Research on the application of electrode materials for batteries

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Abstract. In the world, ecological environment and energy problems seriously restrict the sustainable development of each country and society. Therefore, it is essential to eliminate fossil energy dependence and develop and utilise new energy, especially in electric vehicles. This requires the use of secondary batteries to achieve efficient energy storage. In this paper, several potential energy storage technologies Ni-HM, Li-ion and PEMFC, are compared, and the application prospect, existing problems and the primary performance of these three battery technologies are analysed. This paper examines the standard preparation technology, reaction mechanism, background and advantages and disadvantages of these three kinds of batteries. Then the problems faced by the application of these three battery technologies, including specific energy, energy density, specific power, energy storage cost, cycle life, energy efficiency, safety, etc., are analysed, and through the main performance comparison of these three battery technologies, to provide a new idea in the battery area. Through the analysis and comparison of these batteries, the Li-ion battery has the greatest all-around performance, so it is also the optimal solution to solve environmental and energy problems. Secondly, Ni-MH batteries in all aspects of the commission are very general; the current technology still lacks competitiveness, and many vital areas need further research. Finally, the PEMFC have significant advantages in energy density, energy storage cost, and specific energy, so this technology is a potential technology worthy of further study.

Keywords: electrode materials, energy storage technologies, preparation technology, reaction mechanism.

1. Introduction

With the global popularisation and the rapid electric vehicle industry development, energy storage technology will become the critical link to significant promoting energy development. There are promoting differences in the maturity of various technologies in the energy storage field, like chemical fuel energy storage, heat storage technology, and electrochemical storage. Therefore, building an energy storage technology layout with multiple energy complementation is necessary; learning from each other's strengths, adapting measures to local conditions and giving priority to benefits are required. Among them, electrochemical energy storage technology can effectively solve the peak-valley difference in power supply and new energy consumption and provide the power system's stability, reliability and economy. Compared with pumped storage, electrochemical energy storage technology has significant advantages in response speed, site selection conditions, environmental impact, construction cost, safe operation, power loss, regulation efficiency, construction period, etc.

As a carrier of energy conversion and storage, batteries have never been interrupted in recent decades. It has always been a hot spot of scientific research [1]. With repeated charging and discharging characteristics, the secondary battery is more economical and practical than the primary battery, in line with sustainable development. In many different kinds of secondary batteries, represented by the lithium battery of the electrochemical energy storage technologies have been preliminarily into the vast commercialisation, large-scale application, and has enormous development space, is the promising power technology in the energy storage area, so it is widely used in portable electronics, energy storage power station and electric vehicles, etc. [2]. For example, energy storage and conversion devices for electric cars mainly include nickel-metal hydride (Ni-MH) batteries, lithium-ion (Li-ion) batteries, Proton Exchange Membrane Fuel cells (PEMFC) and so on. Although Li-ion batteries currently dominate energy storage technologies, the restricted amount of lithium stored in the world and the climbing cost each year significantly impose its potential for next applications [3]. However, nickel metal hydride battery, as a mature secondary battery, has the advantages of high safety, excellent low-temperature performance, good assembly performance, abuse resistance, high recyclable value, and environmental friendliness. It has been widely used in new energy vehicles, power tools, consumer electronics, emergency devices, military equipment and other fields. However, due to the relatively low specific energy, it is at a disadvantage in the market competition for Li-ion. It is essential to improve the Ni-MH battery’s discharge cycle life and its capacity to enhance the market competitiveness of Ni-MH. In addition, fuel cell vehicles have the advantages of long-range, short energy replenishment time and less pollution emission. In particular, PEMFC has been recognised as the development direction of the next generation of vehicle power because of its many advantages, such as high power density, only water emission product high and efficiency and promising low-temperature start-up. However, the operation of fuel cell vehicles requires large-scale refuelling stations, which hinders large-scale promotion and application [4].

Based on the present situation and development trend for electrochemical energy storage technology, in this paper, the electric car involved in the field of different materials generalises the secondary batteries, Ni-MH, Li-ion battery, fuel cell, and other forms of the corresponding principle, preparation methods, at the same time inventory of all kinds of secondary battery application status and technological, economic development trend.

