



# POLITECNICO

## MILANO 1863

SCHOOL OF INDUSTRIAL AND INFORMATION ENGINEERING  
MASTER OF SCIENCE IN ELECTRICAL ENGINEERING

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# **Analyze the state of the art of lithium-ion and sodium-ion batteries for electric vehicles**

## **1. Research background**

As a kind of renewable energy, the power battery of new energy vehicles has relatively high sustainability and environmental protection, which can alleviate the pressure brought by the energy crisis. In addition, the zero emission characteristics of the power battery of new energy vehicles can significantly reduce the degree of environmental pollution and help to improve the environmental quality. Energy, pollution, safety and congestion are the four major public hazards recognized worldwide, which can be effectively alleviated through the development of new energy vehicles based on power batteries. First, power batteries can use energy more efficiently and reduce unnecessary energy consumption. Secondly, batteries provide energy in a way that can reduce the harm of automobile exhaust. Finally, smart cars based on power batteries can realize the purpose of intelligent interconnection, reduce urban congestion, and reduce human-caused safety accidents. Therefore, new energy vehicles based on power battery technology can efficiently solve the problems caused by traditional vehicles, and promote the automobile industry to

achieve industrial low-carbon and intelligent. Automotive power batteries, also known as electric vehicle batteries, high energy density lithium-ion batteries, are a type of battery used to power electric vehicles.

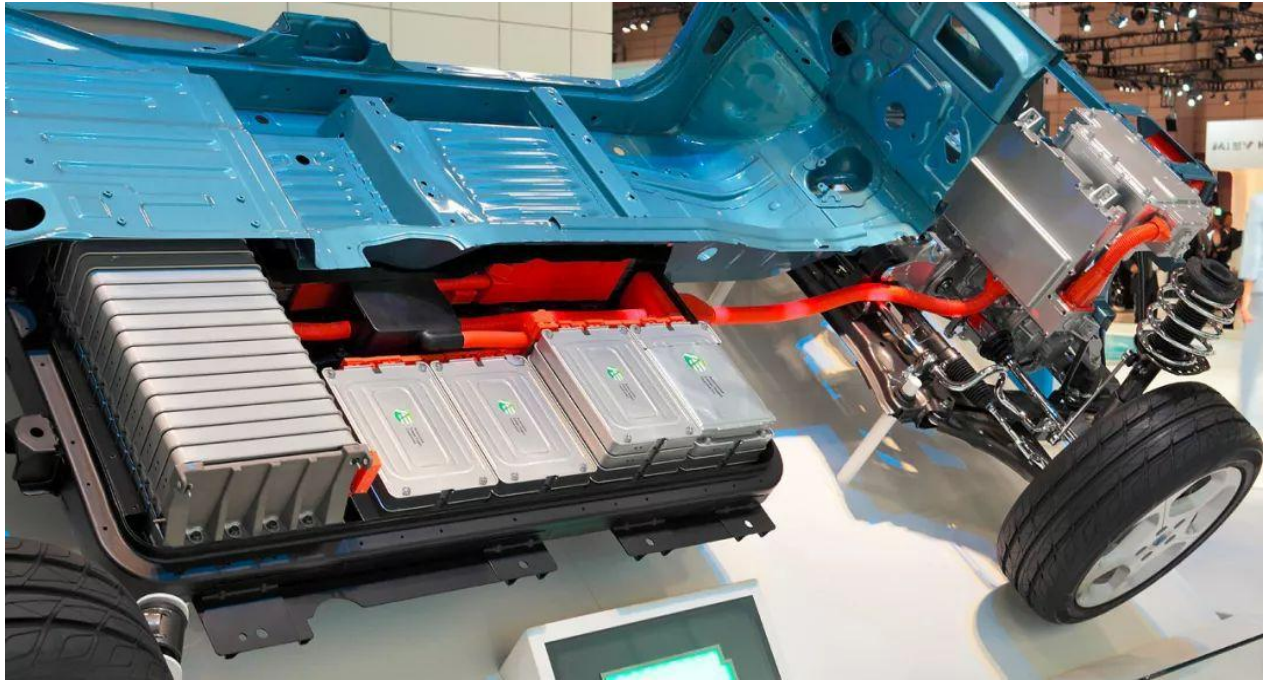
Among them, the traditional lead-acid battery as a relatively mature technology, low cost, can be high rate discharge is its advantage, but lead-acid battery specific energy, specific power and energy density are very low, short life, mass, pollution, do not adapt to the driving requirements of modern new energy electric vehicles, almost has been eliminated by the market.

In addition, nickel-cadmium batteries and nickel-metal hydride batteries, although they have better performance than lead-acid batteries, still have the disadvantages of large pollution, low capacity and short life. Although some manufacturers still use these two types of batteries, but in the long run, this type of battery will gradually be phased out by the market.

Lithium-ion battery energy storage has been well applied in new energy, electronic market and other fields because of its outstanding green advantages. However, with the increasing demand for lithium ion batteries, the shortage of lithium resources and cost problems affect the development of lithium ion batteries. In this context, due to the similarity of physical and chemical properties between sodium ion and lithium ion, abundant sodium resources and low cost, it has become a new

energy storage material to replace lithium ion batteries. The most important energy source is fossil fuels, but because of the non-renewable characteristics of fossil fuels, and will bring greater pollution to the environment, therefore, manufacturers began to pay attention to the development of green energy. The emerging electrochemical energy storage technology has become a research hotspot. Due to the similarity of physical and chemical properties between sodium ion and lithium ion, it is a new energy storage system to replace lithium ion battery and has a good application prospect.





## 1.1 The advantages of the new battery

Sodium ion resources are relatively rich, the cost is low, has high safety and energy conversion rate, long service life, in the field of new energy batteries, can meet the safety and cost-effective aspects of the higher requirements. From the periodic table, sodium is an alkali metal element closely following lithium. There are certain differences in physicochemical properties between sodium and Lithium, so the corresponding electrode materials will also have certain differences in electrochemical performance. Due to the larger radius and mass fraction of sodium ions compared with lithium ions, there will be a gap in mass and volume energy density compared with lithium ion batteries. Moreover, because of the larger radius of sodium ions, there will be differences in interface properties, phase structure evolution and ion transport of electrode materials. In order to make sodium ion batteries better show their advantages, The material system of sodium ion battery needs to be studied.



## **1.2. The development status of new batteries**

From a worldwide perspective, at present, technical research breakthroughs related to sodium ion batteries are mainly reflected in electrolyte materials, electrode materials, sodium storage mechanism, characterization analysis and cell technology, and so on. The number of patent inventions related to sodium ion batteries and the number of published articles is gradually increasing. In 2020, the Department of Energy of the United States published the layout of battery research plan, mainly focusing on the research of power batteries and energy storage batteries, and sodium ion batteries were explicitly included in the development system of energy storage batteries. The European Union's "Battery 2030" energy storage project puts sodium-ion batteries at the top of the list of non-lithium-ion battery systems.

For the application field of lithium ion battery, lithium material has always been the first choice of green battery materials, lithium battery production technology is constantly improved, the cost is constantly compressed, so lithium battery has been widely used in recent years. Depending on the application scenario, lithium-ion batteries can be roughly divided into power, consumer and energy storage types. Based on application scenarios, root can be divided into three types: power, consumption and storage. This paper mainly analyzes the

application of lithium battery in the field of electric vehicles. Currently, most of the electric vehicles produced by companies use lead-acid battery as the main power battery, so the weight of the battery itself will be about 12 kilograms. With the use of lithium-ion batteries, the weight of the battery will be significantly reduced, to about five kilograms at most. So lithium ion battery is the inevitable trend to replace lead acid battery. The use of lithium-ion batteries could make electric cars lighter, safer and cheaper. It is bound to be more popular. In addition, from the perspective of environmental protection, car pollution is becoming more and more serious, exhaust gas, noise and other environmental damage is becoming more and more serious, especially in some densely populated, traffic congestion of large and medium-sized cities, this situation is not to be ignored. Therefore, the new generation of lithium-ion battery with its pollution-free, low pollution, energy diversification and other characteristics, has been vigorously developed in the electric vehicle industry, so the application of lithium-ion battery is a good way to solve such problems.





## **2. Lithium-ion battery**

### **2.1 Lithium-ion battery energy storage technology, lithium-ion battery principle**

Lithium ion battery is a new type of environmental protection and high performance battery, its initial application is reflected in the small capacity of the battery application, related to lead-acid battery and nickel metal hydride battery, it has a small size, high capacity, no pollution, good safety several advantages, with the emergence of new lithium ion cathode materials, lithium ion battery application range continues to expand, It has expanded from simple mobile phone battery applications to large, medium and small electric vehicles, electric energy storage, backup power, power tools and airplane models.

Due to the characteristics listed, lithium-powered batteries have their own unique advantages:

With high energy and high working rate, the working voltage of a single battery can reach 3.7V, which is 3 times that of nickel-cadmium battery and nickel-metal hydride battery, and nearly 2 times that of lead-acid battery. This is also an important reason for the high specific energy of lithium-powered batteries.

In terms of charge and discharge rate, lithium-powered batteries can charge and discharge very quickly, which can

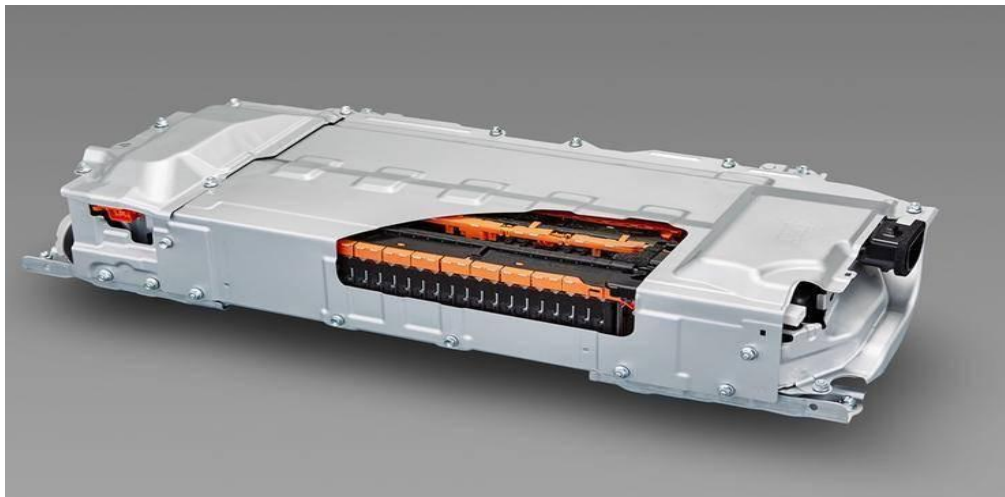
provide sufficient power to the device in a short period of time.

