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Study of preparation technology for high performance AA size Ni–MH batteries

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Abstract

By optimum selecting of materials, optimizing electrode composition and preparation technology of electrodes, modifying battery assembly process, AA size Ni–MH batteries with 600–660 mAh/cm^3 volume specific capacity of nickel hydroxide electrode and 1350–1525 mAh rated capacity were prepared. The battery has high discharge voltage platform, good high rate charge and discharge characteristic and long cycle life of large current.

Keywords: Ni–MH battery; Electrode composition; Preparation technology; Volume specific capacity

1. Introduction

The major application market of nickel hydride battery is communication equipment, such as portable mobile telephones, which require Ni–MH batteries with not only high capacity, but also high rate discharge property, high discharge voltage platform and long high rate charge and discharge life. These are all the technical indexes the consumers are concerned with. Therefore, whether a Ni–MH battery can enter the international market to take part in the competition depends on the overall level of the Ni–MH battery itself. The aim of this research is to improve the overall characteristics and homogeneity of the products.

2. Experimental

2.1. Selection of materials

For obtaining high performance of electrode and battery, it is important to choose materials with good properties. So the properties of a large number of electrode and battery materials were tested and compared. Some materials with good properties were selected for use.

The foamed nickel, spherical active $Ni(OH)_2$ and hydrogen storage alloy selected are made by General Research Institute for Non-ferrous Metals, Koly Advanced Material Plant, Jizhou Hebei China, and China Liaoning Suppo Battery Co., Ltd., respectively.

The conductors used in this study are nickel powder with a radius of 0.2 μm and acetylene black. Superfine powder Co, CoO and Zn were chosen as additives. PTFE and CMC mixed solution and a new type of binder prepared by Institute of Chemistry, Chinese Academy of Science were chosen as binders.

2.2. Technological process for electrode preparation

The technological process for electrode preparation is shown in Fig. 1.

2.3. Battery assembly

A series of modifications for electrode sizes and matching of positive and negative electrode chips was carried out in order to reach optimum ratio, and suitable assembly degree of tightness, in addition, short circuit was prevented in the battery bottom, internal core, neck and electrode lip.

2.4. Sealed formation

In order to simplify process, reduce cost and improve battery performance, the sealed formation technique, developed in this project, was applied. The technique mainly included: (1) choosing suitable raw materials; (2) preparation of high active electrode; (3) alkaline solution injection method and amount, we used centrifugal alkaline injection way of which alkaline could be permeated quickly in a

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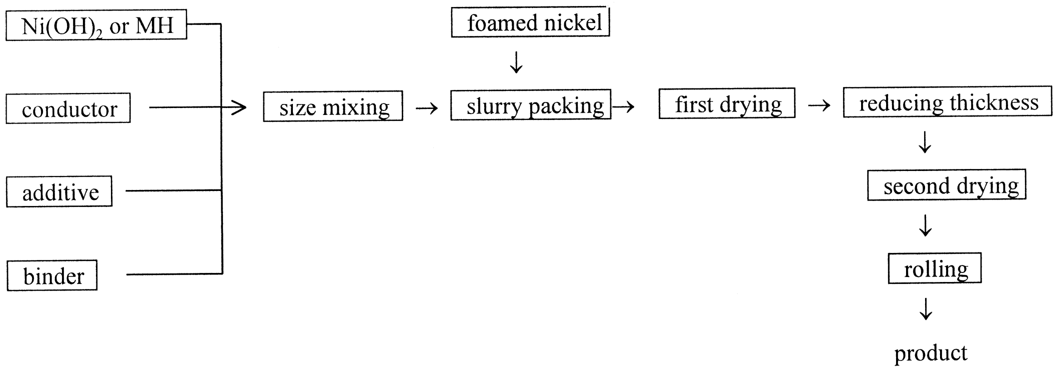

Fig. 1. Technological process for electrode preparation.

short time and enough alkaline absorption ensured. Besides, the effect of alkaline amount on the stability of the battery was investigated; (4) determination of formation system. After using the technique to charge and discharge battery two or three times, the activation could be succeeded.

3. Results and discussion

3.1. Application of additives

A small amount of additive should be added into the raw material in order to improve the properties of the electrodes, especially the properties of the positive electrode. The additives applied commonly are Co power, Co compound and elements of II group, Cd, Zn, Ba and etc.. The main functions of additives to the positive electrode are as follows: (a) to increase the activity and utilization factor of active material [1]; (b) to suppress the formation of γ-$Ni(OH)_2$ and increase the operating time; (c) to increase the conductivity of the electrode; (d) to enhance the oxygen separation polarization, decrease the quantity of oxygen gas separated out, raise the charging efficiency etc. [2]. For example, the main function of adding CoO is that, during the dissolving and separation process in the alkaline solution, the additive can clad over the surface of $Ni(OH)_2$ uniformly in the form of β-$Co(OH)_2$, and then the β-$Co(OH)_2$ is oxidized into CoOOH during the charging process. This reaction is irreversible, but the active product CoOOH has good conductivity. Therefore, the CoO acts as a high conductivity connector between the foamed nickel matrix and $Ni(OH)_2$, while the utilization factor of $Ni(OH)_2$ increases evidently.