2. Preparation of secondary batteries

At present, the research field of anode materials for secondary batteries is generally designed into different morphologies and structures, such as hexagonal shapes and flower-like shapes, through other chemical synthesis methods (such as solid phase pyrolysis, water/solvothermal method, chemical/physical vapour deposition method, etc.) to increase their surface area and improve their active reaction sites. Reduce the dramatic volume change and improve its structural stability.

2.1. Solid phase pyrolysis preparation method

Generally, the powder samples are prepared by the solid-phase thermal decomposition approach. This method has the advantages of a simple process and high efficiency and simplifies and accelerates the synthesis of multiple steps. Because the reaction can be carried out in a simple reaction vessel, it can avoid the loss caused by manual operation and repeated transfer of materials; However, the significant problems of this method are high synthesis temperature, high energy consumption and high production cost. In particular, the products are prone to agglomerate, which reduces the exposure of active reaction sites, thereby increasing the volume increase caused by the ion de-embedding process and destroying its stability.

2.2. Water/solvothermal preparation method

Hydrothermal solvent-thermal means that under a certain specific temperature (100-1000℃) and pressure (1-100mpa), water or other solvents are in a critical or supercritical state, the reactivity is improved, and the physical and chemical properties of other substances in the solvent are considerably significantly changed. Therefore, the thermal solvent-thermal chemical reaction is different from usual. A of various inorganic materials, inorganic compounds with unique composition and structure and unique condensed matter materials can be synthesised.

2.3. Preparation method of vapour deposition

The vapour deposition method includes the physical and chemical vapour deposition methods. Chemical Vapor Deposition (CVD): A technology that employs gaseous substances such as gas or Vapor to generate solid sediments through Chemical reactions on the gas phase or gas-solid interface. Physical Vapor Deposition (PVD) vaporise a technique in which atoms or molecules, or parts of a material source (solid or liquid surface) in the gaseous state are evaporated to ions under vacuum to deposit a thin film with a specific function on the substrate surface by a low-pressure gas (or plasma) process.

3. Classification of secondary battery materials

3.1. Nickel metal hydride battery

Nickle metal battery (Ni-MH) was born in the 1970s and commercialised in the 1990s. In this system, the anode material is nickel hydroxide, hydrogen storage alloy as anode material, porous polymer material as diaphragm material, and the electrolyte is KOH aqueous solution; its working voltage is at 1.2V. Ni-MH, disposable dry batteries, and nickel-cadmium batteries have similar operating voltage, higher energy density and better environmental protection, so they are widely used in power tools, portable electronic devices and other fields nickel-cadmium batteries and disposable batteries. In figure 1, the Ni-MH working principle is illustrated. According to other reports, the reaction in the battery is eq.(1)-(3) [6]:

$$\text{Anode: } Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \tag{1}$$

$$\text{Cathode: } M + xH_2O + xe^- \rightarrow MH_x + xOH^- \tag{2}$$

$$\text{Battery reaction: } M + xNi(OH)_2 \rightarrow MHx + xNiOOH \tag{3}$$

where, M and MHx are hydrogen storage alloys and their corresponding hydrides, respectively.
When the Ni-MH battery is overcharged, the reaction occurs as eq. (4)-(5):

$$\text{Anode: } 4OH- \rightarrow 2H2O + O2 + 4e- \tag{4}$$

$$\text{Cathode: } 2MH + 1/2O_2 \rightarrow 2M + H_2O \tag{5}$$

$$\text{Reaction: } 2M + 2H_2O + 2e^- \rightarrow 2MH + 2OH^- \tag{6}$$

In over-discharged, the reaction in Ni-MH battery, as shown in eq. (7)-(8):

