustration of the iron electrode test cell used in the example.

The invention will now be illustrated with reference to the following Example:—

EXAMPLE

Approximately 80 grams of substantially pure iron particles, made from Fe_2O_3 powder thermally reduced in H_2 at 900°C for 2 hours, having an average particle size of between about 150 microns to about 250 microns was mixed with 0.8 gram of $MgSO_4$ and 0.8 gram of $3CdSO_4 \cdot 8H_2O$. After thorough mixing was achieved, 40 grams (40 ml.) of deionized water was added. Using a spatula for mixing, a creamy, homogeneous paste was obtained and the iron particles were uniformly covered with the water soluble metal sulfates.

The blend was placed into a flat container and air dried in an oven at 60°C for 1 hour. The solid mass was then crumbled to form a powder and then sized through a set of screens, so that the average particle size was below 250 microns diameter. The iron-magnesium sulfate-cadium sulfate hydrate powder was then placed into a 100 sq. cm. square mold and flat bed pressed at 25 tons pressure, to form a loosely consolidated plaque structure that could be handled. The plaque, consisting of only the iron particles coated with the metal sulfates, with no additional supporting structure, was then placed in a Burrel Model #200 hydrogen reduction muffle furnace, similar to that shown in Figure 1 of the drawings.

While coming up to temperature, the furnace was purged with argon gas until it reached 100°C. Then hydrogen gas was turned on at a rate of about 5,000 cc./min. When the furnace reached 900°C, it was held at this temperature for 30 minutes to reduce and sinter-activate the plaque, and produce an activated, completely consolidated iron active electrode. The furnace was then shut-off and the hydrogen gas left on until the temperature reached 100°C. At this time the hydrogen reducing gas was turned off and argon was again used to purge the system until it reached 25°C.

This method provided a self-supporting electrode, containing interconnected, bonded, iron particles substantially covered with a thin film of magnesium and cadmium, with a possible alloy of the metals, and trace amounts, about 0.1 weight percent, of substantially free sulfur. The rest of the sulfur by-products of the reduction-sintering were removed through a hood.

The electrode contained the iron activated battery particles, sintered together without any substantial melting. The electrode was structurally firm and very strong and needed no further support materials. The electrode had a density of 3.3 g./cu. cm., a porosity of from 80% to 90% and a thickness of 100 mils (0.1 inch).

The electrode was trimmed to about 4 cm. x 4 cm. and a lead wire was attached to one end. The electrode was evaluated using a standard half-cell configuration shown in Figure 3 of the drawings. This consisted of two 10 mil thick dummy nickel electrodes spaced approximately 3/4 inch from each face of the iron electrolyte. A Hg/HgO reference electrode was positioned near one of the faces of the iron electrode. On the first discharge, without any charge-discharge cycling, the electrode delivered about 0.4 Ah/g. output (0.85 volts—vs.—Hg/HgO at 25 mA/sq. cm. in 25 wt.% KOH at 35°C.).

This test showed the usefulness of this activated iron electrode in an electrochemical cell, and illustrates its capability of immediate discharge. A number of such cells could be connected to provide a high output battery. The high output, low weight, ultrathin electrode properties of this invention, coupled with the low cost and ease of construction, make this electrode uniquely suitable as a commercial product. The other sulfates or their hydrates and mixtures described hereinabove could also be used to produce the activated, self-supporting iron electrode of this invention.

WHAT WE CLAIM IS:—

1. A method of making a self-supporting and fully activated electrode structure consisting of iron active material particles consisting of essentially pure Fe, which comprises the steps of:— (A) mixing 100 parts of metallic iron particles with from 0.5 part to 5.0 parts of a water soluble metal sulfate additive effective to activate the iron and consisting of at least one of $MgSO_4$, $CdSO_4$, $MnSO_4$, $ZnSO_4$, $BaSO_4$, $Cr_2(SO_4)_3$, $CuSO_4$, $CaSO_4$, Li_2SO_4 and a hydrate thereof, and an amount of water effective to form a thin coating of the metal sulfate on the surface of the metallic iron particles; (B) drying the mixture and sizing the mixture to provide particles having an average particle size of from 10 microns to 275 microns diameter; (C) pressing the coated metallic iron particles to provide a plaque; and then (D) reducing and sintering the plaque consisting of the coated metallic iron particles at from 700°C to 1,000°C, in a reducing atmosphere, to provide an interconnected, self-supporting metallic electrode structure consisting solely of fully charged metallic iron particles consisting of essentially pure Fe, coated with the activator metal of the additive, said electrode being capable of immediate discharge.

2. A method according to claim 1, wherein the additive is at least one of $MgSO_4$, $3CdSO_4 \cdot 8H_2O$, $MnSO_4$, $ZnSO_4$, $BaSO_4$, $Cr_2(SO_4)_3 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, $CaSO_4 \cdot 2H_2O$ and $Li_2SO_4H_2O$, and the iron particles are made from Fe_2O_3, thermally reduced in H_2 gas at from 400°C to 1,000°C.