It was found in experiments that miscellaneous additives had better results than a single additive. The effect of CoO additive content on the electrode properties is shown in Fig. 2.

From Fig. 2, it is obvious that the electrode properties could be improved greatly by adding CoO. When the CoO content increases, the mass specific capacity and the volume specific capacity increase continuously in the initial stage, but when the CoO content approaches to 7%, the former no longer goes up whereas the later tends to go down. Because the over-added CoO couldn't raise the volume specific capacity, on the contrary, it occupied some place of the electrode, thus the filling quantity of $Ni(OH)_2$ reduced comparatively.

A small amount of Co compound was added into the negative electrode. The effect of Co compound content on the battery performance is shown in Table 1.

From Table 1, adding a small amount of Co compound in the negative electrode can enable the electrode to increase the discharge voltage platform, achieve high rate discharge and decrease the discharge reserve. To consider the effect on electrode cost and specific capacity etc., it is suitable that the Co compound content of negative electrode is about 1%.

3.2. Types and content of binders in positive electrode

The types and content of binders intensively affect the electrical and mechanical properties of the electrode. Binders of PTFE, CMC and a new one prepared by the Institute of Chemistry, Chinese Academy of Science, were investigated thoroughly in this study. Work was focus on the mixed binder, which consists of both PTFE and CMC. After PTFE becomes fibre, the fibrous-net structure has efficient containment and cohesiveness to the active material, so that the intensity of electrode is enhanced and its operating life is extended. Since the existence of hydrophilic characteristic of CMC, the electrolysis solution can wet the active component thoroughly to overcome the lack of solution in local area caused by using a single PTFE binder. Hence the utilization factor of active material rises. Table 2 shows the effect of the binder content on the properties of nickel electrode.

From Table 2, it can be seen that the specific capacity of electrode reduces with the increase of binder's content. The increase of binder's content, as a matter of course, leads to slowing down the active rate and raising inherent resistance. Thus the battery properties of voltage platform,

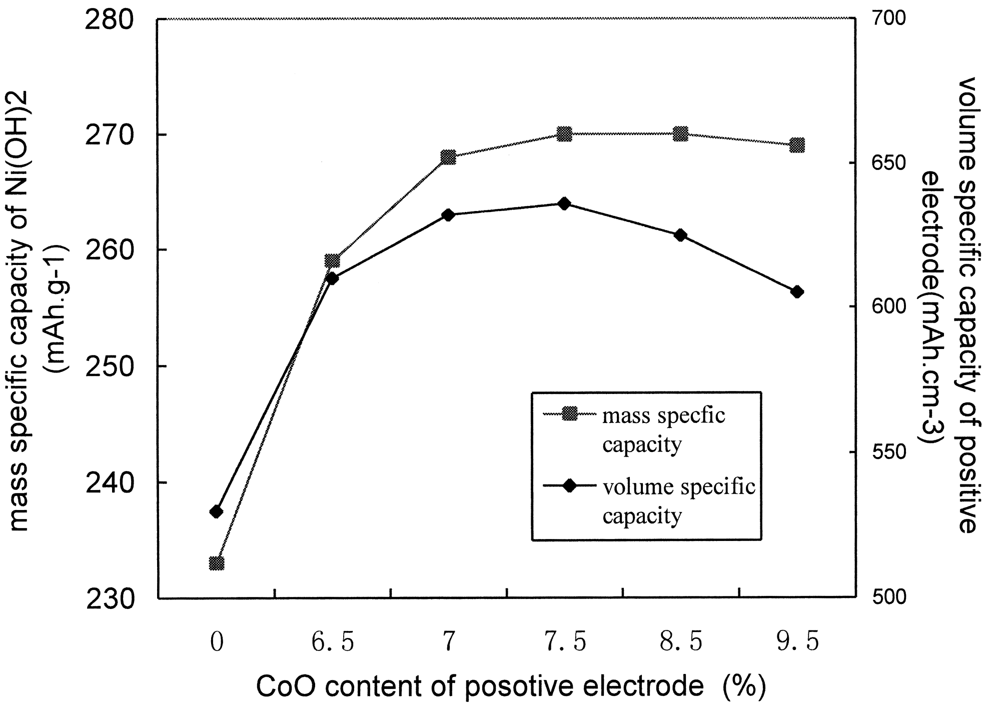

Fig. 2. Effect of CoO content on electrode properties.