In terms of service life, long cycle life, cycle times up to 1000 times. If the capacity is maintained at 80%, the number of charge and discharge cycles can reach more than 800 times, and the service life can reach 3-5 years, about 2-3 times that of the lead-acid battery. With the technological innovation and the improvement of the quantitative production process of lithium battery, the life of lithium battery will be longer and longer, and the cost performance of lithium battery will be higher and higher.

In terms of operating temperature, lithium power battery allows a wide range of operating temperature, low temperature performance is good. It can operate between  $-20\text{ }^{\circ}\text{C}$  and  $+55\text{ }^{\circ}\text{C}$ , especially suitable for low temperature use. At low temperature, the performance of lead-acid battery and nickel-metal hydride battery will be greatly reduced due to the poor fluidity of electrolyte.

Lithium-ion batteries are rechargeable batteries that rely primarily on lithium ions moving between positive and negative electrodes to work. In the process of charge and discharge,  $\text{Li}^+$  is inserted and deembedded between the two electrodes. In the charging battery,  $\text{Li}^+$  is removed from the positive electrode and inserted into the negative electrode through the electrolyte. The negative electrode is in a lithium-rich state. The opposite is true for electrical discharge. Batteries are often called lithium-ion

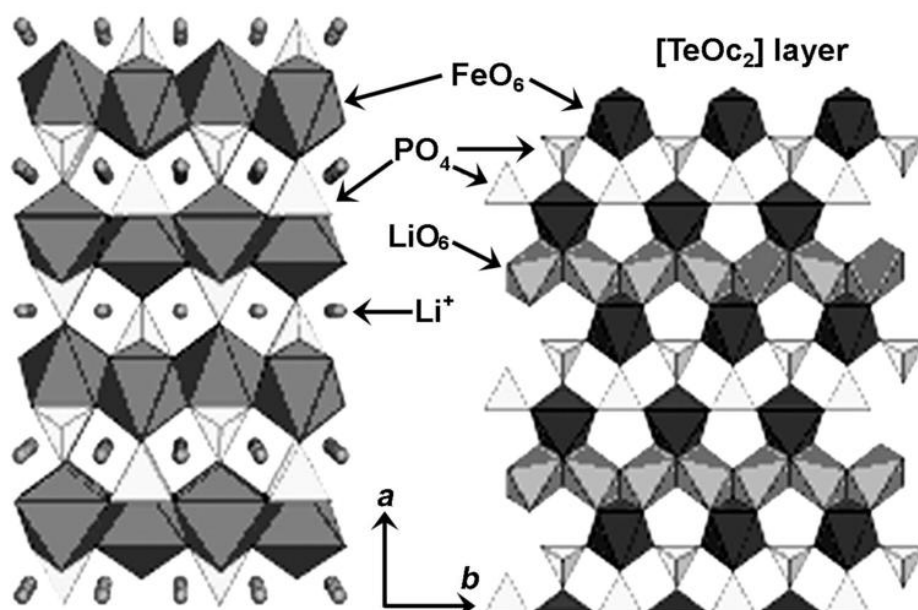
batteries because they typically use materials containing lithium as electrodes.



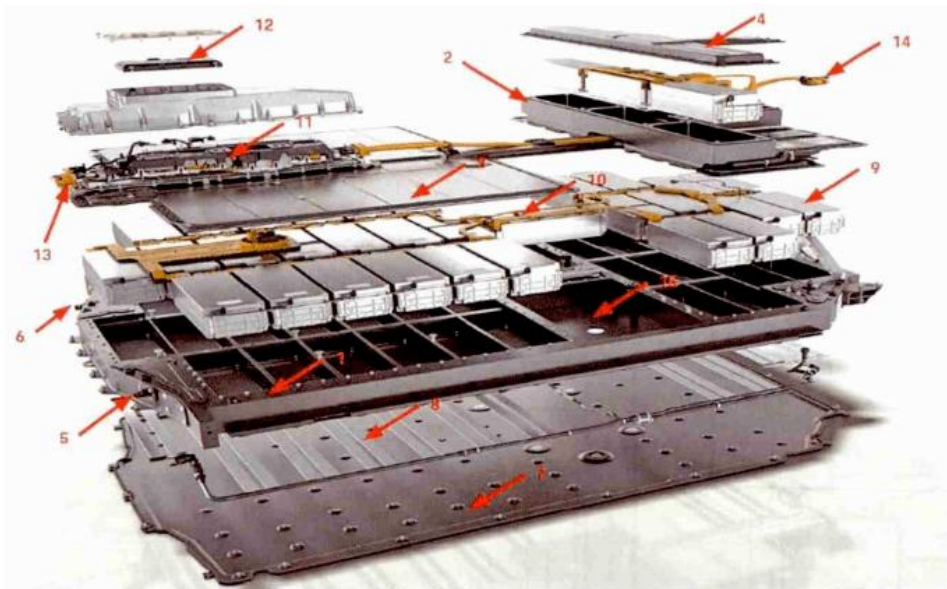
## 2.2 Selection of electrode materials

(1) Safety of anode materials. At present, commercial lithium-ion batteries mostly use carbon material as negative electrode. In the process of charging and discharging, lithium is embedded and removed in carbon particles, thus reducing the possibility of lithium dendrite formation and improving the safety of batteries. However, this does not mean that carbon negative electrode has no safety problems.

(2) Safety of positive electrode materials. The safety of cathode material includes thermal stability and overcharge safety. At present, the common active materials for the positive electrode of lithium ion battery are  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ,  $\text{LiFePO}_4$  and  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . Studies show that  $\text{LiMn}_2\text{O}_4$  and  $\text{LiFePO}_4$  have better safety performance.

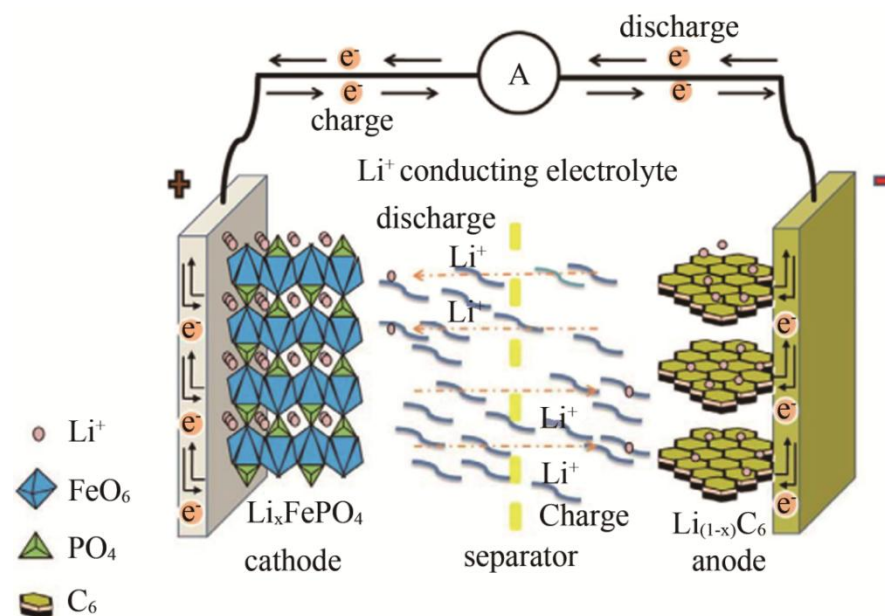


(3) The influence of electrolyte. In the electrolyte, the use of organic solvents with low melting point, high boiling point and high decomposition voltage is one of the effective ways to improve the safety performance of lithium-ion batteries. Currently, LiPF<sub>6</sub> is mostly used as a conductive agent for commercial lithium-ion batteries, but LiPF<sub>6</sub> also has safety risks, so it is urgent to find a conductive agent with better safety performance to replace LiPF<sub>6</sub>. Electrolyte additive is currently recognized as an effective means to improve the safety of lithium-ion batteries. By adding different additives, it can improve the performance of SEI film, protect positive active substances, stabilize LiPF<sub>6</sub>, improve the safety of overcharge and flame retardant.





### 2.3 Structure of lithium ion battery



The following from the lithium battery charging process, discharge process and battery protection board three major parts to introduce its working principle:

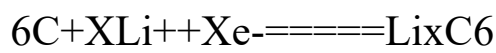
## 1) Lithium battery charging process

The positive electrode of the battery is made of lithium ions, which flow from the positive electrode into the electrolyte, through which they travel through small holes in the polymer electrolyte membrane to the negative electrode, where they bond with electrons that travel to the negative electrode via an external circuit.

- The reaction on the positive electrode is:



- The reaction on the negative electrode is:



In the process of charging,  $\text{Li}^+$  exits from the positive electrode  $\text{LiCoO}_2$ , enters the electrolyte, moves to the negative electrode under the action of the additional external electric field of the charger, and enters the negative electrode composed of graphite or coke successively, where  $\text{LiC}$  compounds are formed.

## 2) Discharge process of lithium battery

When discharging, the electrons and  $\text{Li}^+$  both move at the same time, in the same direction but with different paths. The electrons run from the negative electrode to the positive

electrode through the external circuit.  $\text{Li}^+$  enters the electrolyte from the negative electrode, flows through small holes in the polymer electrolyte membrane, passes through the electrolyte to the positive electrode, and bonds with electrons from an external circuit.

