Grid-Grade Rechargeable Batterie and Predication in Future

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Abstract. China is in a period of the energy transition; more renewable energy is used to replace coal which has caused more and more environmental issues. Researches on energy storage play a significant role in the government's future sustainable development plans. In this article, four types of rechargeable batteries' characteristics will be explored and their applications for grid-scale energy storage. The Lithium-ion battery is the most well-established with the less exploring room one. Then Nickel-metal hydride battery, due to the complexity of its reaction condition and electrode materials, still retains room for exploration after decades of development. Mn-Cu battery and Mn-H battery have the shortest development cycle and are mostly still in the experimental research stage. The rechargeable battery is one of the most promising energy storage technologies in the future, but there are many kinds of rechargeable batteries, only part of which can be applied to hydropower storage. In this article, four types of rechargeable batteries are listed in different development stages. By analyzing and comparing their performance, the feasibility of grid-level energy storage is summarized, and the future development direction of them is predicted.

Keywords: Energy storage, Sustainable development, Rechargeable battery, Grid, Environmental protection.

1. Introduction

Energy storage is a critical component of future sustainable development. Along with the electrification of society's infrastructure, electricity generation, storage, and conversion are becoming increasingly crucial. At the same time, the energy storage for electricity also needs to be green (based on certain metrics, waste emission, cost) [1]. For energy transformation and reservation, the rechargeable battery is a potential option. Specifically, the grid needs to be altered to undertake the input of renewable energy, for example, solar power. This is a significant issue for a power station, and it is required to select a technology of rechargeable battery for both long-term and short-term energy conversion and storage. This article is aimed to evaluate 4 types of rechargeable batteries for the Hunan Liu yang hydropower station as well the related power grid.

To date, extensive research has been conducted on rechargeable batteries for the power grid-scale, using different materials, including Manganese-Hydrogen, and Manganese-Copper Battery [2, 3]. Because of the booming development of such technology and the improvement for future power-grids, many researchers also produced various review articles to analyze and predict the future. Some papers focus on the big picture of the grid and battery, combined with the general evaluation of up-to-date markets and situations. With the rise of renewable energy, distributed energy resources, plug-in electric vehicles, and photovoltaic installations, the future seems bright. The future electric power grid, regardless of its size, is turning into a duplex flow of data and electricity between demand and provide [4]. In addition, the status of existing energy storage has also been discussed comprehensively [5], which offers good indications for policymakers. For future green grid, Yang and his colleagues

provide a thorough discussion on energy storage and analysis of various batteries from 11 years ago [6].

In the review, a microscopic perspective is to evaluate 4 potential applicants for the use of energy conversion and storage of hydropower. Given the demand for future energy storage facilities for the hydropower station, the advantages of reversible batteries, and the rapid advancement of power storage technology, this article focuses on selecting relatively suitable technologies for reversible batteries, based on the future expansibility and key metrics for assessing a battery (voltage for every cell, life span, safety, energy density, financial issue, and energy capacity). This article will mainly analyze 4 recent breakthroughs of grid-scale rechargeable batteries for future practice. And there are lots of trials and improvements that can be conducted on these technologies for real-world grid applications.

2. Lithium-ion battery

2.1. Description of Lithium-ion battery

It has been about a half-century since the lithium-ion battery was invented. There are several kinds of lithium-ion batteries on the market, such as Li-Al-FeS battery, $LiFePO_4$ battery, and so on. Nowadays, it has become an indispensable part of our lives because of its many advantages, such as high energy density, high energy efficiency, and being environmentally friendly. It helps us store energy for phones, computers, cars, and so on. The working temperature of the Li-Al-FeS battery is limited to 375-500℃ means it will suitable to store energy in some special environments [7, 8]. The $LiFePO_4$ battery discharges quickly to meet most of the power demand, costs less than the other lithium-ion batteries for common materials, and reacts stably [9, 10]. Although different kinds of lithium-ion batteries have its feature, their principles are similar. Fig. 1 shows the charge and discharge of the lithium-ion battery. When it is charging, the electric field forces the lithium-ion to move toward the anode electrolyte. Then an electron combines with this lithium-ion into a lithium atom and it adheres to the carbon layer. When it is discharging, it is reverse of the previous process.