$$\text{Anode: } 2H_2O + 2e- \rightarrow H_2 + 2OH^- \tag{7}$$

$$\text{Cathode: } H_2 + OH- \rightarrow 2H_2O + 2e^- \tag{8}$$

$$\text{Reaction: } H_2 + 2M \rightarrow 2MH_x \tag{9}$$

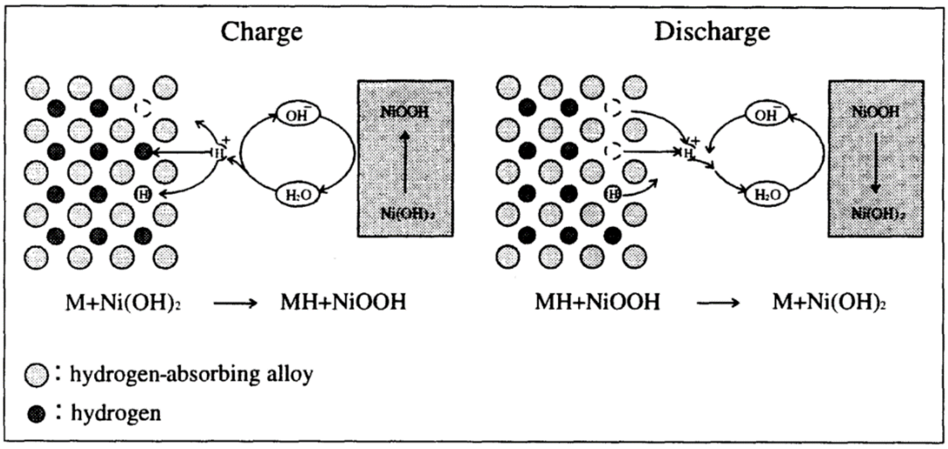

Figure 1. The reaction mechanism of the Ni-MH battery [5].

The Ni-MH battery's reactions are carried out in the solid state. In the response, water-soluble metal ion intermediates are not formed, and there is no solution-precipitation reaction problem that often occurs in other aqueous solution batteries. Therefore, this battery has good structural stability in its electrode materials. In addition, in the battery reaction, the electrolyte components are protected, so that the battery is maintenance-free and airtight. When the battery is overcharged, on the hydride electrode surface the oxygen transfers to water via the diaphragm. When over-discharged, the hydrogen rained poured from the anode is absorbed by the hydride electrode through the diaphragm. Therefore, theoretically speaking, a nickel-metal hydride battery in overcharge or over-discharge will not produce gas aggregation problems, with excellent properties in over-discharge/charge and related resistance abilities, which make the secondary battery safer. Nickel metal hydride battery products are widely used in portable power tools, retail electronic devices, hybrid electric vehicles, military equipment and other fields [7].

Ni-MH, as the mature secondary battery technology, has the following technical advantages [7]: (i) good safety even under conditions of abuse; (ii) good consistency; (iii) excellent high and low-temperature performance; (iv) good environmental friendliness; (v) high recoverable value.

At the same time, nickel-metal hydride batteries also have many disadvantages, such as relatively low specific energy (for lithium-ion batteries), poor self-discharge performance, general cycle life, and high cost of raw materials (compared with lithium-ion batteries, the price advantage is obvious apparent), which makes it in an inferior position in the market competition with lithium-ion batteries.

3.2. Lithium-ion battery

The core components of a Li-ion battery are the negative and positive terminal, the diaphragm and the electrolyte. They store energy by moving Li-ion forth and back into the cathode and anode during the cycling process. The cathode of graphite and the anode of lithium cobalt acid ($LiCoO_2$) is used for commercial lithium-ion batteries. The working principle is like figure 2 (eqs. (10) and (11)).

$$\text{Anode: } LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^- \tag{10}$$

$$\text{Cathode: } 6C + xLi^+ xe^- \rightarrow Li_xC_6 \tag{11}$$

Ions are removed from the cathode material lithium, move from the anode to the cathode, and are finally embedded in the graphite layer to form Li-carbon interlayer compound $LixC_6$ (eqs. (12) and (13)).

$$\text{Cathode: } Li_xC_6 \rightarrow 6C + xLi^+ + xe^- \tag{12}$$

$$\text{Anode: } Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2 \tag{13}$$