Generally speaking, the battery capacity refers to the discharge capacity.

Lithium battery capacity, defined as the battery can be given under certain discharge conditions, commonly expressed in C, the unit is Ah or mAh. Capacity is an important indicator of battery electrical performance. Lithium battery capacity is usually divided into rated capacity, actual capacity and theoretical capacity. The capacity of lithium battery is determined by the capacity of the electrode, especially the positive material. By improving the performance of the positive material, the capacity of lithium battery can be greatly increased and the volume of the battery can be reduced.

### 3) Battery protection plate

As the name suggests, battery protection board is mainly for rechargeable battery (generally refers to lithium battery) to protect the integrated circuit board. Lithium battery (rechargeable type) needs protection, because the material of lithium battery itself determines that it can not be overcharged, overdischarged, overcurrent, short circuit and ultra-high

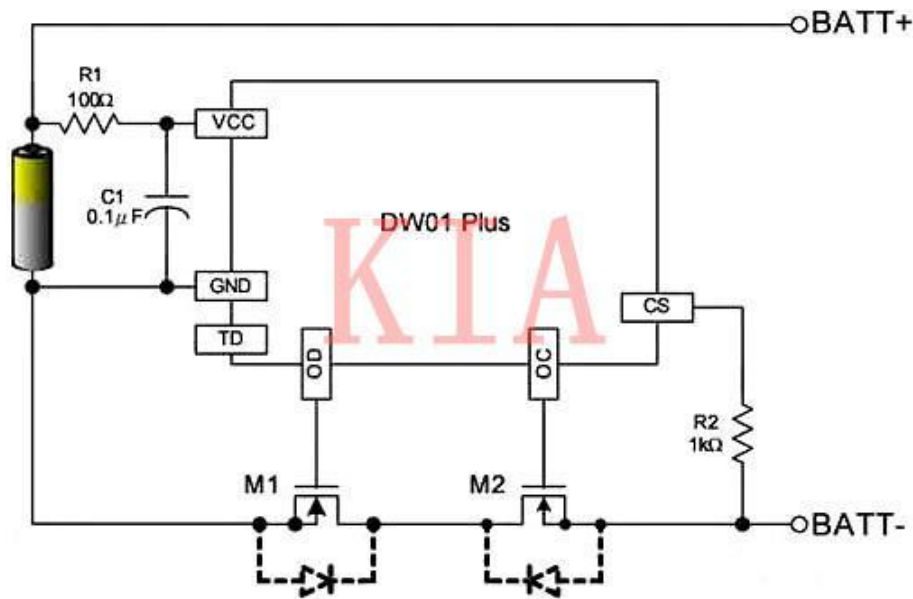


temperature charge and discharge, so lithium battery will always have a protection plate and a current insurance device. Generally speaking, the protection function of lithium battery is carried out by the cooperation of the protection measures circuit board and PTC. The protection board is composed of electronic circuit, which can accurately monitor the voltage of the cell and the current of the charging and discharging control loop at  $-40\text{ }^{\circ}\text{C}$  to  $+85\text{ }^{\circ}\text{C}$ , and timely control the on-off of the current control loop. PTC avoids relatively severe battery damage in the environment of continuous high temperature. The panel protection circuit is shown below.

PTC: positive temperature coefficient thermistor; NTC: negative temperature coefficient thermistor

When the ambient temperature rises, the resistance value decreases, the use of electrical equipment or charging equipment can react in time, control the internal interruption and stop the charge and discharge; U1 is the circuit protection chip, U2 is the two reverse MOSFET switches.

Under normal condition, CO and DO of U1 of the panel output high voltage, Vdd is high level, Vss, VM is low level, both MOSFET are in open state, and the battery can be charged and discharged freely. When any parameter of Vdd, Vss, or VM is changed, the level of the DO or CO terminal changes.



Overcharge protection: When U1 detects that the battery voltage reaches the threshold of overcharge protection, CO pin output low level, MOS tube switch 2 turns from on-off to off, the charging loop is off, the charger can no longer charge the battery, so as to achieve overcharge protection.

Overdischarge protection: in the process of battery discharge, when U1 detects that the battery voltage is lower than the over-discharge protection threshold, the DO pin changes from high level to low level, and the MOS tube switch 1 is closed, so that the battery can no longer discharge; In the state of overdischarge protection, the battery voltage can no longer be reduced, and the current of the protection circuit is required to be very small, and the control circuit enters the low power consumption.

Overcurrent protection: under normal circumstances, the battery discharges the load, and the current passes through two

MOS tube switches in series. The VM pin detects that the voltage drop voltage of the two MOS tubes is U. If the load for some reason causes U abnormal, so that the loop current increases, when U is greater than a certain value, DO pin from high voltage into low voltage, MOS tube switch 1 off, so that the discharge loop current is zero, to achieve the effect of overcurrent protection.

Overcurrent protection measures mainly because of the chemical characteristics of lithium-ion batteries, battery manufacturers usually stipulate that the maximum discharge current cannot exceed  $2C$  ( $C$ = battery capacity/hour), if the battery exceeds  $2C$  current discharge, it will cause permanent damage to the battery or security problems. Lithium battery protection board in the normal discharge process of the load, discharge current after the series of 2 MOSFET, mainly because MOSFET conduction impedance, will cause a voltage at both ends, so as to control the IC on the "V-" foot to detect the voltage value, if the load due to some circumstances caused by abnormal, so that the control loop current increases, When the control loop current is large enough to make  $U > 0.1V$  (the value is determined by the control IC, different IC has different values), its "DO" foot will be converted from high voltage to zero voltage, so that T2 from on-off to off, and then cut off the discharge control loop, so that the current in the control loop is zero, play the role of overcurrent protection measures. There is

also a delay time between the time when the control IC detects overcurrent and the time when it sends off T2 signal. The length of the delay time is determined by C2, which is generally about 13 milliseconds, to avoid misjudgment caused by interference.

## 2.4 Aging decline of lithium battery materials



### 2.4.1 Causes of lithium battery aging

The material inside lithium ion battery includes: positive and negative active material, binder, conductive agent, fluid collector, diaphragm and electrolyte. During the use of lithium-ion batteries, these materials will be accompanied by a certain degree of decay and aging. For example, the factors that may make the capacity of manganese lithium ion battery decline include the formation of SEI film, the dissolution of positive

active material, electrolyte decomposition, anode and cathode REDOX reaction and the generation of side reactions.

(1) The formation and subsequent growth of negative SEI film will lead to the continuous reduction of lithium activity. SEI film, full name is solid electrolyte interface, is a passivation film with solid electrolyte properties. In addition, SEI membrane does not have the function of real solid electrolyte. In addition to lithium ions, the diffusion and migration of other substances will lead to the appearance of gas and particle rupture. In addition, the change of material volume and the precipitation of lithium metal during cyclic charging and discharge also lead to the loss of capacity.

(2) Overcharge and overdischarge of lithium battery, lithium battery overcharge will damage the battery, that is to say, continued charging under the condition of full charge of lithium battery will lead to changes in the structure of the cathode material inside the battery, resulting in the loss of the total capacity of the battery, and if more serious, it will automatically decompose and release oxygen and electrolyte, violent chemical reactions will occur, and finally lithium battery will directly explode. A fire broke out.

(3) In addition, lithium batteries cannot be charged in a high temperature environment, because lithium batteries

themselves will produce high temperature during the charging process. If charged in a high temperature environment, the lithium ions inside lithium batteries will become more active and produce extraordinary high temperature, and then they will directly explode. In addition, not only lithium batteries, but also other batteries will have explosion risks. According to the data, lithium battery is the most explosive battery of all batteries, of course, the probability of explosion is very small, as long as the normal use of lithium battery is still safe under the specified conditions.

(4) The electrolyte reacts at a high voltage. If the charging voltage of the lithium battery is too high, it will lead to the REDOX reaction of the electrolyte and generate some by-products, blocking the electrode pores and preventing the migration of lithium ions, thus reducing the number of circulating ions. The concentration of electrolyte is inversely proportional to the variation trend of electrolyte stability. The higher the electrolyte concentration, the lower the stability of electrolyte, thus affecting the capacity of lithium-ion battery. During the charging process, the electrolyte will be consumed to some extent, so it needs to be replenishment during assembly, resulting in the reduction of battery active materials and affecting the initial capacity of the battery.

(5) The decomposition of electrolyte will also affect the service life of lithium battery. Electrolytes include electrolytes, solvents and additives. Its properties will affect the battery life, specific capacity, charge-discharge performance and safety performance. The decomposition of electrolyte and solvent in electrolyte will cause the loss of battery capacity. In the first charge and discharge, the solvent and other substances will form SEI film on the negative surface, which will lead to irreversible capacity loss, which is unavoidable. Especially if there are impurities such as water or hydrogen fluoride in the electrolyte, the electrolyte may decompose at a high temperature, and the resulting product reacts with the positive electrode material, resulting in the battery capacity is affected. At the same time, some of the products will react with solvents, which will affect the stability of the SEI film on the surface of the negative electrode. In addition, if the electrolyte decomposition products do not contain electrolytic liquid phase, then it may block the positive electrode gap in the process of ion migration, resulting in battery capacity attenuation.

#### (6) Self-discharge phenomenon

Lithium batteries generally suffer capacity loss, a process known as self-discharge, which is classified into reversible capacity loss and irreversible capacity loss. The solvent

oxidation rate has a direct influence on the self-discharge rate, and the active materials of positive and negative electrodes may react with the solute during the charging process, leading to the attenuation of lithium ion migration. In short, the occurrence of side reactions between the electrolyte and the positive and negative electrodes of the battery, as well as the by-products produced, are the main factors causing the capacity attenuation of the battery.

