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NASA TECHNICAL MEMORANDUM

NASA TM-76944

### METHOD OF PROCUCING NICKEL ELECTRODE

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Translation of Japanese Patent No. 55-32192, April 17, 1975.



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This invention provides a large capacity nickel electrode in which the charging efficiency and discharge utilization coefficient are improved in comparison to nickel electrodes which are produced by the conventional method, specifically by immersion of nickel electrodes retaining nickel active material or nickel active material and cobalt compounds on a porous nickel substrate in a cobalt sulfate aqueous solution whose pH is adjusted in the range of 3.5 to 6.0, followed by crystallization of the hydroxide or oxide by pyrolysis or immersion in alkali, thereby coating the surface of the nickel active material with cobalt crystals and simultaneously promoting alloying of the nickel-cobalt				
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### METHOD OF PRODUCING NICKEL ELECTRODE Yutaka Ikeda, Tsukasa Ohira, Yasuyuki Kumano, Toshio Nakao

#### Scope of Patent Claim

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1. A method of producing nickel electrodes in which nickel electrodes retaining nickel hydroxide or nickel oxide on a porous nickel substrate are immersed in a cobalt sulfate aqueous solution whose pH is adjusted in the range of 3.5 to 6.0, thereby impregnating cobalt sulfate on the nickel electrode, followed by alteration of the aforementioned cobalt sulfate into cobalt hydroxide or cobalt oxide.

Detailed Description of the Invention

Conventional nickel electrodes have been produced by immersion of a porous nickel substrate, produced by sintering nickel metal powder for 0.5 hours at approximately 900°C in a reducing atmosphere, in an aqueous solution of nickel nitrate or in a blended aqueous solution of nickel nitrate and cobalt nitrate, followed by immersion in an alkali solution or pyrolysis. The nickel nitrate or cobalt nitrate which is impregnated on the nickel substrate by means of this is then converted into nickel hydroxide or nickel oxide which does not dissolve in alkali. The nickel charging efficiency is improved by alloying the cobalt compound with nickel, and the discharge performance is also improved.

The method of simultaneously packing cobalt when nickel active material is packed in conventional porous nickel substrates is believed to be effective in forming fine crystalline alloy particles by blending nickel ions and cobalt ions followed by alkali immersion and activation of material by

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pyrolysis or crystallization, but the actual electrode capacity is only 500 mAH per 1 cc of electrode capacity. This electrode capacity is more strongly dependent on the charging capacity of nickel active material than on the effects of cobalt.

This invention provides a large capacity nickel electrode in which the charging efficiency and discharge utilization coefficient are improved in comparison to nickel electrodes which are produced by the conventional method, specifically by immersion of nickel electrodes retaining nickel active material or nickel active material and cobalt compounds on a porous nickel substrate in a cobalt sulfate aqueous solution whose pH is adjusted in the range of 3.5 to 6.0, followed by crystallization of the hydroxide or oxide by pyrolysis or immersion in alkali, thereby coating the surface of the nickel active material with cobalt crystals and simultaneously promoting alloying of the nickel-cobalt.

This invention is explained in detail below through actual examples.

Figure 1 compares the capacity of sintered nickel electrodes produced by the conventional method with that of nickel electrodes produced by this invention. A nickel substrate with 85% porosity, in which 250 mesh nickel powder on the electrode substrate was sintered for 30 minutes at 900°C in a hydrogen reducing atmosphere, was used. This substrate was immersed for five minutes in a saturated nickel nitrate aqueous solution, followed by immersion for 60 minutes in a potassium hydroxide solution at 80°C with specific gravity of 1.3. After water washing for four hours, it was dried for six hours at 60°C. The course from immersion in saturated nickel nitrate aqueous solution until drying was repeated six times, producing nickel /172 electrodes with a charging capacity of 1,000 mAH. This electrode

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was charged for 15 hours at 100 mA current using a nickel electrode in potassium hydroxide solution of 1.3 specific gravity as the opposing electrode. Curve A in Figure 1 illustrates the discharge properties in the case of discharge at 200 mA. Curve B illustrates the performance of the nickel electrode produced identically to that in A except that a blended aqueous solution of saturated nickel nitrate aqueous solution in which was dissolved 0.4 mols/liter of cobalt nitrate was used instead of the saturated nickel nitrate aqueous solution of A.

