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ARTICLE

Review on Comprehensive Recovery of Valuable Metals from Spent Electrode Materials of Nickel-Hydrogen Batteries

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Abstract: In spent battery materials, there exist plenty of valuable metals, such as nickel, cobalt and rare earth element. The recovery of valuable metals from them not only protects the environment, but also improves the utilization of resources and lowers the cost of battery production. Similarly to many other batteries, random dumping of spent nickel-hydrogen batteries would lead to serious pollution; the recovery of valuable metals from them is of great significance. A review on recycling of spent nickel-hydrogen batteries was presented in the present paper, and several recovery technologies were introduced in detail. In addition, the prospect on comprehensive recovery of valuable metals from spent electrode materials of nickel-hydrogen batteries was made.

Key words: spent nickel-hydrogen battery; leaching; valuable metal; recovery

Nickel-hydrogen battery (Ni-*M*H battery) is one type of new batteries largely developed by many countries worldwide in the 1990s. In recent years, the average annual growth rate of its market in the world is about 13%. As for our country, driven by National High-Tech Research and Development Program of China ("863" program), it is gradually realizing the goal that its Ni-*M*H battery and related industries develop from scratch and catching up with and even surpassing the advanced level in the world. Although it is gradually replaced by lithium-ion battery and lithium-polymer battery, Ni-*M*H battery still has a big share in the secondary battery market due to its comprehensive advantages[1-4]. As all batteries have a problem of serving life, the number of waste batteries will increase with the increasing of consumption of batteries, and there is no exception for Ni-*M*H battery[5-7]. Recovery of valuable metals from spent Ni-*M*H batteries and development of recycling technology with high efficiency can not only reduce its pollution in environment[8,9], but also promote recycling of resources, thus meeting the requirements of sustainable development.

1 Overview of Ni-*M*H Batteries

1.1 Classification and working principle

Ni-*M*H battery is one type of secondary batteries. According to different encapsulations, they can be divided into ones with or without plate cassette, and seal Ni-*M*H batteries. And they can also be divided into cylindrical and square types[10].

Coating the active material, nickel hydroxide on the nickel base materials makes the positive electrode of Ni-*M*H battery. The negative electrode of this battery is hydride electrode using hydrogen storage alloys as the active substances. Usually the porous polyamide or polypropylene fleece or gauze is used as diaphragm between electrode plates. The electrolyte is generally an aqueous solution of potassium hydroxide with a small amount of lithium hydroxide and sodium hydroxide. Each electrode reaction in the charging and

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discharging process is shown in the following equations from (1) to (6).

In the charging process,

Positive reaction: $Ni(OH)_2+OH^- - e^- \rightarrow NiOOH+H_2O$ (1)

Negative reaction: $M+H_2O+e^- \rightarrow MH+OH^-$ (2)

Overall reaction: $M+Ni(OH)_2 \rightarrow MH+NiOOH$ (3)

In the discharging process,

Positive reaction: $NiOOH+H_2O+e^- \rightarrow Ni(OH)_2+OH^-$ (4)

Negative reaction: $MH+OH^- - e^- \rightarrow M+H_2O$ (5)

Overall reaction: $MH+NiOOH \rightarrow M+Ni(OH)_2$ (6)

In above equations, *M* indicates hydrogen storage alloys, and *M*H indicates metal hydride. For the charging process, the hydrogen atom dissociates from $Ni(OH)_2$ and is combined with the *M* alloy, forming *M*H alloys. For the discharging process, the hydrogen atom dissociates from the *M*H alloys and joins with NiOOH, forming $Ni(OH)_2$ [10]. In the charging and discharging processes of Ni-*M*H battery, electrochemical reactions occur in the two electrodes. In the charging process, the positive active substance $Ni(OH)_2$ release a H^+ and e^-, among which the e^- will be derived through the external circuit and H^+ will be transferred to the surface of negative electrode through diaphragm (including electrolyte). Then the H^+ will combine with another e^-, and contact with hydrogen storing alloys, forming metal hydride (*M*H). The discharging process is a reverse reaction of the charging process. Thus, the electrolyte is just playing a role of transferring H^+, and it does not join in the electrode reactions in itself. Therefore, Ni-*M*H battery has no need to consume electrolyte, which is the promise of battery seal and maintenance-free.

If overcharging of Ni-*M*H battery happens, oxygen will be generated in the positive electrode, but the negative electrode will soon absorb it. The overcharging reactions can be shown in the following equation (7) and (8).

Overcharging reaction of positive electrode:

$4OH^- \rightarrow O_2+2H_2O+4e^-$ (7)

Overcharging reaction of negative electrode:

$4MH+O_2 \rightarrow 2H_2O+4M$ (8)

Therefore, the internal pressure of Ni-*M*H battery will not increase too high to be dangerous, and even if the battery pressure exceeds the designed pressure, the battery safety valve will be open to release a part of gas to ensure the internal pressure remain at a level of relatively low, so as to ensure the safety performance of battery.

1.2 Background of recycling spent Ni-*M*H batteries

1.2.1 Harms of spent batteries

Spent batteries include spent primary battery and spent secondary battery, and the former is mainly zinc manganese battery, which contains harmful substances such as mercury and alkali[11]. And the harms of the latter are mainly derived from the substances of large amounts of heavy metals, acids and alkali. If these spent batteries were handled improperly, the harmful substances in them would be penetrated out, entering into soil and water. Then these harmful substances would be accumulated in the bodies of animals and plants, and be transferred to the human body through biologic chain, making damages to nerve, blood, digestive system and so forth[12]. In brief, there are various harms caused by spent batteries[13-16].

1.2.2 Signification of recycling spent Ni-*M*H batteries

Based on the discussion above, it is very favorable to carry out the recycling of spent Ni-*M*H batteries to protect the environment and ensure human health. In addition, no matter what kind of batteries, they are not just rubbish, but renewable secondary resources. As for spent Ni-*M*H batteries, they contain a large number of valuable metals with high economic value. The recycling of valuable metallic elements from them can not only reduce the hazard of waste substances to the environment, bringing environmental protection effect, but also has economic benefits. Metal or non-metal components in spent batteries are derived from mineral resources. And the valuable metal content in spent batteries is much higher than that of primary ores. It will cause a tremendous waste of resources if we don't conduct effective recycling. With the gradual exhausting of mineral resources, it is imperative for us to carry out recycling of non-ferrous resources such as spent Ni-*M*H batteries having high content of valuable metals.

2 Recovery Technologies

Recovery technologies of spent Ni-*M*H batteries should consider the particularity of spent material components, the feasibility and the economical efficiency. According to different recovery purposes, the existing recovery technologies of spent Ni-*M*H batteries at home and abroad are shown in the following sorts.

2.1 Pyro-metallurgy processing technology

In the pyro-metallurgy processing technology[17,18], spent Ni-*M*H batteries are firstly crushed. After removing the electrolytes, the obtained materials are dried at a certain temperature. After drying, organic materials such as diaphragms and adhesives are separated, and the remained materials can be used to produce nickel-iron based alloys by reduction smelted. According to different targets, retreatments of the obtained alloys can be conducted. For instance, the smelted products obtained after impurity elements, such as Mm, Mn and V are removed by oxidation, can be applied in the smelting of alloy steels or cast irons again.

A combined process of machinery and metallurgy can reflect the development of existing pyro-metallurgy processing technology. Steel shells, organic materials and spent electrode materials of Ni-*M*H batteries would be separated in the crushing process. With the aid of electric arc furnace and specialized fusing agent, nickel-cobalt alloys can