#### **2.4.2 Methods for slowing down debilitation and aging**

The battery life is affected if the battery temperature is too high or too low. Therefore, when the temperature of the device is too high during charging, you can remove the charging cable and temporarily stop using it to reduce its temperature. Similarly, when the temperature is too low, the activity of lithium ions will be reduced, and the battery performance and charging performance will also be significantly reduced. At this time, if forced to charge, the battery life will also be affected. Therefore, in the cold environment, before the lithium battery is used, it is necessary to preheat the battery, and it can work normally after reaching a certain temperature. There are a number of factors that cause batteries to age, starting with natural aging. Even with normal use, lithium ions will detach themselves from the anode and gradually age, but at a slower rate. In daily use,



overcharging and overloading of batteries will accelerate the aging of lithium batteries. The current lithium battery usually has the design of rectifier voltage regulation. When the charger is fully charged, it will disconnect the charging circuit and directly use the power cord to supply power to the device. Low voltage overdischarge or self-discharge reaction will lead to decomposition and destruction of lithium ion active substances, and this loss is difficult to recover. Any form of overcharge of lithium-ion batteries will cause serious damage to battery performance, or even explosion. Therefore, overcharge of lithium battery must be avoided during the charging process. If you are not using the original charger, it is likely that you will not cut off the power in time to continue charging a fully charged battery. If the device is likely to be unused for a long time, the best thing to do is to charge the device once in a while to keep the lithium battery alive.

With the popularization of fast charge, some people think that fast charge will also affect the applicable life of the battery. But we know that the fast charge of the battery is actually to improve the power of the charger, so that the current and voltage increase, in theory is not to cause the acceleration of battery aging. But in the process of fast charging, it will bring a lot of heat generation, high heat will lead the battery to work in a high temperature environment, but also accelerate the aging of the battery. So based on this consideration, we can try not to use the

fast charge function to extend the use cycle.

## **2.5 Advantages and disadvantages of lithium battery**

### **2.5.1 Advantages of lithium-ion batteries**

1) The advantages of lithium-ion batteries are long life, light weight and small size. The power performance of lithium-ion battery electric vehicles is similar to that of lead-acid batteries. They can charge for six to eight hours and run for 30 to 45 kilometers, depending on the battery capacity. However, the weight of lithium-ion battery electric vehicles is only about one fifth of that of lead-acid batteries.

Lithium ion batteries have the characteristics of non-activation, in the use of lithium ion batteries should be noted that the battery placed for a period of time, the battery will enter the state of hibernation, at this time the capacity is lower than the normal value, the use time is also shortened. But lithium-ion batteries are easy to activate, and it only takes 35 normal charge and discharge cycles to activate the battery and return it to normal capacity. Because of the nature of lithium-ion batteries, they have almost no memory effect. Battery memory effect refers to the phenomenon that if a nickel-cadmium battery is not fully charged or discharged for a long time, it is easy to leave traces in the battery and reduce the battery capacity.

Therefore, the user's new lithium-ion battery in the activation process, is not a special method and equipment.

2) In addition to its advantages in performance, lithium-ion battery has more obvious advantages in environmental protection compared with lead-acid battery. No matter in production, use or scrap, lithium-ion battery does not contain or appear any toxic and harmful heavy metal elements and substances such as lead, mercury and cadmium, so it is a clean and green chemical material.

### **2.5.1 Disadvantages of lithium-ion batteries**

#### 1) Structural advantage

The high cost of lithium battery is mainly due to the high price of cathode material  $\text{LiCoO}_2$ , because the Co resources are less, and the electrolyte system is difficult to purify.

#### 2) Need to have protection measures to protect the line.

A. Overcharge protection: overcharge of the battery will damage the positive electrode structure and affect the performance and life; At the same time, overcharging makes the electrolyte decompose, and the internal pressure is too high, leading to leakage and other problems; Therefore, it must be

charged at a certain constant pressure;

B. Over-discharge protection: Over-discharge will lead to the recovery of active substances becomes difficult, so it also needs to be protected line control.

### 3) The influence of temperature is obvious

At low temperature, the battery performance deteriorates obviously, the discharge capacity decreases, the output power decreases, and the available power decreases.

Because the electrolyte of lithium ion battery is organic solvent, its conductivity is much lower than the aqueous solution electrolyte of nickel cadmium battery and nickel metal hydride battery, so the internal impedance of lithium ion battery is about 11 times larger than nickel cadmium battery and nickel metal hydride battery. The operating voltage varies greatly. For example, when the battery is discharged to 80% of its rated capacity, the voltage change of nickel-cadmium batteries is small (about 20%), while that of lithium-ion batteries is large (about 40%).

### 4) Safety hazard

Lithium-ion battery has safety risks of explosion during use. Due to the active composition of lithium-ion battery, if used

incorrectly, electrolyte decomposition and high temperature will occur, which may even lead to explosion in serious cases, thus threatening the personal safety of users. The danger of lithium-ion batteries catching fire, subsiding and exploding remains. The collision of the vehicle may cause the battery positive and negative data to break through the gap, and the ultra-high current at the moment when the energy is quickly recharged to the battery when braking will cause the battery to short-circuit, temperature rise, causing the calm and even blasting. The cause of fire is bump, short circuit caused by lithium ion precipitation, and air contact will cause fire, calm. In addition, the electrolyte in lithium-ion batteries is organic, which makes it easier to quell the fire when it comes into contact with air.



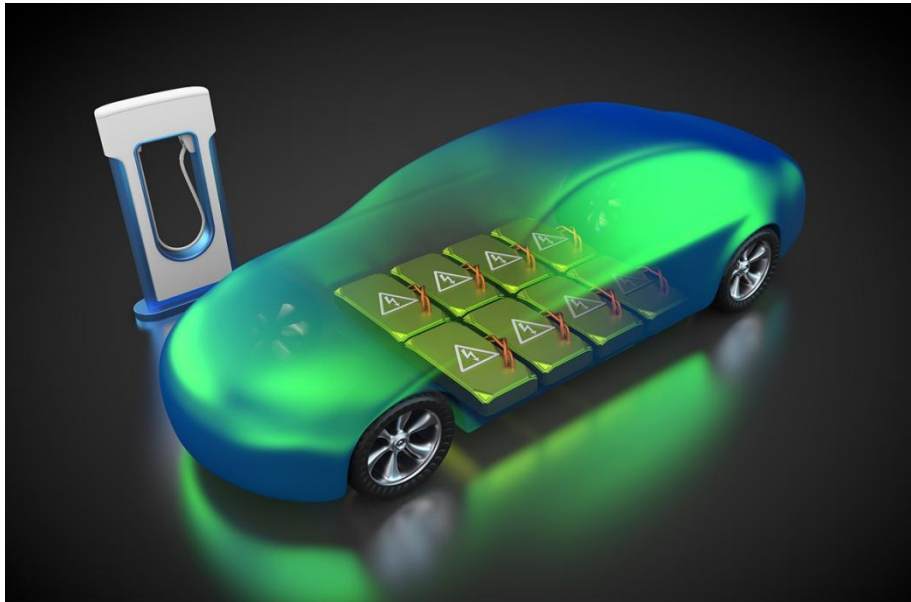


### **3.Sodium-ion batteries**

The concept of sodium-ion batteries began in the 1980s, around the same time as lithium batteries. However, since consumer batteries (such as laptops, mobile phones, etc.), power batteries (mainly automobiles, and some two-wheelers) and other categories of batteries in the 1990s focused on high energy density and service life, lithium-ion batteries were successfully commercialized with better performance. Meanwhile, carbon-based materials such as soft carbon and graphite had better lithium embedding performance, but weak sodium embedding ability. Lithium battery from the technical maturity

into the industrialization stage faster, the development of sodium ion battery is very slow. In recent years, the development of electrochemical energy storage has focused more on economy and safety, rather than energy density. At the same time, sodium battery technology is more mature than ever before, and the cost is further reduced, the energy density has been significantly increased, and the engineering feasibility has been verified. In addition, the price of lithium carbonate, the core raw material of lithium ion batteries, has skyrocketed. The high cost makes sodium ion batteries regain the focus of attention.

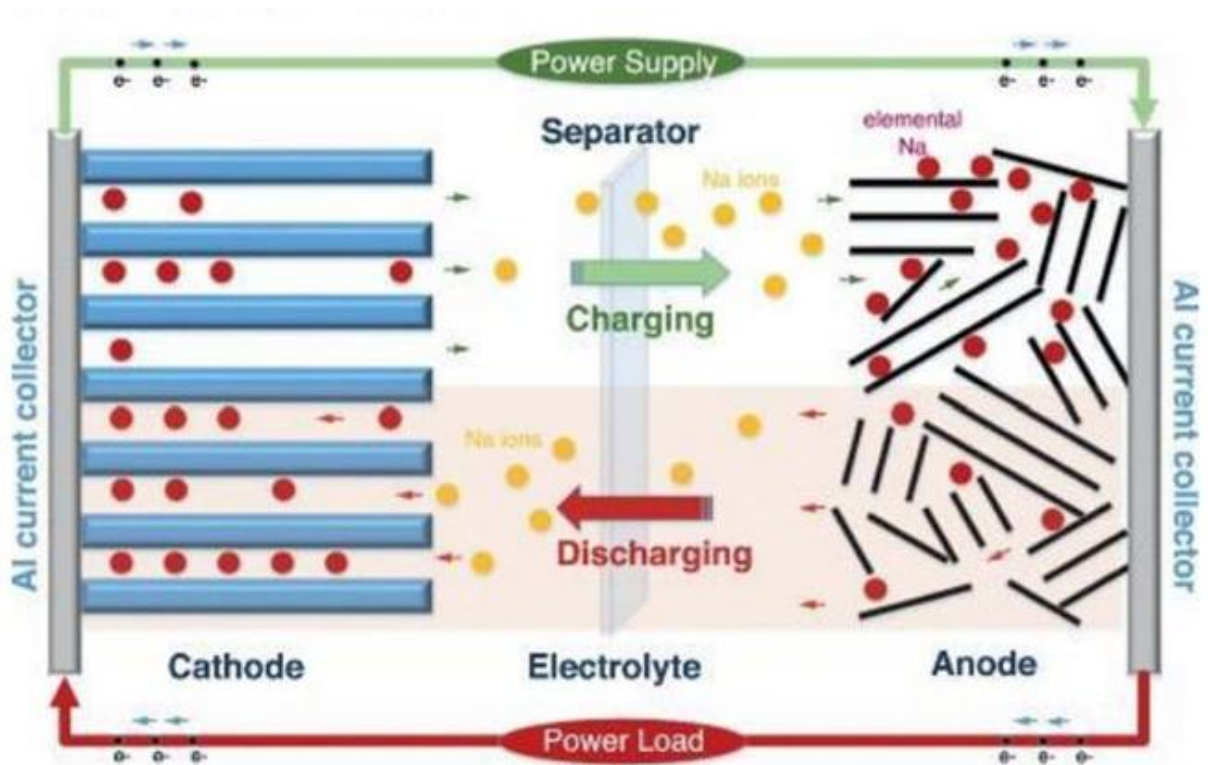
In theory, a sodium-ion battery can be recharged in one-fifth the time of a lithium-ion battery. The most important characteristic of sodium ion battery is the use of sodium ion instead of lithium ion, in order to adapt to sodium ion battery, positive material, negative material and electrolyte need to change accordingly. The advantage of sodium-ion batteries over lithium is that they are abundant. The crustal abundance of sodium is about 2.6%, much higher than the 0.0065% of lithium. Therefore, in contrast, sodium elements come from a wide range of sources, making it cheap and less affected by demand fluctuations, which can meet the needs of large-scale applications, and has gradually become a high-quality substitute and potential competitor of lithium ion batteries.