3. A method according to claim 2, wherein the additive is a mixture of $MgSO_4$ and $3CdSO_4 \cdot 8H_2O$ and the metallic iron particles are mixed with from 0.8 part to 3.0 parts of metal sulfate.

4. A method according to claim 1, 2 or 3, wherein the mixture is dried in step B for from 30 minutes to 120 minutes at from 25°C to about 75°C, and the reducing atmosphere in step (D) is H_2 gas.

5. A method according to any of claims 1 to 4, wherein the electrode is from 50 mil to 150 mil thick, and from 70% to about 95% porous.

6. A method of making a self-supporting, fully activated electrode structure consisting of iron active material, said method being substantially as described herein with particular reference to the foregoing Example.

7. Electrode structures when made by a method according to any of claims 1 to 6.

8. Electrode structures substantially as described herein with particular reference to Figure 2 of the accompanying drawings.

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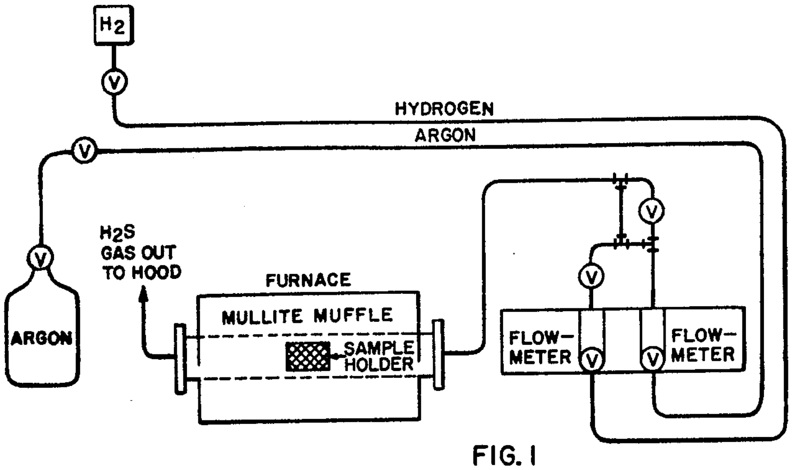
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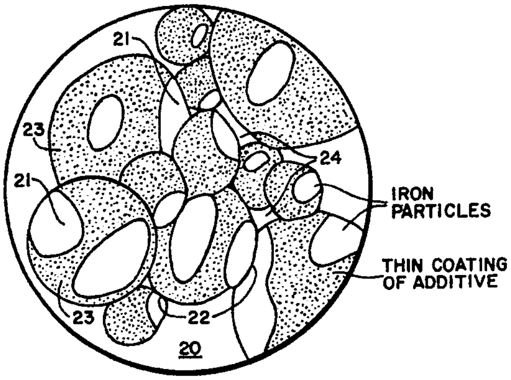
FIG. 1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23
21
24
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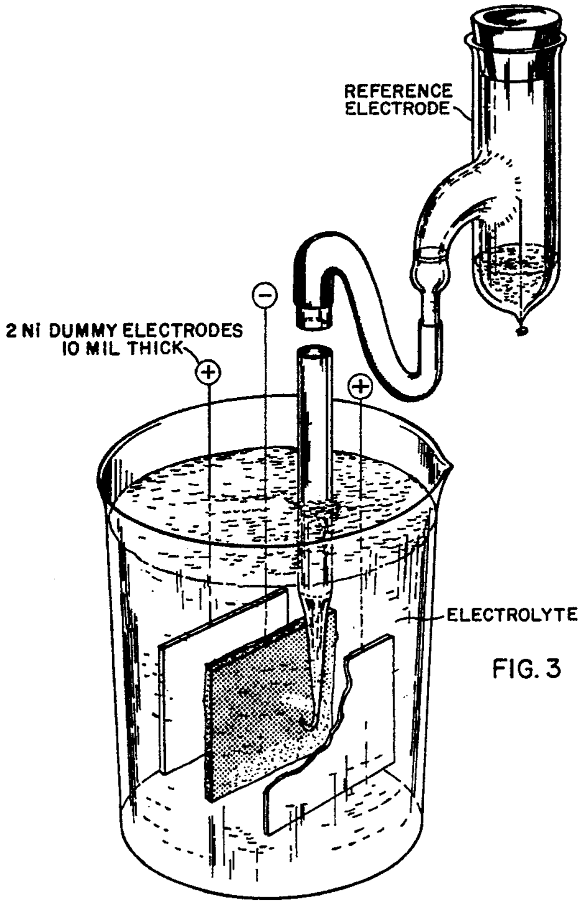
THIN COATING OF ADDITIVE
23
22
20

FIG. 2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2 NI DUMMY ELECTRODES 10 MIL THICK
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FIG. 3