

No. 882,144.

PATENTED MAR. 17, 1908.

T. A. EDISON.
STORAGE BATTERY ELECTRODE.
APPLICATION FILED MAR. 30, 1905.

Fig. 1

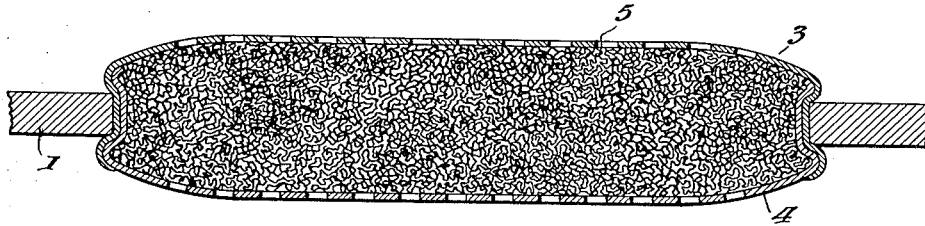
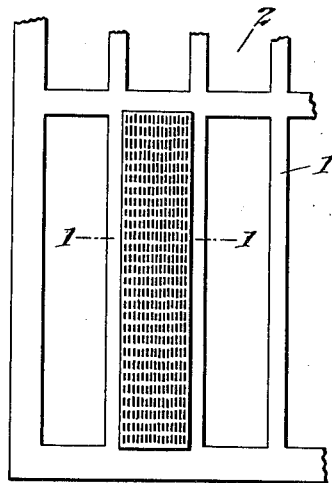


Fig. 2



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UNITED STATES PATENT OFFICE.

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STORAGE-BATTERY ELECTRODE.

No. 882,144.

Specification of Letters Patent.

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To all whom it may concern:

Be it known that I, THOMAS A. EDISON, of Llewellyn Park, Orange, in the county of Essex and State of New Jersey, have invented a certain new and Improved Storage-Battery Electrode, of which the following is a description.

My invention relates to an improved storage battery electrode, wherein the active material is associated with minute flakes or foils of an insoluble metal or metals, preferably cobalt or an alloy of nickel and cobalt, or nickel alone.

In using metallic conducting flakes for admixture with the active material, difficulties have been experienced, due in the first place, to the fact that electrical contact between the metallic flakes and between the flakes and the pocket walls is generally poor and difficult to maintain, except under considerable pressure, and in the second place, to the fact that opportunity is offered within the mass for the tapping of gas, resulting in separation of the active particles and bulging of the pocket walls, to further increase the difficulties of contact. The latter objection is more pronounced when the battery solution employed is quite concentrated and hence in the best condition for high economy, owing to the viscous character thereof. Consequently, there has heretofore been a limit at which the further concentration of the solution cannot be carried without serious objection.

My object is to provide an improved storage battery electrode, wherein metallic contacts within the electrode are entirely done away with, and wherein very much less opportunity is offered for gas pressure due to solution viscosity, and for trapping of gas with the objections noted.

To this end, the invention consists of a storage battery electrode, wherein the flakes of conducting metal or metals are welded together and to the pocket walls, if used, presenting a highly diversified cellular integral structure with a very small weight of metal, in which the active material is intimately contained, the process of manufacture being such that the active material is introduced within the cellular structure after the formation of the latter, so that obviously, free passage will be allowed for the escape of any gas generated *in situ*. By so constructing the

conducting metal that it shall constitute a honeycomb or sponge-like cellular structure within the pocket or other electrode element and by allowing free opportunity for the escape of gas generated therein, the tendency of the electrode mass, as a whole, to swell is very largely reduced, and for this reason the necessity of employing expensive and highly elastic steel is overcome; moreover the cheaper steel, if used, can be more readily and economically perforated. Furthermore, by employing an integral metallic sponge-like conducting system, as explained, the conductivity of the latter will be always constant and as it presents cells of minute size, the thickness of active material in contact with any part of the conducting system will be relatively slight (probably not greater than one or two particles thick) so that it will be necessary for the current to traverse paths of the minimum length through the active particles, thus allowing an enormously high discharge rate.