### 3.1 Principles of sodium ion batteries

Sodium-ion batteries work in much the same way as lithium-ion batteries, with  $\text{Na}^+$  moving back and forth between the two electrodes during charging and discharging. During charging,  $\text{Na}^+$  is detached from the positive electrode and embedded into the negative electrode through the electrolyte. On the contrary,  $\text{Na}^+$  is detached from the negative electrode and embedded into the positive electrode through the electrolyte.



Sodium ion batteries usually take  $\text{Na}_x\text{MO}_2$  as the positive electrode material and hard carbon as the negative electrode material. The reaction formula of electrode and battery can be expressed as:

The positive reaction:  $\text{Na}_x\text{MO}_2 \rightleftharpoons \text{Na}_x y\text{MO}_2 + y\text{Na}^+ + ye^-$

The cathode reaction:  $n\text{C} + y\text{Na}^+ + ye^- \rightleftharpoons \text{Na}_y\text{C}_n$

Cell response:  $\text{Na}_x\text{MO}_2 + n\text{C} \rightleftharpoons \text{Na}_x y\text{MO}_2 + \text{Na}_y\text{C}_n$

### **3.2 Selection of electrode materials**

Sodium ion battery can be divided into sodium sulfur battery, sodium salt battery, sodium air battery, water sodium ion battery, organic sodium ion battery, solid state sodium ion battery. There are two kinds of sodium battery systems that have been applied in the field of energy storage, namely, high temperature sodium-sulfur battery based on solid electrolyte system and sodium-metal chloride battery system. Their negative active material is metallic sodium, more accurately known as sodium batteries. We now often say that sodium ion batteries are mainly the latter three.

The packaging form and manufacturing process of sodium batteries are not different from that of lithium-ion batteries. They can be divided into three forms: cylinder, soft pack and

square hard shell, which are completed by pole plate manufacturing and battery assembly equipment.



### 3.3 Structure of sodium ion batteries

The main components of sodium ion battery are positive electrode, negative electrode, diaphragm, electrolyte and fluid collector. The structure and performance of positive electrode and negative electrode materials determine the sodium storage performance of the whole battery. The positive and negative electrodes are separated by a diaphragm to prevent short circuit. The electrolyte infiltrates the positive and negative electrodes as the medium for ion flow. The fluid collection plays the role of collecting and transmitting electrons.

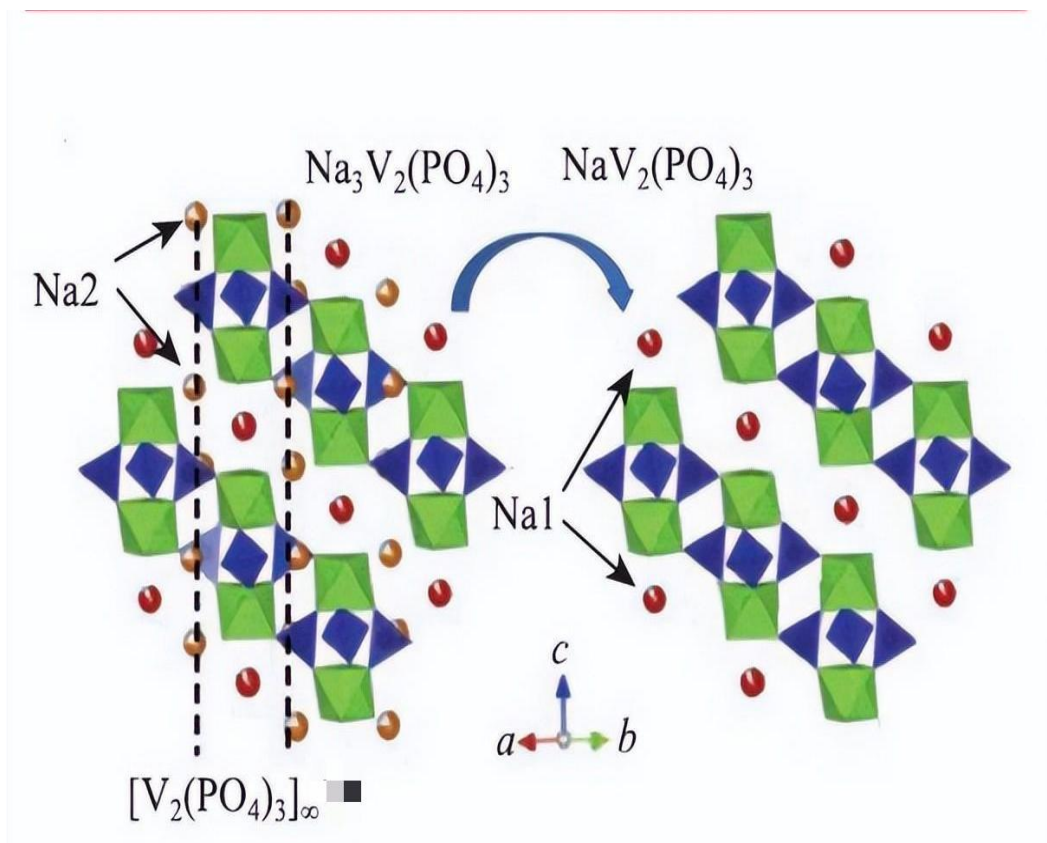
The core difference between sodium-ion batteries and lithium-ion batteries lies in the difference between positive and negative charge carriers, mainly because the radius of sodium ions is larger than lithium ions, compared with lithium ions, sodium ions will be larger, which means that during the operation of the battery, sodium ions in the material embedding and removal of structural stability and dynamics of materials put forward higher requirements. As a result, sodium ions cannot be embedded in graphite materials, and the reversible charge and discharge of sodium ions do not depend on rare metals such as nickel, cobalt and manganese. Therefore, the positive and negative electrode materials and electrolyte of sodium ion batteries need to be changed accordingly to adapt to sodium ion batteries. However, it has minimal impact on the diaphragm and does not affect the current diaphragm system





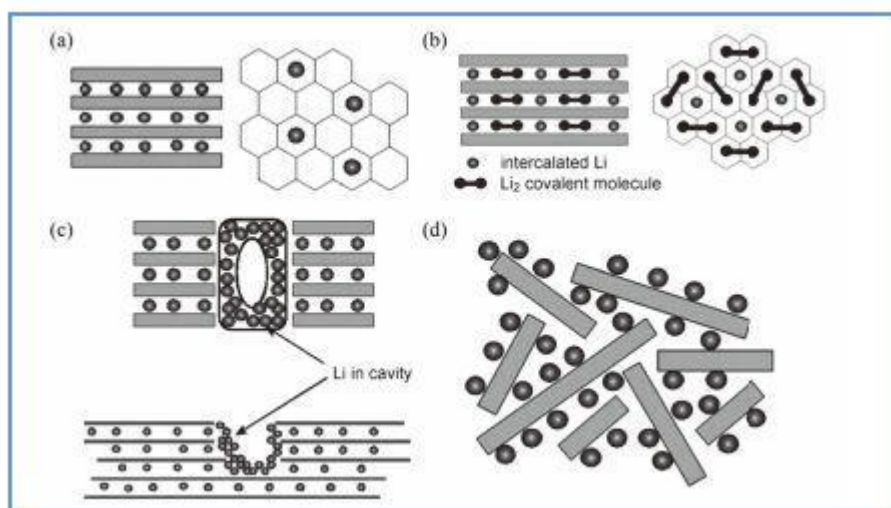
1) In terms of positive electrode materials, Prussian white and layered oxide materials have potential commercialization value at present, which are similar to the existing positive electrode materials of lithium ion batteries. Prussian white is a Prussian blue compound, which is called Prussian white because of its high sodium content. It is a positive electrode material containing cheap metals such as copper, iron and manganese. Prussian white has an open skeleton structure, abundant REDOX active sites and strong structural stability. Due to its large ion channels and lattice gaps, Prussian white is easy to carry out reversible ion insertion/removal reactions, as it is one of the few positive substrate materials capable of accommodating larger basic cations such as Na and K ions. At the same time, Prussian white's outstanding advantages and characteristics lie in its low cost of raw materials and easy access. Layered transition metal oxide  $\text{Na}_x\text{MO}_2$  (M is transition

metal elements, such as Mn, Ni, Cr, Fe, Ti and V and their composites) has high specific capacity and is easy to process and mass produce. It can be divided into single metal oxide, binary metal oxide, ternary metal oxide and polymetallic oxide. It is similar to lithium battery in terms of synthesis and battery manufacturing. Among them, monolayer metal oxide is based on the research of lithium battery  $\text{LiCoO}_2$ , but the structure is unstable, while binary or ternary metal oxide mixed with various elements can have higher reversible capacity and better cycle life, but also increase the cost.