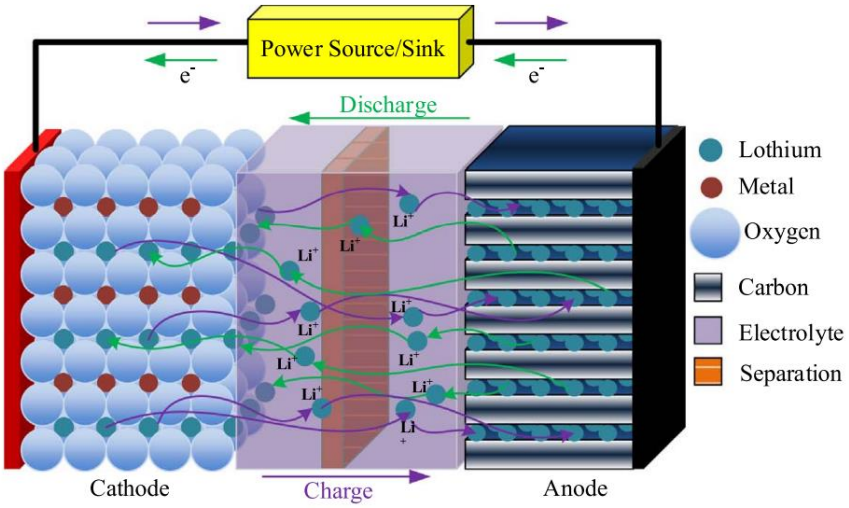


Figure 1. Lithium-ion battery during charge and discharge [11].

2.2. Main Features

Lithium -ion is a stable store system. Because of different materials, they have different energy densities. Generally, the energy density of the lithium-ion battery is about 300Wh/kg. As for energy efficiency, it is about 95% in general [13]. It only losses about 2% to 3% of energy per month [14]. It is just a little loss for storage, which can prove the surplus electric energy from wind and solar to store almost without any loss. The lifetime is more than 10 years [14]. To meet the project's demand of generating storage power for usage, the battery can generate energy in less than 20 milliseconds

[15]. The temperature in most places can reach -10℃ and 40℃. This will challenge lithium-ion battery because most lithium-ion batteries on market can only work at 0-40℃. Then the price of lithium-ion batteries in the market is more than 110$/kWh. In the last few years, the research on the storage properties of lithium-ion battery develops quickly. The lithium-ion battery recycling also got a breakthrough recently. Now, most of the metal in the battery can be recycled by environmentally friendly procedures [16]. Just like LFP powder, put them in a certain concentration at 25℃ to stir for 20 min [16]. More than 99% of Li can be refined from it [16]. And some other electrode materials also can be processed into industrial materials or row metal. As is known to all, the lithium resource is scarce on the earth. This will solve the problem of the lack of lithium. Then one more way to recycle the battery is to reuse them at the end of their lifecycle. A second synergistic effect will give them a second life [16]. This second life battery retention storage capacity still has 80-85% of the original one [16]. This technology has been applied widely in EVs batteries. The price of this battery is less than $100/kWh, which is cheaper than the new one [16]. So, the development of this technology will further improve the combination of lithium-ion battery and sustainable development.

2.3. Review and future perspective

As of this year, the lithium-ion battery has been invented for about 100 years. The most of research about it is well-established. The room that scientists can explore is less and less. Just like the energy density, a report shows that the energy density improve by less than 3% in the last 30 years [17, 18]. So, taking this trend, it can be roughly predicted it will reach 400 kWh/kg. Although the storage for surplus energy doesn't matter much to the energy density, this proves researchers have faced much more challenges in lithium-ion battery improvement than before. Another problem needing to solve urgently is the working temperature. Now, there is a solid electrolyte lithium-ion battery that can work from -50℃ to 200℃, and the technology of adding some additives to extend the range of working temperature [19]. But they still need time to further investigate and prove its safety. In general, the future of lithium-ion batteries will be challenging, but it still has much room to create more possibilities.