C illustrates the capacity of the nickel electrode of this invention which was produced by immersion of the same nickel electrode as was produced in A into a cobalt sulfate aqueous solution of 0.4 mols/liter in which the pH was adjusted in the range of 3.5 to 6.0, thereby impregnating cobalt sulfate, followed by immersion in potassium hydroxide of 1.3 specific gravity, thereby producing cobalt oxide or cobalt hydroxide, washing with water and drying. D illustrates the capacity of nickel electrodes of this invention in which the nickel electrodes produced in B were impregnated with cobalt sulfate in the same process as that in C, thereby forming cobalt oxide or cobalt hydroxide.

The figure indicates that nickel electrodes of this invention which are produced by immersion of nickel electrodes, which retain nickel hydroxide or nickel oxide in the sintered nickel substrate, in cobalt sulfate aqueous solution whose pH was adjusted in the range of 3.5 to 6.0 exhibit far superior discharge capacity in comparison to conventional nickel electrodes.

Figure 2 illustrates the discharge capacity of nickel electrodes produced by immersion of nickel electrodes produced in B of figure 1 in 0.4 mol/liter cobalt sulfate aqueous solutions

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with pH of 2.5, 3.0, 3.5, 4.0, 5.0, 6.0, 6.5 and 7.0, followed by immersion in alkali. The hydrogen ion concentration in the aqueous solution had a clear effect on the capacity of nickel electrodes although the cobalt ion concentrations were uniform.

The capacity of nickel electrodes was best when the pH of the cobalt sulfate aqueous solution used ranged from 3.5 to 6.0. At pH less than or equal to 3.0 or pH greater than or equal to 6.5, the results were virtually identical with those of untreated electrodes, and the effects of cobalt sulfate were not seen. This is because corrosion of the nickel substrate does not occur when the pH is high, and as a result, the nickel substrate is not activated. Furthermore, nickel activation occurs due to sulfate anions when the pH is low, and corrosion takes place, ultimately reducing the discharge capacity. The marked improvement in the effects of cobalt sulfate only in a specific pH range is due to partial corrosion of the nickel substrate, with precipitation occurring simultaneously due to substitution of cobalt ions. Alloy formation is promoted, and alloying of cobalt and nickel active material is promoted due to simultaneous adsorption of sulfate anions of cobalt sulfate in relation to nickel active material, thereby raising the activity. In the aforementioned example, alkali aqueous solution was used to convert the cobalt sulfate impregnated in the nickel electrode into cobalt hydroxide or cobalt oxide, but pyrolysis may also be employed.

Since the bond strength of anions and cobalt ions varies with the type of anion of cobalt salt, the range of concentration of hydrogen ions activated by the cobalt salt used would also vary.

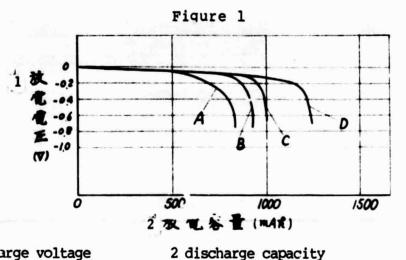
As indicated above, a large capacity nickel electrode can be produced by this invention.

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Simple Explanation of the Figures

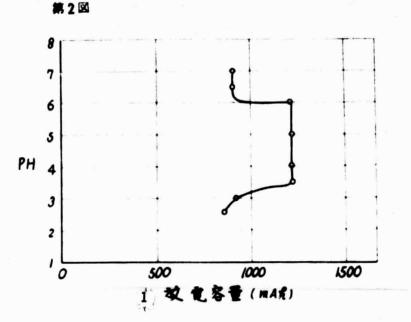
Figure 1 compares the discharge properties of nickel electrodes produced by various methods. Figure 2 illustrates the relation between the hydrogen ion concentration of cobalt salt aqueous solutions and the discharge capacity of nickel elect odes.



1 discharge voltage







1 discharge capacity