2) In the anode material, the commonly used graphite is cheap and easy to use, but it is inconsistent with sodium ion,

sodium ion is easy to lose electrochemical activity after embedding. Hard carbon materials are considered to be the most practical anode materials for sodium ion batteries because of their abundant carbon sources, low cost, non-toxic and environmental protection, and low sodium storage potential. Hard carbon materials are generally considered as a general term for carbon materials that are difficult to graphitize. The microstructure of hard carbon materials is composed of short-range ordered micro regions stacked by bent graphite-like sheets, with many nanoholes left by random and disordered stacking of each micro region. Due to the large layer spacing (usually greater than 0.37 nm), more nanopores, and more defect sites, it can store more sodium ions and has a higher specific capacity.



3) In terms of electrolyte, electrolyte is the carrier of ion transport and is composed of electrolyte, solvent and additive.

The electrolyte of sodium-ion batteries is very similar to that of lithium-ion batteries, substituting sodium compounds for lithium compounds, such as sodium hexafluorophosphate for lithium hexafluorophosphate. Solvents are divided into water and non-water systems, most of the use of lithium electricity esters of organic solvents. Additives are almost the same as lithium-ion batteries.

4) In the diaphragm, on the one hand, the diaphragm is used to separate the positive and negative electrode, on the other hand, the formation of charge and discharge circuit to make ions through, sodium ion battery and lithium ion battery in the diaphragm technology is similar. The PP/PE membranes widely used in lithium batteries can be reused, but sodium-ion batteries use more fiberglass membranes, which are cheaper.

5) Sodium electric collector uses aluminum foil, the cost is much lower than lithium electricity. Fluid collection is used to connect the powdery active substance, and the current generated by the active substance will be collected and output, input electrode current to the active substance. In graphite-based lithium batteries, because lithium reacts with aluminum to form an alloy, copper foil must be used as a collector for the negative terminal. In sodium-ion batteries, however, sodium and aluminum do not react to form alloys, so aluminum foil can be



used for both positive and negative collector fluids at a much lower cost than lithium-ion batteries.

### **3.4 Causes of aging decline of sodium ion batteries**

1) Increase in the number of cycles. As the battery is used more and more, the chemical reactions inside the battery will continue, leading to the loss of electrode materials and the degradation of electrolytes, which will lead to the reduction of battery capacity.

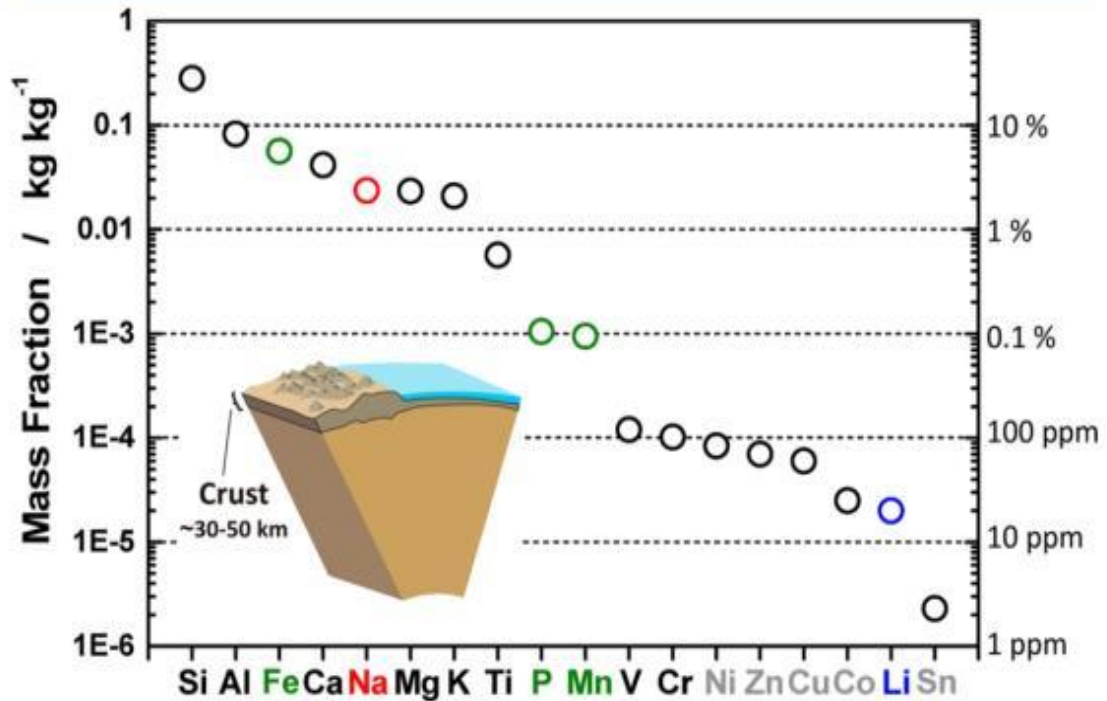
2) The influence of temperature. This is because the battery generates heat during the process of charging and discharging, which causes the temperature to rise. Under high temperature condition, electrode material is easy to lose activity, electrolyte will become unstable, thus affecting the service life and capacity of sodium ion battery.

3) The effect of charge and discharge rate. Too fast a rate of charge and discharge can lead to incomplete chemical reactions inside the battery, which reduces the capacity of the battery.

## **4. Comparison between sodium-ion batteries and lithium-ion batteries**

### **(1) Sodium resources are richer than lithium resources**

Both sodium and lithium are alkali metal elements, which share similar physical and chemical properties. Both can be used as carriers of metal ions in batteries. In recent years, with the large-scale application of lithium ion batteries, lithium resources have entered the supply and demand pattern. By 2022, the price of battery grade lithium carbonate in China is about 47,000 yuan/ton, an eight-fold increase compared with the beginning of 2021. In 2022, the annual output of new energy vehicles in China will be about 590,000, with a penetration rate of 23.6 percent. Lithium will remain in short supply in 2022-2023, which could lead to even higher prices. However, sodium resources are more abundant in the Earth's crust and cost less. As of 2022, the price of sodium carbonate is only 2,782 yuan/ton. In addition, the sodium ion battery positive and negative electrode of the fluid collection can use inexpensive aluminum foil, which can further reduce the battery system cost.



(2) The performance of sodium ion batteries is excellent

From the point of view of battery performance, sodium-ion batteries are also excellent. The solvation energy of sodium ion is lower than that of lithium ion, that is, it has better interfacial ion diffusion ability. At the same time, the electrolyte with the same concentration of sodium ion has higher ionic conductivity than that of lithium ion. Higher ion diffusion capacity and higher ion conductivity mean that the rate performance of sodium ion batteries is better, the power output and acceptance capacity is stronger, and the publicly available sodium ion batteries have 3C and above charge and discharge rates, which can be used well in large-scale energy storage frequency modulation.

In terms of fast charging capacity, the charging time of sodium-ion batteries only takes about 10 minutes, in comparison, the current mass production of ternary lithium batteries even under the DC fast charge, the power from 20% to 80% usually takes about 30 minutes, if it is a lithium iron phosphate battery, it takes about 45 minutes.

Values																		Colors																	
Fraction of Earth's Crust																		Type B Conversion Anodes																	
5 Year Price Range (USD lb <sup>-1</sup> )																		Type B Conversion Cathodes																	
Commonly used Transition Metals for Intercalation Electrodes																		Type B Conversion Cathodes																	
H 1.52E-3																		He																	
Li 1.80E-5 30	Be 2.00E-6																	B 9.00E-6	C 1.80E-4 0.2-1.5	N 1.90E-5	O 4.55E-1	F 5.44E-4	Ne												
Na 2.27E-2	Mg 2.76E-2 1-1.5																	Al 8.00E-2 0.5-1.5	Si 2.72E-1 0.5-2	P 1.12E-3	S 3.40E-4 .001-0.3	Cl 1.26E-4	Ar												
K 1.84E-2	Ca 4.66E-2	Sc 2.50E-5	Ti 6.32E-3 5-15	V 1.36E-4 10-20	Cr 1.22E-4 3-7	Mn 1.06E-3 1-2	Fe 6.2E-2 0.1-0.25	Co 2.90E-5 10-25	Ni 9.90E-5 5-15	Cu 6.80E-5 1-5	Zn 7.60E-5 0.5-1.5	Ga 1.90E-5	Ge 1.50E-6	As 1.80E-6	Se 5.00E-8 15-25	Br 2.5E-6	Kr																		
Rb 7.88E-5	Sr 3.84E-4	Y 3.10E-5	Zr 1.62E-4	Nb 2.00E-5 15-25	Mo 1.20E-6 10-20	Tc	Ru 1.0E-10 1.2k-6k	Rh 1.0E-10	Pd 1.5E-8	Ag 8.00E-8 1k-3.5k	Cd 1.60E-7 0.5-2.5	In 2.40E-7	Sn 2.10E-6 5-15	Sb 2.00E-7 1-10	Te 1.00E-9 50-200	I 4.60E-7	Xe																		
Cs 6.60E-5	Ba 3.90E-4	Lu	Hf 2.80E-6	Ta 1.70E-6	W 1.20E-6 10-25	Re 7.0E-10	Os 5.00E-9	Ir 1.00E-9	Pt 1.00E-8	Au 4.00E-9 10k-30k	Hg 8.00E-8	Tl 7.00E-7	Pb 1.30E-6 0.5-1.5	Bi 8.00E-9 5-15	Po	At	Rn																		



(3) The high and low temperature performance of sodium ion batteries is better

Sodium ion ion conductivity is high, the concentration of the electrolyte is lower, the viscosity of the electrolyte is lower

than that of the lithium-ion battery at low temperature, and the overall performance of the battery is better. The normal operating temperature range of sodium-ion batteries is  $-40^{\circ}\text{C}$ - $80^{\circ}\text{C}$ , and the capacity retention rate of some products can reach 88% at  $-20^{\circ}\text{C}$ , which is significantly better than the capacity retention rate of about 60-70% of lithium iron phosphate. However, sodium-ion batteries can release more than 70% of their capacity at a low temperature of  $-40^{\circ}\text{C}$ , and can still be recycled at a high temperature of  $80^{\circ}\text{C}$ . This will reduce the power quota of the air conditioning system at the energy storage system level, and can also reduce the online time of the temperature control system, thereby reducing the primary input cost and operating cost of the energy storage system.