3. Mn-Cu battery

3.1 Description of Mn-Cu battery

This Mn-Cu rechargeable battery has two different running modes, general charging and discharging, and generating hydrogen and electricity separately. For a grid-scale application, the first mode will be analyzed mainly. The battery is employed with raw materials of Copper sulfate pentahydrate, Manganese (II) sulfate monohydrates, Sulfuric acid, Copperplate and carbon electrode. [3] The diagram is shown in Fig. 2, because of its additional function, the electrode can be altered, which will be explored later. The general principle of the battery is by changing the oxidative state of Copper and Manganese to absorb and release electricity. Specifically, during the charging process, Mn^{2+} will turn into MnO_2 and deposit near the carbon electrode, while the Cu^{2+} is reduced in the Copperplate. Here is the electrochemical reaction, the double head arrow suggests that from left to right is charging and right to left is discharging (Eqs. (1)-(3)).

$$\text{Cathode: } Mn^{2+} + 2H_2O \leftrightarrow MnO_2\downarrow + 4H^+ + 2e^- \quad (1)$$

$$\text{Anode: } Cu^{2+} + 2e^- \leftrightarrow Cu\downarrow \quad (2)$$

$$\text{Overall equation: } Mn^{2+} + Cu^{2+} + 2H_2O \leftrightarrow MnO_2\downarrow + Cu\downarrow + 4H^+ \quad (3)$$

It is very easy to scale up the battery for higher electrochemical parameters for the power storage system, because of its concise structure [3]. This kind of flexibility can be a significant part of future power grid use and is easy to maintain or repair.

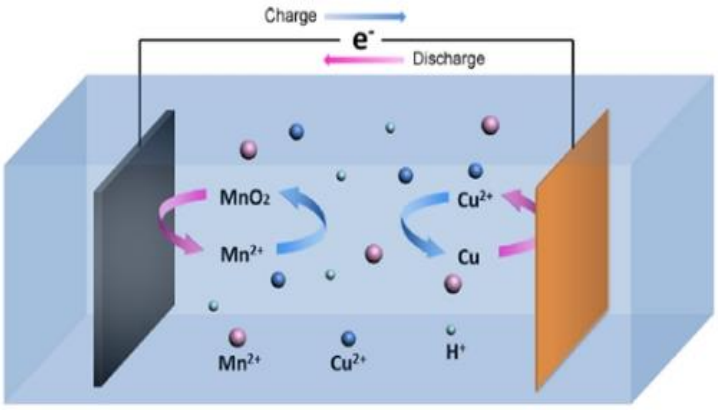


Figure 2. the structure and working reaction in schematic illustration [3].

3.2 Main Features

For the battery used in the grid for energy storage, safety and stability are the priorities. The devices produce no explosive products during working and can withstand severe conditions Because the highly complex power grid is fragile to some degree, it can suffer no sudden changes. For industrial use like a grid, it is required to have easy maintenance and repair. The duration of the technology should be high because the grid cannot be constructed very frequently. The Mn-Cu battery has quite a simple structure and common parts and reagents which may satisfy that criterium. Whereas the grid scale is less sensitive to the energy density, unlike electric cars because the shortage can be mitigated by scaling up the storage with larger batteries and facilities. As for the storage, low energy loss is less important but not the priority, since normally grid energy storage does not take a very long time, because storage receives extra energy produced day time. By the background of hydropower back up, it may also need low energy loss.

In the experiment of Huang and his colleagues, the demonstrative battery was conducted pressure test by drilling and thermal damage and expressed outstanding safe properties [3]. the energy efficiency for this kind of battery is above 70%, and up to 81.7% after 100 h open-circuit voltage (OCV) measurement which is sufficient for grid use. The battery underwent a life of 10000 cycles with no noticeable capacity decay and was maintained stable. What's more, the batteries were examined under a voltage of 1.2 V with a different energy input of 1, 5, 10, 20,30, and 50 $mAh \cdot cm^2$. The results show that the charge current is able to achieve a maximum of 100 mA cm^{-2} which suggests that the cell has impressive adjustability and can endure intensive energy input. That is one of the most critical factors for the grid and can be satisfied by the Mn-Cu battery. The average operating voltage for the battery is 3V, the value is only for the prototype and may vary by scaling up. The paper observed the speed of potential increment as 1mV/s; thus, the speed of energy generation is about 50 minutes. For the duration and energy loss, the Mn-Cu battery shows impressive performance. In the 100h test, the storage ability has declined only 0.7%, and capacity withhold is 99.3%, roughly estimate, the battery may probably function in 11 years. Starting with reagents, they all have predicted properties and safety. the metal Manganese is fairly abundant on the planet, for the past few decades, many researchers have been developing it [20]. Mn has been widely used as an electrode. Copper and Sulfuric acid are components that are both cheap and non-explosive. When the battery is running it produces no explosive hydrogen byproducts. Also, ion-selective membrane, catalysts, extreme gas-sealed requirement, and high running temperature are not required for this situation, compared to the flow battery and lithium – antimony liquid metal battery [21, 22].