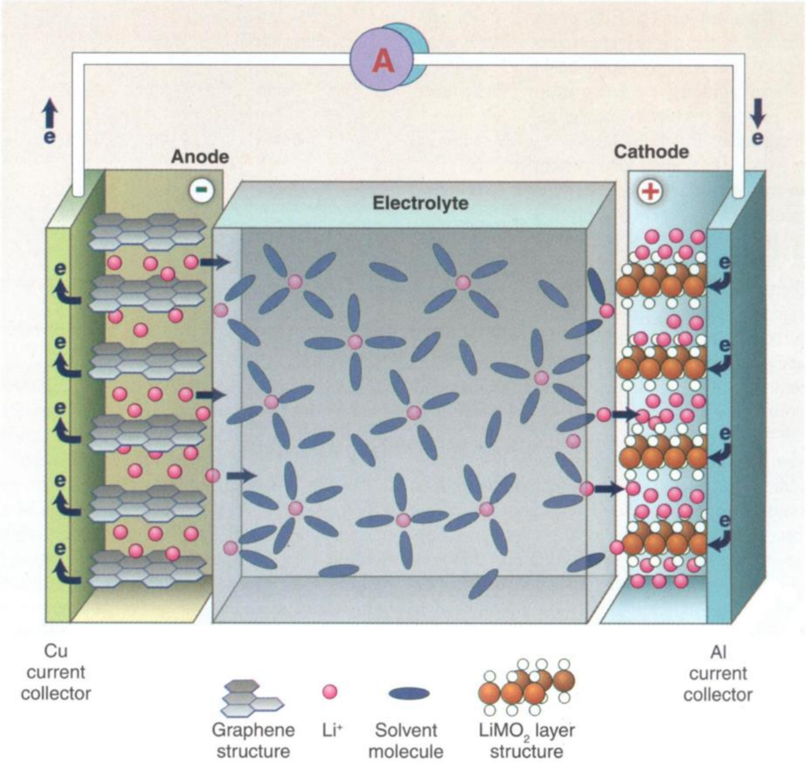

Figure 2. Lithium-ion battery working principle [8].

Li-ion battery material systems are rich and diverse, among which lithium iron phosphate, ternary (lithium nickel-cobalt manganate), lithium titanate and so on are the main ones suitable for power storage. In addition, some new lithium-ion battery systems with high energy density have been developed recently. New lithium-ion batteries, including lithium-air and lithium-sulfur batteries, are more forward-looking lithium-ion battery technologies mainly targeted at ultra-high energy density applications. At present, it is still in its infancy. When the technology is mature in the future, it will have a disruptive impact on the lithium-ion battery industry and related industries.

3.3. Proton exchange membrane fell cell (PEMFC)

It is well-known that a fuel cell can transfer energy from chemicals to electricity. In addition, it has a comprehensive source of raw materials like hydrogen, natural gas, methanol, ethanol and formic acid. The PEMFC is a fuel cell which uses a proton exchange membrane as a solid electrolyte.

Figure 3 shows the structure of the PEMFC. The outermost part of the fuel cell is the collector plate. The layer is the catalytic layer that exists inside of the gas diffusion, where the chemical energy is converted into electric power in the fuel cell, and the catalytic reaction occurs. A proton exchange membrane in the catalytic layer plays a solid electrolyte to isolate the responses on both sides and transfer protons. On the other side is the cell structure on the other side of the same order as described above.

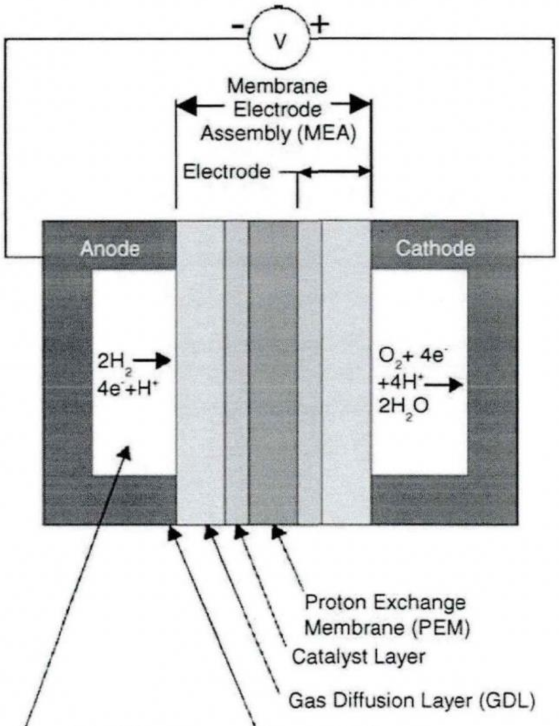

Figure 3. The structure of PEMFC [9].