Table 1
Effect of Co compound content on the battery performance

Co compound content (%)	0	0.5	1	2
K (%)[a]	80	85	89	90
$C_{1C}/C_{0.2C}$ (%)	88	92	95	96

[a] Note: K is a ratio between the discharged capacity under the state of voltage $\geq$1.200 V and the total discharge capacity.

high rate charge and discharge get poorer. It indicates that the binder content must be controlled strictly on premise that the operating life is enough long. The study results suggest that the binder content values presented in other Ni–MH battery research reports are all more than necessary. The misunderstanding is due to the same worry that the electrode may drop powder if the binder content is not high enough. Our proposal is that, since the battery has compact structure and charge discharges unceasingly, the electrode will expand in various extents, hence the electrode components will combine more closely. It is determined that the binder content is about 1% in this study. No phenomenon of powder-drop was observed during the charge and discharge circulation of more than 350 times.

Table 2
Effect of the binder content on properties of positive electrode

Binder content/%	1	2	3
Mass specific capacity of $Ni(OH)_2$ (mAh g^{-1})	272	250	230
Volume specific capacity of positive electrode (mAh cm^{-3})	636	580	525

3.3. Technology of electrode preparation

3.3.1. Size mixing and slurry packing

The technology of size mixing and slurry packing is very important in the process of electrode preparation. The main parameters in it are as follows: (1) pre-rolling thickness of foamed nickel, generally, the thickness of foamed nickel is 2.0$\pm$0.2 mm. If it was used directly, the amount of slurry packed would be too high, and the thickness of the electrode would be difficult to reduce. So, in order to obtain suitable amount of slurry packed, the foamed nickel must be pre-rolled. The pre-rolling thickness in this study is less than 1.5 mm. (2) viscosity of slurry, because it is not easy to coat when slurry is too sticky, and the composition of slurry would not be well-distributed when the slurry is too thin. So the viscosity of slurry must be suitable. (3) time of size mixing, in order to assure that the composition of slurry, especially super-fine conductors and additives, would be well-distributed, the time of size mixing must be enough. In addition, in order to assure the homogeneity of slurry packing, a small type of equipment for slurry packing made by ourselves was used in this study.

3.3.2. Forming and pliability of electrode

Two times drying and rolling were used. The main parameters in this technology are as follows: drying temperature, time, content of water reserved after first drying, thickness of reducing, pressure of forming etc. These parameters affect directly the thickness and porosity of electrode, and yet the thickness and porosity of elec-

Table 3
Main properties of common battery

Volume specific capacity of positive electrode (mAh/cm^3)	$0.2C_5$ discharge		$1.0C_5$ discharge		Internal resistance (mΩ)	28d self-discharge ratio (%)	1C cycle life[b] (times)
	Capacity (mAh)	K[a] (%)	Capacity (mAh)	K[a] (%)			
600–630	1350–1400	88–92	>1250	70–82	13–16	<30	>350

[b] The charge/discharge rate used to measure the 1C cycle life is as follows: charge to t=75 min and $-\Delta V$=10 mV, lay aside for 30 min and then discharge to 1.0 V under a current of 1200 mA, repeat until the 1C capacity reduces to 80% of its initial value.
[a] K is a ratio between the discharged capacity under the state of voltage ≥1.200 V and the total discharge capacity.

Table 4
Main properties of high capacity battery

Volume specific capacity of positive electrode (mAh/cm^3)	$0.2C_5$ discharge		$1.0C_5$ discharge		Internal resistance (mΩ)	28d self-discharge ratio (%)	1C cycle life[b] (times)
	Capacity (mAh)	K[a] (%)	Capacity (mAh)	K[a] (%)			
630–660	1450–1525	85–90	>1350	65–75	14–18	<30	>250

[b] The charge/discharge rate used to measure the 1C cycle life is as follows: charge to t=75 min and $-\Delta V$=10 mV, lay aside for 30 min and then discharge to 1.0 V under a current of 1200 mA, repeat until the 1C capacity reduces to 80% of its initial value.
[a] K is a ratio between the discharged capacity under the state of voltage ≥1.200 V and the total discharge capacity.

trode affects the performance of electrode largely [3]. The thickness of positive and negative electrode prepared in this study is 0.6–0.62 mm and 0.3–0.33 mm respectively. The electrodes prepared have good pliability.

4. Properties of batteries

Tow types of AA size Ni–MH batteries were prepared by using the above mentioned technique. The properties of the batteries are shown in Tables 3 and 4.

5. Conclusions

1. Battery with twin-foam structure has advantages of simple preparing process, low cost and high packing ratio of active material;
2. The cruxes of fabricating high property battery are to optimize materials, electrode composition, preparing process and to rationalize the battery structure;
3. The positive electrode which has volume specific capacity of 600–660 mAh.cm^{-3} and AA size Ni–MH battery which has nominal capacity of 1350–1525 mAh were prepared. The battery has high discharge voltage platform, good large current charge/discharge characteristic and long high rate cycle life.

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