3.3 The applicant for sustainable development

Hydrogen energy is the most promising energy for society in the future with its high energy density and non-pollution properties [1, 23]. The redox potential for the Oxygen generation is higher than MnO_2/Mn couple, and the Cu^{2+}/Cu is higher than the H_2 release potential, which indicates the

possibility of generating electricity and H_2 without O_2. The Mn-Cu battery can be incorporated into the hydrogen generation process. As Fig. 3 described, the first step is to convert protons to H_2 and produce MnO_2 (the oxidants for the next step) through charging. Then, replace the HER electrode with another reducing electrode and start the reaction as a power release to generate electricity. Therefore, H_2 and electricity are separately produced. In addition, the negative electrode can be replaced by other reductants, for instance, benzyl alcohol. In that case, during the discharge process, valuable products can be generated spontaneously. This will not only bring economical income but also meet the goal of green chemistry. In that case, many factories can employ the technology to manufacture other products sustainably.

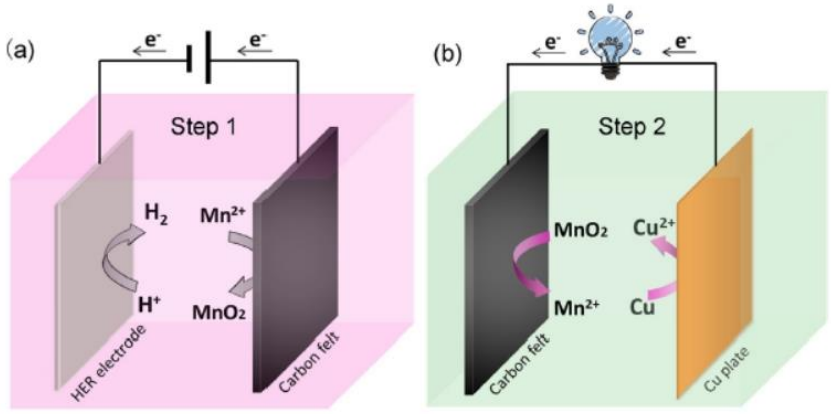


Figure 3. Producing hydrogen and power alternatively [3].

3.4 Review and future perspective

Based on the above analysis, for grid energy storage, the Cu-Mn fit the criteria as a demonstrative prototype. It possesses advantages including safety, stability, low energy loss, high duration, and being able to merge with renewable hydrogen production. But the field pressure test for a real grid has not yet been performed. The Cu-Mn battery is a prospective option for energy preservation and conversion. There is still a long road between labs and practical use. In the next few years, the demand to improve the grid may be strong [6].

4. Hybrid Nickel-Metal Hydride battery

4.1 Description of Hybrid Nickel-Metal Hydride battery

Ni-MH battery stores electric energy by plugging in external hydrogen gas, transferring electrons through the reaction and retaining the energy in the form of solid metal hydrides eventually. This battery can be used for large-scale stationary energy storage by hydrogen as well as lithium-ion battery, but more security, better performing, environmentally friendly and low-budget. As the conceptive picture is shown in Fig.4, it contains a positive electrode with $Ni(OH)_2$ and a hybrid negative electrode consisting of an alloy hydride which determines itself being a complex category to study and high-pressure H_2 as the active material [1].

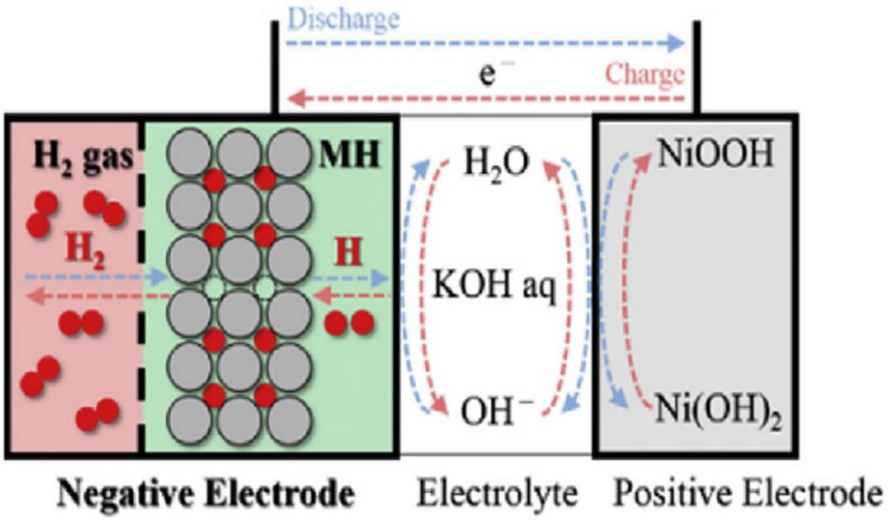


Figure 4. Reaction principle concept diagram of nickel-metal hydride battery [24].