Figure 4 illustrates the one-half schematic representation of the proton exchange membrane electrode assembly. In figure 4, the membrane electrode assembly (MEA) catalytic layer (CL) core component is not a single composition. In general, the catalytic layer is made up of a catalyst, a proton conductor. The triggers are generally composed of noble metal (Pt or Pt alloy) supported on high specific area carbon materials. Proton conductor generally refers to perfluorinated sulfonate resin (Nafion). Some catalytic layers contain a hydrophobic bonding agent, commonly polytetrafluoroethylene resin (PIPE).

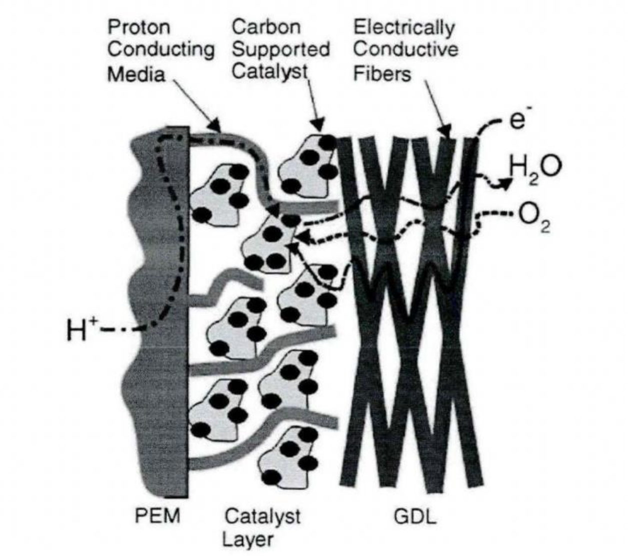

Figure 4. A schematic representation of one-half of the electrode assembly of the proton exchange membrane [9].

The merit of PEMFC can be concluded as follows: (i) highest power density among all fuel cells; (ii) high battery performance can be obtained at lower temperatures.

The disadvantages of PEMFC can be summarised as follows: (i) the use of noble metal catalysts dramatically increases the overall construction cost of fuel cells; (ii) proton exchange membrane and other components are relatively expensive; (iii) good water management ability is required to timely discharge the water on the cathode side; (iv) the low concentration of CO and S compounds will cause PEMFC catalyst poisoning.

4. Challenge and expectation

4.1. Current problems with these batteries

4.1.1. Nickel-metal hydride battery

Ni-MH often is used in the following aspects. First, Ni-MH is commonly used in civilian products, such as solar photovoltaic systems, communication systems and field emergency backup power, electric toys, cameras, and other digital equipment. Ni-MH is also commonly used in pure electric cars as the only energy source to provide power demand; In a hybrid electric vehicle includes peak power to start the vehicle and acceleration energy as extra auxiliary energy. In fuel cell vehicles, it also serves as an additional energy source to provide peak power to begin the car and provide acceleration energy. Third, Ni-MH batteries have specific applications in military portable power supplies [10]. At the same time, nickel-metal hydride batteries still need improvement, including relatively low specific energy, poor self-discharge performance, general cycle life, and high cost of raw materials [10]. At present, nickel metal hydride battery is in a disadvantageous position in the market competition with lithium-ion batteries.

4.1.2. Lithium-ion battery

Although Li-ion is the most widely used battery technology in the electric storage field, the increasing cost and the number of lithium storage in the world restrict the development of this technology and its broad applications in the future [11]. Hence, exploring low-cost energy storage technologies using materials plentiful as substitutes for lithium is critical.

4.1.3. Fuel cells of proton exchange membrane

At present, PEMFC mainly faces the following problems.

High cost [12]. PEMFC's high cost is mainly reflected in the PEM and CL; PEM materials usually use perfluorinated sulfonic acid resin; perfluorinated sulfonic acid resin in the production process is complex, and the process is cumbersome lead to expensive. The catalyst Pt in CL belongs to the precious metal; its price is costly.

Short effective working time [13]. The adequate working time of PEMFC is short. On the one hand, the Pt/C in CL will agglomerate when working for a long time, and the oxidation of Pt will reduce the catalytic efficiency of Pt. On the other hand, because the PEM is relatively thin, hydrogen leakage and other problems will occur after a long time, eventually leading to PEMFC's inability to work for a long time.