By impregnating the cells of the conducting structure, as hereinafter described, I am furthermore enabled to remove the active material whenever necessary, after which the conducting structure may be cleaned by hydrogen and re-used with fresh active material. Furthermore, the process of forming the conducting metallic sponge or cellular structure within the pockets, as explained, also results in the welding of the pocket sections so that a structure will be secured wherein all metallic contacts are eliminated, the advantages of which are obvious.

Assuming the mechanical make-up of the electrode to be substantially like that illustrated in my Patent No. 704,305, dated July 8, 1902, I proceed substantially as follows: I first take a suitable refractory material capable of being readily dissolved when desired, such as magnesium oxid, and mix it with a small quantity of water containing a little carbonate of soda or other suitable binder. Only enough water is added to slightly moisten the oxid, so that after thorough mixing the oxid shows a tendency to cake together or pack slightly. This mass is then molded into thin cakes under hydraulic pressure and the cakes are subjected to a white heat, so as to consolidate the same and make them fairly hard. The cakes are then crushed to form granules of fairly defi-

nite size which are then screened. Those particles passing a 20 mesh screen and rejected by an 80 mesh screen are first mixed with water, then dried, and are then mixed with a suitable sticky material, preferably stiff molasses, until the exterior surface of all the particles is coated with the latter. I now add the thin metallic flake-like conducting metal or metals (preferably cobalt or a cobalt-nickel alloy, or nickel alone) in the form of relatively small films or scales in substantially the proportion of twenty-four parts by weight of the granular oxid and five parts by weight of the conducting metal, and intimately mix the same. Owing to the presence of the thin sticky film on each of the oxid granules, the surface thereof will be coated with the flake-like metal, so that when the mixing is complete the resulting mass shows to the eye none of the white oxid, but appears to consist entirely of metallic granules.

The metallic flakes referred to may be made in any suitable way; for example, thin sheets of cobalt or nickel, or a nickel-cobalt alloy made by fusion, may be rolled into flakes, oil being used to prevent sticking, as is well known, for instance, in the art of making bronze powder. Or instead, the hydroxid of either metal, or the mixed hydroxids of both metals in the proper proportion can be precipitated in the usual way, washed, dried and granulated to the proper size, and after reduction by hydrogen or otherwise, passed between rolls with oil to form the flakes, as I describe in my Patent No. 827,717, granted August 7, 1906. In either case, it is desirable to anneal the flakes two or more times between the passes of the rolling operation in an inert gas, preferably hydrogen, at a red heat. After the flakes are formed, it is preferable, in order to increase their bulk, to pass them between very fine crimping rolls by which they will be crimped, corrugated or otherwise distorted, or between rolls of very small diameter by which they will be curled or formed into minute curved flakes. Or instead, the flakes or foils may be made by a process of electro-deposition, as I describe in my Patent No. 821,626, granted May 29, 1906, in which event the subsequent crimping or curling operation may be dispensed with, since electro-deposited films naturally assume curved or coiled forms. For construction of the flakes or scales, or foils, I find that metallic nickel, although perfectly insoluble, possesses the objection that good contact with the active material cannot be secured unless an undesirably high pressure is employed. This fact can be possibly attributed to the formation of an invisible film of non-conducting oxid by the action of electrolysis on the nickel flakes. Metallic cobalt on the other hand, is not open to this objection, for

although its surface is slightly attacked by electrolysis, yet good contact with the active particles is secured, even when no pressure is used other than the weight of the particles themselves. It is possible, however, that the electrolytic action on the metallic flakes, if made wholly of cobalt, might, in a long time gradually disintegrate the same, and for this reason I consider it undesirable to rely on metallic cobalt alone. I therefore prefer to make use of a nickel-cobalt alloy, containing say—60 per cent. of cobalt and 40 per cent. of nickel. With such an alloy good contact with the active material will be secured by the mere weight of the latter without additional pressure, while at the same time, oxidation of the cobalt will not penetrate into the alloy to a harmful extent, so that the flakes will preserve their metallic identity. This desirable characteristic of the nickel-cobalt alloy is present even when the proportions of the two metals are widely varied.

