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NASA TECHNICAL MEMORANDUM

NASA TM-77239

TECHNIQUE FOR MANUFACTURING NICKEL ELECTRODES

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Range of Patent Application

The present invention is a method of manufacturing nickel electrodes distinctive for its use of a composite material for the electrode made up of nickel compound, electrode material, cobalt in metal form or cobalt in compound form. The composite is over-discharged (same as reverse charging) in an alkaline solution. After dealkalization, synthetic resin adhesive is added and the electrode is formed.

The present invention is a method for manufacturing nickel electrodes as described in paragraph 1 of this Range of Patent Application in which selection of the cobalt compound is made from a group consisting of cobalt oxide, cobalt hydroxide, cobalt carbonate and cobalt sulfate.

Detailed Description of the Invention

The present invention is a technique for manufacturing the nickel electrodes used in alkaline storage batteries. In greater detail, this is a method that upgrades plate characteristics by using an active material in a non-sintered type nickel electrode, which is activated by electro-chemical effect.

Sintering is the most well known conventional technique for industrially producing the positive nickel electrodes used in sealed cylindrical alkaline storage batteries. Electrodes manufactured by this method, have many advantages in the characteristics accruing to an electrode, they are normally very durable, have a long plate life, excellent charge-discharge characteristics and high rate of usability, but, on the other hand, the disadvantages with this type battery electrode are the many different steps required in manufacturing require a complex manufacturing process. Also, high operational control costs necessitated by secondary equipment raise the costs of manufacturing.

Tests have been made in recent years on sintered nickel electrodes in an attempt to eliminate the disadvantages in alkaline *Numbers in the margin indicate pagination in the foreign text. /2

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storage battery production. In these tests, a mixture of adhesive synthetic resins is the chief component, nickel compounds such as nickel hydroxide are the active material and the conductor is a graphite or metal powder. This mixture is adhered to a conductive core material to obtain the plate. But in all tests made with nonsintered materials so far, there has been an increase in resistance due to a reduction in conductivity, or worsening in plate characteristics and reduction in reactivity of the active materials caused by the adding of synthetic resins. An upgrade of the rate of usability is desirable due to a low rate of approximately 70% even when there is a good volume of electrical discharge for the filled active material.

This invention improves the rate of usability of non-sintered electrodes that use the electro-chemical method. That is to say, the distinctive feature of this invention is in its being a process of forming electrodes in which the electrode composite material is over-discharged in an alkaline solution. The electrode composite used in the invention consists of a nickel compound, a conductive material, and cobalt in either its original metal or in compound form. After dealkalization, a synthetic resin adhesive is added.

In the following paragraphs, we will explain this invention through its use in prototype examples.

One-hundred (100) parts (in the following, all units are parts by weight) of NiOH₂ are used as the active material, 25 parts of phosphorized graphite and 10 parts of cobalt oxide are used as the conductive material. These ingredients are mixed uniformly and the mixture is pressure-formed in a die with the pressure at 0.5-1.0tons/cm². The formed material is then embedded in a fine wire mesh net of stainless steel or nickel. After embedding, the pressureadhered material is used for the negative electrode and nickel plate is used for the positive. This is inserted into an electrolytic cell through a separator and 7 moles/liter of caustic potash solution are entered. A current is then placed into the cell at a current density

of $4mA/cm^2$ for 1 hour and an electrical volume is then applied that is approximately 5% of the theoretical charge-volume of the active This flows the feedback current to the active material and material. the state is the same as when it is over-discharged. The above mentioned mixture is then recovered, and we weight out 90 parts of the material which has been dealkalized and then dried, 7 parts of polyethylene latex by precipitate, l part of synthetic fiber filament and 2 parts of carboxymethyl cellulose solution by solid matter volume These ingredients are then mixed into a paste consistenreduction. The mixture is then coated on both side of a nickel plate cy. punched in a die, sent through preparatory drying, rolled in pressure rollers, the adhesive is fused at 150°C-200°C and a strong electrode is obtained.

To test the characteristics of the invention we used positive nickel electrodes produced in the manner described above and test produced a nickel cadmium storage battery with a nominal chargevolume of 1650mAh.

Figure 1 is a cross-section diagram showing the configuration of the battery used here. Number 1 is the negative electrode plate which is a paste type made from cadmium oxide, synthetic filaments and binder. It has a charge-volume in the negative electrode that is approximately twice that of the positive electrode. Number 2 is the separator made from a polyamide nonwoven fabric and it is the interstice between negative electrode plate 1 and positive electrode plate 3. Number 3 is the positive electrode place of this invention. It is a nickel electrode with a positive electrode charge-volume of 2000-2500mAh and is made using an active material which has been subjected to prior over-discharge processing during its phase as a raw Number 4 is the lead plate of positive electrode plate 3, material. 5 is the sealing plate which sets safety valve 11 and 6 is the lead plate for negative electrode plate 1. Number 7 is the external casing, 8 is the lower insulating plate and 9 is the upper insulating Number 10 is the insulating gasket and it preserves the plating. sealed structure by being seamed between the edges of external

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container 7 and sealing plate 5. It should be noted that a caustic potash solution of 7 moles/liter was used for the electrolytic fluid.

One of the most important features of this invention is that in the battery of the above configuration, an active material containing a cobalt compound is filled into electrode plate 3. And, that active material has been subjected to the process of over-discharging (equivalent to reverse charging) during the stage when it is still a raw material.

The following table shows calculations of the us bility rate based on the ratio of real charge-volume to theoretical charge- volume. Theoretical charge-volume was calculated as 289mAh per gram of Ni(OH)₂. Real charge-volume was calculated after a charge of 10 hours and an over-discharge of 5 hours, taking the time until battery voltage reaches 1.0 V.

	Usability Rate	
Conventional Non-sintered electrode	65%-70%	
This Invention's Non-sintered Electrode	83%-88%	

Figure 2 is a graph showing the results of tests made on battery life according to JIS standards. Line A in the graph is the result with the present invention, B is the result for a conventional nonsintered electrode containing cobalt oxide and C is the result when electrode B is over-discharged by the same electrical quantity as A. The initial charge-volume for A is 18% above the nominal chargevolume, and although we can see some decline in charge-volume at the 250 cycle point, there are no large degradations. Even though B fulfills the theoretical charge-volume of 2400mAh, as the above table shows, it does not output the nominal charge-volume since its rate of usability is low at 65%-70%. C has a large initial .ume similar to A, but because the core generates hydrogen gas due to over-charge being applied during the electrode state, contact resistance at the boundary between core material and composite material increases, there is a gradual, but marked degradation of charge-volume and

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resistance sharply worsens at the 150 cycle boundary. The reader should note that cobalt hydroxide, cobalt in metal form, cobalt carbonate and/or cobalt sulfate may be added instead of cobalt oxide. But it must also be mentioned that none of the desired effects were obcained without the addition of a cobalt compound.

In the ways we have outlined above, the present invention vastly improves the characteristics of non-sintered nickel electrodes.

Simplified Description of Charts

Figure 1 is a cross-section diagram of the nickel cadmium battery made possible by this invention. Figure 2 is a graph showing the characteristics demonstrated in the relation between chargevolume and cycle life.

1.....negative electrode plate
2....separator
3....positive electrode plate

Figure 1