Water management problems [14]. GDL is the critical component of water management in PEMFC, and the battery will produce more water when working at a high current density. When the design of GDL is not reasonable, the moisture generated will not be able to discharge generally from the battery, resulting in water filling in the contact surface between CL and GDL and in the holes of GDL. If the spot of GDL is blocked by water, the gas transmission will be affected. Moreover, a large amount of water gathered at the CL side of the cathode will cover the active site of Pt and reduce the catalytic efficiency of CL, which will eventually lead to an increase in material transport loss and even force the battery to stop working because water cannot be discharged from the storm. Therefore, the design and optimisation of GDL play an essential role in improving the water management capability and gas transport efficiency of the battery

4.2. The direction of battery development

Figure 5 shows the different aspects of these batteries. Firstly, it can be found that the PEMFC specific energy is over 3000Wh Kg^{-1}. Compared with other power supply technologies, hydrogen energy shows a "clean " specific energy, far higher than other power supply technologies. In terms of energy storage cost, it is also the most competitive. However, PEMFC has no advantage in specific power, which is the worst of the three batteries.

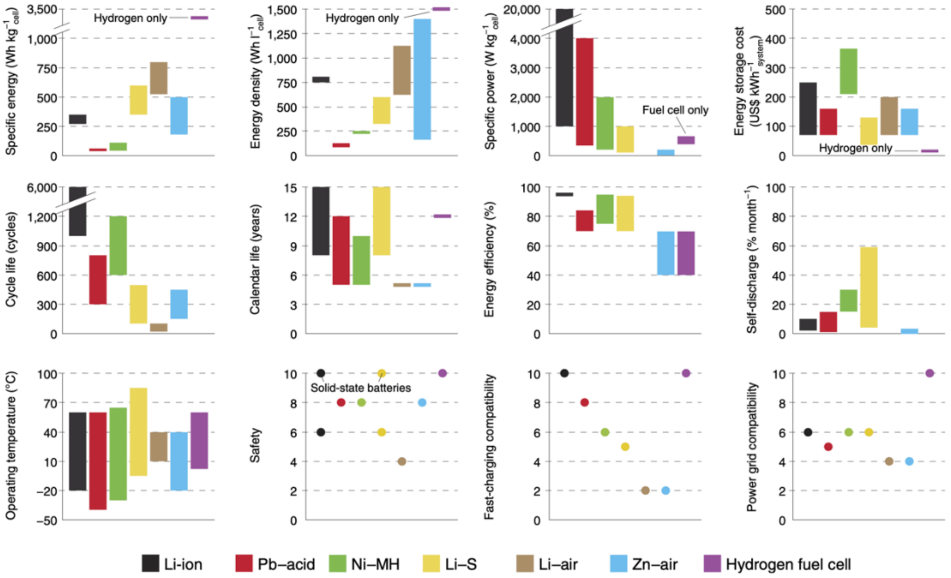

Figure 5. Several typical battery technology comparisons on the market [15].

The Li-ion battery has the highest specific power at 20000 W kg-1 and cycles life of 6000 cycles, far higher than the Ni-MH and PEMFC batteries. Moreover, energy efficiency, calendar life and self-discharge have the best performance. Finally, for Ni-MH, except for operating temperature, this battery has no apparent advantages. And it has the highest energy storage cost.

5. Conclusion

With the increasingly severe energy problem, it is becoming increasingly essential to promote the application of new energy technology in the field of transportation, and the application of new battery technology in this field is playing an increasingly important role. In conclusion, compared with other energy technologies, PEMFC is far superior to other power technologies in terms of energy storage cost, security, fast charging capability and grid compatibility. In addition, the fuel cell in the life, energy efficiency, battery operating temperature range also better performance. It was found that hydrogen's high specific energy and energy density and PEMFC exhibit extremely mismatched specific power. At the same time, the special ability of fuel cells is almost the lowest compared to other power supply technologies. Therefore, the typical low power of PEMFC seriously limits fuel cell commercialisation and large-scale application. Therefore, improving the specific strength of fuel cells is of great significance in promoting the large-scale commercialisation of PEMFC. Lithium battery has excellent performance in specific power and cycle life, and other aspects also have good performance in these three battery technologies. So lithium battery is the most worthy of large-scale commercial battery technology and the best-extended version of the battery technology. Ni-MH batteries it has no particular advantages over the other two kinds of batteries in all aspects, so their application and implementation are worthy of further research and exploration.

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