#### (4) sodium ion batteries have high safety

In terms of safety, due to the relatively high internal resistance of sodium-ion batteries, the instantaneous heat output when short circuit occurs is relatively small compared with lithium batteries, and the temperature rise is relatively low, with higher safety. The reason why sodium-ion batteries are relatively safer is that the higher the current density of lithium-ion batteries, the faster the growth of dendrite lithium, which punctures the internal structure of the battery, causing short circuit spontaneous combustion. The probability of sodium ions

producing dendrites is very low, so the probability of spontaneous combustion is very low.

(5) Sodium-ion batteries are more environmentally friendly

The positive and negative electrodes of the sodium ion battery are collected by aluminum foil. The structure and composition of the battery are simpler, and it is easier to recycle and reuse, so that the sodium ion battery has green environmental protection properties. In contrast, lead-acid batteries contain lead and acid components that will cause pollution to the environment, so the environmental protection is poor.

(6) Low cost of sodium ion batteries

index	Sodium-ion battery	Lithium-ion battery	Lead accumulator
Energy cost per unit of raw material	0.29RMB/ (W.h)	0.43RMB/ (W.h)	0.40RMB/ (W.h)
Mass energy density	100-150W.h/kg	120-180W.h/kg	30-50W.h/kg
Volume energy density	180-280W.h/L	200-350W.h/L	60-100W.h/L
Cycle life	More than	More than	300-500

	2000	3000	
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Although the core energy density and cycle life index of sodium battery are weaker than lithium battery, its cost advantage still makes it more economical in downstream application scenarios such as energy storage. Taking lead batteries, lithium iron phosphate batteries, lithium ternary batteries and sodium ion batteries as examples, significant differences can be found by comparing the life-cycle KWH cost of these batteries in different application scenarios. Under the calculation of power loss, the upper limit of kilowatt-hour cost of sodium battery is 52.2%, 32.4% and 54.3% lower than that of lead battery, lithium iron phosphate battery and ternary lithium battery, respectively.

project	Lead accumulator	Lithium iron phosphate	Ternary lithium battery	Sodium ion battery
Calculate the cost per kilowatt-hour of power lost	0.95-1.234 RMB	0.739-0.873 RMB	1.07-1.29 RMB	0.512-0.59 RMB
The cost per kilowatt-hour of electricity is not calculated when power is lost	0.85-1.13 RMB	0.7-0,834 RMB	1.404-1.26 RMB	0.465-0.543 RMB
The cost per kilowatt hour	0.629-0.806	0.469-0.543	0.82-0.98	0.32-0.366

without counting power loss and with a discount rate of 0	RMB	RMB	RMB	RMB
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### (7) Application scenarios of sodium ions

At present, the energy density of sodium-ion batteries can reach about 150Wh/kg, which is close to that of lithium manganese batteries. And the cycle life can reach 3000~6000 times, which is equivalent to lithium iron phosphate, better than lithium manganese and ternary materials, and the thermal stability and safety are basically equivalent to lithium iron phosphate. Sodium-ion batteries have unique advantages in low temperature performance, fast charge and environmental adaptability, and can be compatible and complementary with lithium-ion batteries. Sodium-ion batteries will first be used in areas that are less sensitive to energy density, such as energy storage and two-wheeled electric vehicles.

## 5. Current issues

The current problems of sodium-ion battery and lithium-ion battery are mainly in three aspects: poor material, high cost and undetermined standard.



(1) Material research needs to be in-depth: hard carbon mechanism, performance improvement, safety assessment

At present, the mechanism of sodium storage in hard carbon is still controversial and has not been fully clarified. In order to improve the low first-cycle efficiency of the existing hard carbon anode, the dynamic mechanism of sodium storage must be deeply understood to provide the most fundamental theoretical guidance for technology research and development. The material properties of existing sodium-ion batteries still have great room for improvement. In general, the energy density of current sodium-ion batteries is far from the theoretical value, and its cycle performance needs to be further improved. On the one hand, continuous improvement of active materials is needed. On the other hand, also need to consider its overall system design and integrated management. The actual operation safety of sodium ion batteries needs careful evaluation. At present, the safety test experiment of sodium ion battery is on the level of cell, the results show that although the safety is high, but the actual operation of the safety needs to be observed, should not be blindly optimistic. In particular, the Prussian blue cathode will release hydrocyanic acid, cyanide gas and other highly toxic gases in the case of thermal runaway.

(2) Cost advantage to be realized: technology research and development and scale effect are indispensable

The reduction in the cost of sodium-ion batteries depends on the reduction of variable costs through continuous technology iteration and the dilution of fixed costs through mass production. Theoretically, sodium-ion batteries do have a great material cost advantage, but the actual total cost of the current product is more than 1 RMB /Wh, higher than lithium iron phosphate, this is mainly due to the current technical maturity is not enough and has not yet appeared scale effect. On the one hand, the type and manufacturing process of electrode materials are not standardized, and the precursor lacks a stable and reliable supply chain, which leads to low yield and consistency of electrode materials and high actual cost, which can only be improved through continuous technological exploration. On the other hand, the price of production equipment is high and the depreciation loss is large, accounting for about 20~30% of the manufacturing cost, which can only be diluted through large-scale production.

(3) Technical standards to be formulated: standardize market order and promote healthy development

The sodium-ion battery industry needs to establish a

scientific and unified standard to standardize the production activities of enterprises and promote the healthy and orderly development of the industry. At present, the technical routes of the manufacturers engaged in the research and development of sodium ion batteries are different, which one is better than the other is controversial. At present, manufacturers mainly refer to lithium-ion batteries, combined with the characteristics of sodium ion batteries and industrial development, to develop standards or product specifications suitable for their own enterprises, and to guide the product design and manufacturing process, to ensure the product yield and consistency, which leads to the product performance and technical level between different enterprises. The unified formulation of industrial technical standards can play a better leading role in the industry and is the necessary guarantee to achieve scale effect. Safety standard, in particular, is an important basis for restricting product quality, but also an important means to regulate market order and promote the healthy and sustainable development of industry.

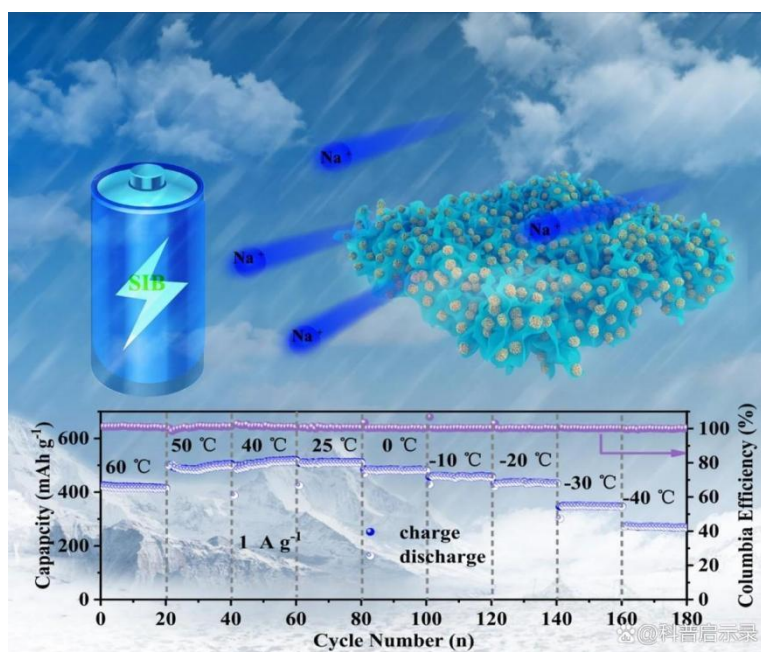
## **6. Future development**

From the perspective of resources, the reserves of sodium elements are very rich, which makes the manufacturing cost of sodium ion batteries greatly reduced. The abundant reserves can fully meet the material supply of sodium ion batteries, which

can be used in a wide range of energy storage systems. The availability of this advantage is very high, because the energy supply is actually very unstable right now, and if you have enough storage systems, you can solve this headache. As mentioned above, many people have been injured when electronic devices exploded during charging. The main reason is that the temperature of the devices is too high. Sodium ion batteries have good low-temperature performance, can be a good solution to this problem, and the charging speed is very fast, to meet our fast pace of life. Although the sodium-ion battery has obvious advantages when taken apart, it has a fatal disadvantage: its short life. Compared with the current use of more three-way batteries and lithium iron phosphate batteries, the service life is not long. Therefore, sodium ion battery is difficult to enter the mainstream power battery field has become an industry consensus.

As we all know, energy storage has been taking an increasing share of the market in recent years, and the scale of investment is getting bigger and bigger. If the use of sodium ion batteries, the initial capital investment does not need to be particularly much, many small enterprises or emerging enterprises are very attractive. Therefore, it will be more inclined to use sodium ion batteries as power batteries. In addition, such as ternary batteries and lithium iron phosphate batteries are difficult to apply to high cold areas, but sodium ion

batteries are not afraid of cold, in this case, of course, sodium ion batteries are more suitable.