The mixture secured by adding the flakes to the coated particles is dried, and is preferably introduced within the usual sectional pockets which are assembled in the grid, and hydraulic pressure applied, as I describe in my said patent, to engage the pocket sections together and lock the latter firmly in the grid. The grid is now immersed in slightly alkaline water (say—a two per cent. solution of potassium hydroxid) until the molasses has entirely percolated out of the mass, which can be effected by several changes of the solution, after which the electrode is again subjected to pressure. The electrode is now dried, and is placed in a retort through which hydrogen is passed, and brought to a bright yellow heat. The presence of the hydrogen atmosphere prevents any oxidation of the metal at the heat used, and the two sections of each pocket will be thus welded to one another, and the metallic flakes or foils distributed throughout the mass will be also welded together and to the pocket sections. In other words, by this welding operation, integrality of the entire metallic parts of the electrodes is secured, so as to entirely eliminate metallic contacts in the electrode system. Furthermore, by welding together the metallic flakes within the pockets, free opportunity for the escape of gas is allowed, reducing the danger of gas pressure arising in the active mass, and permitting a much cheaper grade of steel to be employed. It will of course, be understood that the heat applied is sufficient only to effect a welding operation and not sufficient to result in melting the metal enough to cause it to flow. After the welding operation thus described has been effected, it becomes necessary to remove the granular magnesium oxid, since the function of the latter as a support for sustaining the metallic films prior to and during the weld-

ing operation has now been fulfilled. This removal can be secured by dissolving out the oxid in any suitable way, as for example, in dilute acetic acid, which does not sensibly attack the metallic parts.

As a result of the operations so far followed, I obtain a structure in which the usual perforated pockets are loosely filled with a fine, quite soft, pithy, readily compressible, sponge-like or honeycomb mass of insoluble metal or alloy, presenting innumerable cells all connected together, and, in bulk occupying only a fraction of the available space inclosed by each pocket and of such a character as to make good contact with the active material. After the acid has been washed out and the electrode dried, the electrode plate is preferably subjected in a hydrogen atmosphere to heat, insufficient to effect a further welding, but sufficient to effectively clean all the metallic surfaces and reduce any oxids present, so as to permit perfect contact with the active material (for example, nickel hydroxid) which it now becomes necessary to introduce within the cellular mass. This is done by introducing the electrodes in a closed chamber connected to a vacuum pump, and whose walls may be heated, for instance, by a steam jacket. I now introduce within the inclosed chamber by means of a pump, a saturated solution of a suitable nickel salt, preferably an ammoniacal solution of nickel hydroxid made by dissolving to saturation, nickel sesquioxid in ammonia. This saturated ammoniacal solution enters at the bottom of the chamber and as the level rises all the pores or cells of the sponge-like structure will be filled with the same. The surplus solution is now withdrawn from the impregnating chamber, capillarity preventing the escape of the solution from the sponge-like structure, the vacuum pump is operated, and heat is applied to quickly evaporate the ammonia and water, leaving a deposit of nickelous hydroxid on the walls of the many cells, the ammonia being absorbed in water or otherwise recovered. By repeating these operations many times, the cells may be almost entirely filled with the active hydroxid, care being of course taken to use at all times a saturated solution, in order that the active material deposited within the cells shall not be dissolved out during the succeeding operations. By depositing the active material in successive layers on the walls of the cells, as explained, it is possible to so regulate the amount of active material thus introduced, as to provide numerous minute connected channels, extending in all directions throughout the mass and leading to the surface thereof, and through which any gas generated within the mass may freely escape. The electrodes thus formed are now removed, the exterior surfaces freed from any oxid which may adhere to the same, and

after being subjected to pressure to consolidate the metallic sponge on the active material, are ready for use.

It will be understood that the requisite cellular structure can be secured in other ways than by the process above indicated. For instance, any other suitable inert refractory granular material capable of being dissolved or otherwise removed may be employed, instead of a magnesium oxid, such as ignited tricalcic phosphate, in granular form. With this material the operations are the same as those followed with magnesium oxid. It is also possible to omit the granular material, and introduce the corrugated or curved flake or foils loosely into the pockets by jarring and tamping, followed by welding in hydrogen, and impregnation with active material, as described in my Patent No. 854,200, granted May 21, 1907.

Improved results will be secured when the pocket sections and grid of each electrode are plated with cobalt-nickel alloy, instead of with nickel alone, as heretofore, since such an alloy materially increases the character of contact. Such an alloy may be substantially 50 per cent. cobalt and 50 per cent. nickel, and may be applied by electro-deposition in any suitable way. After this cobalt-nickel plating has been applied, the metal parts are preferably welded by the application of heat in an inert gas, such as hydrogen, so as to relieve any condition of tension in the deposited coating.