4.2 Main features

The alloy materials inside this battery have been the focus of scholars' research, as a result of different kinds of alloys having different properties and the surface composition and morphology of hydrogen storage alloys have a significant influence on the electrochemical cycle properties of metal hydride electrodes. Apart from that, it is worth mentioning that the same alloy under different reaction conditions can also have different impacts on the energy storage efficiency of the cells. In the following data elaboration, here are the specific conditions, and all data on battery performance are only for the corresponding conditions.

First of all, the energy efficiency of this type of battery is 70~95% [25]. In detail, when NiMH-C_3 cells are charged to 30-70% and then fully discharged at a charge/discharge rate of no more than 0.2C, the calculated energy efficiency exceeds 92% [26]. In terms of the generation speed, the simulation result analyzed in the paper showed that the SOC (state-of-charge) of the battery kept increasing from 40% to 80% during both charging and discharging [27]. It took the battery 280 seconds to discharge from 100% to 40%, and then 220 seconds to recharge to 80% from zero with a load of 50 Ah, 200V [27]. As for the self-discharge, Ni-MH batteries lose about a quarter of their initial capacity in the first month, and then gently drop 10-15% of their capacity each month thereafter [26]. Theoretically, these dates are significantly higher than other rechargeable batteries, which is one of the main reasons causing the non-extensive use in energy storage. A considerable number of scholars have made studies on the influence of the choice of materials on the performance of batteries, and here is an example of AB_2-type and AB_5-type. With the effects of different micro-alloying of both A and B or applying other compatible alternatives, the performance of the entire battery pack will change dramatically with a rise in energy density, capacity retention and life-cycle, and a decrease in self-discharge rate. The variation of alloy materials gives this kind of battery a fair amount of exploration.

4.3 Review and future perspective

Ni-MH batteries have been gradually developed and utilized since the end of the last century. It is not similar to the comprehensive and in-depth lithium-ion battery that has been explored, even today, it has a high potential for development. Although both AB_2 and AB_5 type alloys have been commercialized, neither is satisfactory due to certain intrinsic drawbacks, such as the difficulty of activation of AB_2 alloy and the relatively low specific capacity of AB5 alloy [24]. An increasing number of new materials used for hydrogen storage have been discovered even considered as the substitutions for the cathode of Ni-MH battery [28]. To be more specific, not merely the electrode metal, the reaction condition with solvent of water is also the research direction of many scholars. It's the same as the MN-H battery we'll cover below, it has a lot of untapped potentials that numerous

scholars commit to improving energy conversion and cyclic stability to make it more suitable for industrial applications.

5. Manganese hydrogen battery

5.1 Description of Manganese hydrogen battery

The newest manganese hydrogen battery is shown in this part. The new type of rechargeable water-based manganese hydrogen battery. Recent studies have shown that the negative electrode is through a two-electron reaction cycle between Mn^{2+} and MnO_2, and the negative electrode is through a hydrogen evolution and oxidation catalytic reaction cycle in the middle of H_2 and H_2O [2]. When the Mn-H battery is charged, Mn^{2+} in the dielectric spread to the negative pole and is stored on the carbon mat as solid MnO_2, while the platinum catalyst on the anode drives the conversion of H_2 and H_2O. During battery discharge, the uniformly deposited MnO_2 layer on the negative pole solvent retreat into the soluble Mn^{2+} dielectric, and the H_2 on the positive pole is oxidized [2].

5.2 Main Features

Studies show that the discharge pressure of MN-H battery is about 1.3V. Theoretically, the discharge rate is 100 mA cm^{-2}, and more than 10,000 cycles lifetime can give it a longer service cycle [2]. According to the tests conducted by Professor Cui Yi and his team in 2018, they achieved an energy density of about 139 $Wh \cdot kg^{-1}$ body weight, a volume energy density of about 210 $Wh \cdot L^{-1}$. Theoretically, the energy density for weight is approximately 174 $Wh \cdot kg^{-1}$ and for volume is about 263 $Wh \cdot L^{-1}$ [2]. Theoretically, the energy efficiency of manganese-hydrogen battery is about 71% [2].