In the accompanying drawing, forming part of this specification, and in which similar parts are represented by the same reference numerals, I illustrate in Fig. 1, a sectional view on an enlarged scale, on the line 1—1 of Fig. 2, a portion of a grid with a sectional pocket therein of the type disclosed in my Patent No. 704,305, dated July 8th, 1902, with a sponge-like conducting structure therein obtained as described, and Fig. 2, a plan view of a portion of a grid on a somewhat smaller scale, showing one of the pockets in place. In these drawings, 1 represents the grid, having a series of openings 2 therein, 3 and 4 are the perforated sections of the pocket, crimped in position within each of said openings, and 5 is the sponge-like conducting mass.

While I prefer to employ scales or flakes of a suitable metal or alloy for forming the sponge-like conducting structure surrounding the active mass, as I thereby obtain the greatest porosity with the least weight of metal, the same process may be carried out with the metal or alloy in powdered form, although at a sacrifice of weight, since obviously the relation between the bulk of the metal or alloy and the cubical contents of the cells or pores, would be much less in the case of the metallic powder than in the case of metallic scales, flakes or foils, so that the use

of metallic powder would probably be commercially inapplicable. Finally, it will be understood that the sponge-like conducting structure may be used for supporting the active material independently of the usual perforated pockets in which case the latter may be omitted. I consider it preferable, however, to use the perforated metallic pockets as they materially strengthen the construction of the electrode, and effectively prevent the active material from scaling off or falling out of the exposed cells or pores at the surface of the spongy mass. Furthermore, the perforated pockets protect the spongy mass effectively against accident, since the mass is somewhat fragile and of but slight tenacity.

I do not claim herein the specific method described of forming the spongy or honeycomb structure by the loose introduction of the flake-like or foliated material into the pocket or receptacle, since this specific process is described and claimed in my Patent No. 854,200, granted May 21, 1907. There are, however, claims in my present application, the language of which is generic enough to include the specific process described in my said concurrent case.

Neither do I claim herein any specific processes for making flakes or foils, since such processes are specifically described and claimed in my Patent No. 821,626, granted May 29, 1906, referring to the method of making said flakes by electro-deposition, in my Patent No. 827,717, granted August 7, 1906, referring to the making of said flakes by precipitation, and in my Patent No. 821,627, granted May 29, 1906, referring to the making of said flakes by sublimation. Finally, I do not claim broadly herein, the employment of cobalt or a nickel-cobalt alloy, as material from which to make the flakes or films, since this suggestion is covered broadly in my Patent No. 857,929, granted June 25, 1907. In my present application, however, I make claims to the use of cobalt and cobalt-nickel alloy in the make-up of conducting structures, when the latter are of a sponge-like or honeycomb formation.

Having now described my invention what I claim as new therein and desire to secure by Letters Patent is as follows:—

1. A support for the active material of an alkaline battery, comprising a non-active metallic conducting structure in the form of minute connected irregularly disposed and shaped cells, having filmy or scale-like walls, substantially as and for the purposes set forth.

2. A support for the active material of an alkaline battery, comprising a multitude of conducting metallic flakes welded together to form a cellular integral structure, substantially as set forth.

3. A support for the active material of an alkaline battery, comprising a cellular non-active metallic conducting structure composed wholly or in part of metallic cobalt, substantially as set forth.

4. A support for the active material of an alkaline battery, comprising a multitude of conducting metallic flakes welded together to form a cellular integral structure, composed wholly or in part of metallic cobalt, substantially as set forth.

5. A support for the active material of an alkaline battery, comprising a multitude of conducting metallic flakes welded together to form a cellular integral structure, composed wholly or in part of metallic cobalt, substantially as set forth.

6. A support for the active material of an alkaline battery, comprising a cellular conducting structure composed of nickel-cobalt alloy, substantially as set forth.

7. A support for the active material of an alkaline battery, comprising a multitude of particles of nickel-cobalt alloy, welded together to form a cellular integral structure, substantially as set forth.

8. A support for the active material of an alkaline battery, comprising a multitude of flakes of nickel-cobalt alloy welded together to form a cellular integral structure, substantially as set forth.