5.3 Advantages over other manganese batteries

First, the manganese-hydrogen battery is made in a discharge status, where the cathode only includes a carbon substrate. Because of this, the cathode-less design predigests the fabricating of manganese batteries and avoids the complex preparation of traditional MnO_2 cathodes, thus providing an economical and effective method for battery manufacturing [2]. Second, is the course of dissolution of manganese, which is the degradation mechanism of the traditional water-phase manganese battery [29]. As the main charge storage mechanism of manganese-hydrogen batteries. Yi Cui and his groups in 2018 find that Mn^{2+}/ MnO_2 deposition and dissolution is a highly reversible action, which solves the problems of rechargeable and stable cathode [2]. Third, based on solid MnO_2, the theoretical capacity of manganese due to the Mn^{2+}/ MnO_2 double-electron reaction is twice that of most other single-electron manganese batteries [30]. Fourth, Yi Cui and his groups in 2018 highly invertible hydrogen pole as the positive pole, and utilized platinum-catalyzed HER/HOR reaction to surmount the problem of bad charge-discharge performance at traditional anode [2].

5.4 Suitable for sustainable development

The Manganese-hydrogen battery has the advantages of abundant materials and low cost, which makes it possible to progress into big size power reserve [2]. As a water-based rechargeable battery, a Manganese-Hydrogen battery has the advantages of large output power and safety and environmental protection [31-33]. Manganese in its material has rich chemical properties and has a variant form of loss electrons. The diversified valence states provide great possibilities for the future new Mangan-based battery system [29]. $MnSO_4$ solution was chosen as soluble Mn^{2+} salt solution because of its cheap and great dissolution in aqua pure (at 25℃), and the electrochemical of SO_4^{2-} unaltered below the pressure [34].

5.5 Still existing disadvantages and improvement measures

Because the current manganese hydrogen battery is still in the experimental stage, and its energy density is still low, there are two different methods to expand the energy storage capacity of the manganese hydrogen battery, so as to achieve the effect of increasing the energy density. In the first approach, Yi Cui and his team increased the capacity of the battery by making the cathode carbon layer thicker and the surface area larger [2]. In the second way to expand the storage capacity of manganese hydrogen batteries, Yi Cui and his team make a diaphragm-less columniform battery for a big size reserve in 2018 [2]. The current cost of manganese-hydrogen batteries is still somewhat high. Yi Cui and his team used platinum as a catalyst in an early experiment in 2018, while cheaper alternatives are being sought [2].

5.6 Review and future perspective

In Cui Yi's opinion, the global large-scale energy storage market is worth trillions of dollars. Once manganese hydrogen battery can achieve industrial application as expected, it will make the use of clean energy more stable and bring important promotion to social and economic development. The benefits range from large clean energy plants to small communities and homes. On the other hand, the industrial application of manganese hydrogen batteries will also make electric vehicles more popular. Manganese hydrogen battery can stabilize the power grid, which provides the possibility to achieve this goal [2].

6. Conclusion

Due to the adverse effects of hydropower on ecosystems, it has gradually been replaced by solar energy and wind energy at the request of sustainable development. However, most of this energy generates energy timely so much surplus energy should be stored. This paper selects four rechargeable batteries that are suitable for the background. The Lithium-ion battery has the highest energy efficiency of four batteries. But its advantage in energy density doesn't play an advantage in grid energy storage. The manganese hydrogen battery is safer and has a longer lifetime than the lithium-ion battery. It has paralleled but not as complex development prospects as the nickel-metal hydride battery. Its chemistry, which appeals to researchers, provides a means for the improvement of high energy density, fast charging, and ultra-stable batteries for grid energy storage. A hybrid Nickel-metal hydride battery is cheaper than the other. But its self-discharge will waste much energy in storage. Compared with the traditional cathode materials of Mn-Cu battery, Mn-H battery has a more simplified and cost-effective strategy, it solves the rechargeable and stable problems of the cathode and increases the battery capacity. The new material used for anode overcomes the problem of poor charge and discharge performance of traditional anode, and the combination of cathode and anode improves the rate capacity. In the future, the longer lifetime and environmentally sustainable manufacturing will be essential in the future of storage batteries. A longer lifetime means less consumption, and less pollution in production will further promote sustainable development.

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