9. In a storage battery having an alkaline electrolyte, an electrode, comprising a cellular non-active metallic conducting structure having filmy or flake-like walls and active material carried within the same, substantially as set forth.

10. In a storage battery having an alkaline electrolyte, an electrode, comprising a cellular non-active metallic insoluble conducting structure having filmy or flake-like walls, and active material carried within the same, substantially as set forth.

11. In a storage battery having an alkaline electrolyte, an electrode, comprising a cellular metallic insoluble conducting structure having filmy or flake-like walls and nickel hydroxid carried within the same, substantially as set forth.

12. In a storage battery having an alkaline electrolyte, an electrode, comprising a multitude of conducting metallic flakes welded together to form a cellular integral structure and active material carried within the cells thereof, substantially as set forth.

13. In a storage battery having an alkaline electrolyte, an electrode, comprising a multitude of conducting metallic flakes welded together to form a cellular integral structure and nickel hydroxid carried within the cells thereof, substantially as set forth.

14. A storage battery electrode, comprising an inclosing pocket with perforated walls, a cellular metallic conducting struc-

ture having highly diversified minute cells inclosed by said walls, and an active material carried by the cells thereof, substantially as set forth.

15. A storage battery electrode, comprising an inclosing pocket, having perforated walls, a cellular conducting structure having highly diversified minute cells inclosed by said walls and integral with the same, and active material carried within the cells thereof, substantially as set forth.

16. A storage battery electrode, comprising an inclosing pocket, having perforated walls, a cellular conducting structure having highly diversified minute cells inclosed by said walls and integral with the same, and nickel hydroxid carried within the cells thereof, substantially as set forth.

17. A storage battery electrode, comprising an inclosing pocket having perforated walls, a multitude of metallic flakes or scales within said pocket and welded together to form a sponge-like or cellular structure and active material carried within the cells thereof, substantially as set forth.

18. A storage battery electrode, comprising an inclosing pocket having perforated walls, a multitude of metallic flakes or scales within said pocket and welded together to form a sponge-like or cellular structure and nickel hydroxid carried within the cells thereof, substantially as set forth.

19. A storage battery electrode, comprising an inclosing pocket having perforated walls, a multitude of conducting scales or films within the pocket, welded together and to the walls of the pocket to form an integral sponge-like cellular structure and active material carried within the cells thereof, substantially as set forth.

20. A storage battery electrode, comprising an inclosing pocket having perforated walls, a multitude of conducting scales or films within the pocket, welded together and to the walls of the pocket to form an integral sponge-like cellular structure and nickel hydroxid carried within the cells thereof, substantially as set forth.

21. A storage battery electrode, comprising a sectional inclosing pocket having perforated walls, the sections of which are welded together, a sponge-like metallic conducting structure within said walls and active mate-

rial carried within the cells thereof, substantially as set forth.

22. A storage battery electrode, comprising a sectional inclosing pocket having perforated walls, the sections of which are welded together, a sponge-like metallic conducting structure within said pocket and integral with the walls thereof, and active material within the cells of the conducting structure, substantially as set forth.

23. A storage battery electrode, comprising a sectional inclosing pocket having perforated walls, the sections of which are welded together, a sponge-like metallic conducting structure within said pocket and integral with the walls thereof and nickel hydroxid within the conducting structure, substantially as set forth.

24. A storage battery electrode, comprising a sectional inclosing pocket having perforated walls, the sections of which are welded together, a multitude of metallic conducting flakes within said pocket, said flakes being welded together to form a sponge-like or cellular structure, and active material carried within the cells thereof, substantially as set forth.

25. A storage battery electrode, comprising a sectional inclosing pocket having perforated walls, the sections of which are welded together, a multitude of conducting metallic flakes within the pockets, said flakes being welded together and to the pocket walls to form an integral conducting sponge-like or cellular structure and active material carried within the cells thereof, substantially as set forth.

26. A storage battery electrode, comprising a sectional inclosing pocket having perforated walls, the sections of which are welded together, a multitude of conducting metallic flakes within the pockets, said flakes being welded together and to the pocket walls to form an integral conducting sponge-like or cellular structure, and nickel hydroxid carried within the cells thereof, substantially as set forth.

This specification signed and witnessed this 29th day of March, 1905.

THOMAS A. EDISON.

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