At present, many research institutions prefer to use sodium-ion batteries as a supplement to lithium-ion batteries, rather than as a replacement. Since the sodium-ion battery and lithium-ion battery have their respective strengths, the market prospect of developing together is likely to be broader. For example, Ningde Times Company put forward a solution of AB battery system according to the compatibility of the two batteries, that is, the two ions of sodium and lithium are mixed and integrated into a battery system according to a certain proportion. The balance control of different battery systems is carried out by BMS precision algorithm.

The idea of "mix and match" is actually quite good. It integrates the common advantages of lithium ion battery and sodium ion battery, and realizes that 1 plus 1 is greater than 2. It

is feasible in theory, but there are still many difficulties in practical operation, and technical problems have not been solved. But now both batteries can be fully developed in different fields, there is still a broad space for development to explore.

In terms of cost and cost, sodium ion batteries are definitely more dominant, with abundant reserves of sodium ions and crustal elements ranking the sixth in the world. The crustal abundance of lithium element is 0.0065%, and 75% of the resources are distributed in America, where sodium is several hundred times that of lithium. Again specific to the electrode material, sodium will not react with aluminum, so the anode and cathode of sodium ion battery can use relatively cheap aluminum foil, and lithium ion battery anode material can only use relatively expensive copper foil, lithium ion battery material carbonation price is dozens of times higher than sodium carbonate, anode material is higher than sodium ion, overall or sodium ion cost performance is higher.

### **(1) Broad market prospect**

Current offerings of sodium-ion batteries have outstanding advantages in low temperature performance and safety, but are also limited by their disadvantages in energy density and recycling capacity. In the future, with the gradual completion of the industrial chain and the reduction of cost after scale effect,

as well as the optimization and innovation of power and energy density, it is expected to completely replace the demand for lithium manganate and partly replace the demand for lithium iron phosphate, and be widely used in the fields of low energy density electric passenger cars, electric two-wheelers, energy storage, power tools and so on. China's sodium-ion battery market is expected to reach 58.27 billion yuan in 2027. The potential market of low energy density electric passenger vehicles will reach 5.18 billion yuan in 2027. The bottom line requirements of electric passenger cars for batteries are safety and power, and the main evaluation index is price per unit capacity, taking into account battery energy density. At present, low energy density electric passenger vehicles mainly use lithium iron phosphate batteries. Sodium ion battery safety is better than three-way battery, and lithium iron phosphate close, high charging power cap, is expected to improve vehicle acceleration and fast charging performance, while the unit capacity price has a larger reduction space, and price fluctuations are small, with the basic conditions for electric passenger car application. Although its upper limit of energy density is low, it is difficult to adapt to the long-term driving and functional requirements of high-end cars in the future, but its low temperature performance is far better than lithium iron phosphate, so it can better meet users' use needs in winter and high latitude areas. In addition, China's Ningde Company will

give priority to combining the battery with the sodium-electric solution when the volume and weight allow, and the mixed use of sodium-battery and lithium-battery accelerates the development of sodium-battery.

## **(2) Sodium battery industry chain**

Sodium-ion batteries versus lithium-ion batteries. Material in addition to the diaphragm changes, other equipment can be generally used. The sodium-ion battery system is the same as that of lithium-ion battery. It is composed of positive electrode material, negative electrode material, diaphragm, electrolyte, fluid collector, junction component, etc. However, materials except diaphragm need to be adjusted, and the equipment is common with lithium electric equipment. There are four main cathode materials: transition metal oxide, polyanionic compound, Prussian compound and amorphous material, among which transition metal oxide and Prussian compound are developed faster. The anode materials mainly include metal compounds, carbon-based materials, alloy materials and non-metallic elements, among which carbon-based materials are developing faster. Electrolyte main salt changed from lithium hexafluorophosphate to sodium hexafluorophosphate; The negative collector fluid can change from copper foil to aluminum foil; Isolation film to maintain the original product; The production line of sodium ion battery is consistent with that



of lithium ion battery, and no additional production line is required.

### **(3) Sodium ion cathode material**

Future cathode materials may focus on the route of combining transition metal oxides and Prussian compounds. Because the selection of positive electrode material has five principles: 1) has a high specific capacity; 2) High REDOX potential to ensure that the battery has a high output voltage; 3) Good structural and electrochemical stability; 4) The embedded compounds need to have good electronic and ionic conductivity; 5) Abundant resources, low cost and simple preparation process. Metal oxides and Prussian compounds are the main technological routes. The positive electrode of sodium ion battery mainly includes transition metal oxide, polyanionic compound, Prussian compound and amorphous material. 1) Transition metal oxide is the most popular positive electrode material at present, such as sodium ferric phosphate, sodium ferric manganate, sodium titanomanganate, etc. The technology route is mainly adopted by Sinotec Sodium, sodium Innovation Energy and Faradion. 2) Prussian materials have good electrochemical performance, low cost, good stability and other advantages, but there are some problems in the preparation process, such as difficult to control the content of coordination

water, Ningde Times, Starry Sky sodium electricity and Natron Energy are the main companies; 3) Polyanionic materials have good stability and cycle life, and the compound family has diversity, but the low intrinsic electron conductivity limits the practical application of this kind of materials.

The core material of metal oxides is manganic acid, and the core material of Prussian compounds is cyanide. The main system of transition metal oxides is manganese/iron/cobalt/nickel/copper oxides, among which sodium manganate has better performance and cost comprehensive performance than other materials, and is developing rapidly. The main preparation route of manganic acid is potassium hydroxide or potassium carbonate and manganese dioxide. Prussian materials mainly consist of sodium ferrocyanide, cyanide is widely used in industry, in paint, dyes, rubber and other industries. The field of sodium battery will be the core increment of cyanide in the future. Prussian blue compounds are non-toxic and harmless, but its raw material cyanide is toxic. Therefore, the production of Prussian compounds requires production qualification to prevent the impact on the environment and personal harm to the production personnel.

#### **(4) The cathode of Sodium ion battery**

In terms of anode materials in the future, carbon-based materials are the most cost-effective anode materials for sodium ion batteries. Although there are many technical routes for the negative electrode of sodium ion batteries, the main directions are metal compounds, carbon-based materials, alloy materials and non-metallic elements. Carbon-based material has stable cycling performance and high embedding degree in sodium. Common carbon-based materials include hard carbon, soft carbon, graphite, and graphite-like materials. Graphite-like carbon materials improve the sodium storage capacity of materials by expanding the carbon layer or selecting a matching electrolyte. Soft carbon and hard carbon are the most rapidly commercialized carbon-based negatives. The main difference between soft carbon and hard carbon is whether it can be fully graphitized under high temperature heat treatment at 2800°C. There are graphite microcrystals in both soft carbon and hard carbon, and the graphite microcrystalline structure in amorphous carbon presents parallel and stacked fine graphite sheets. However, the microcrystal size in soft carbon is larger and has higher order. After high temperature heat treatment, soft carbon will be fully graphitized, and the change rate of interlayer distance and microcrystal size will be significantly greater than that of hard carbon, thus reducing the interlayer spacing in soft

carbon. Sodium storage capacity is significantly reduced. The storage modes of sodium ions by hard carbon are mainly microcrystalline intercalation and micropore adsorption. Compared with soft carbon, hard carbon shows stronger sodium storage capacity and lower working potential, so it is more suitable for the negative electrode materials of sodium ion cell.

#### **(5) Negative collector fluid: from copper foil to aluminum foil**

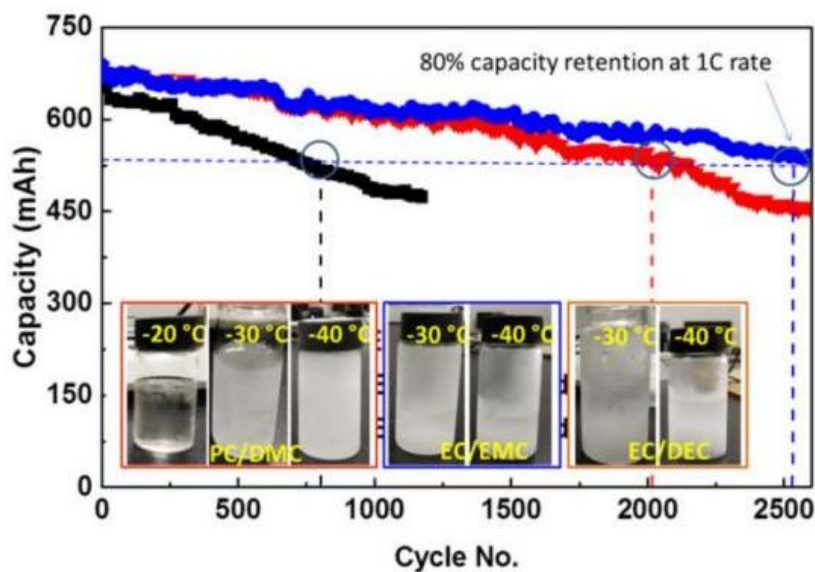
Sodium ion battery set fluid are aluminum foil, existing aluminum foil enterprises benefit. Sodium ion batteries allow the use of aluminum as a fluid collector in the negative electrode, which can effectively avoid the overdischarge problem of graphite-based lithium-ion batteries. The fluid collector plays the role of carrying the positive and negative poles of the battery and collecting electrons in the battery. The selection of materials not only requires good conductivity, soft texture and cheap price, but also needs to be stable in the air. In summary, aluminum and copper are the most suitable material for fluid collection, positive electrode potential is higher, copper foil is easy to be oxidized at high potential, so in lithium ion batteries, copper foil as a negative electrode fluid collection, and hard carbon negative sodium ion batteries can discharge 0V, will not appear any problems such as aluminum dissolution.

## **( 6 ) Electrolyte: sodium hexafluorophosphate for lithium hexafluorophosphate**

The electrolyte of sodium ion battery and lithium ion battery are mainly liquid electrolyte. Because the material of electrolyte needs to be matched according to the positive electrode material, lithium salt needs to be replaced with sodium salt. Currently commonly used salts are sodium hexafluorophosphate ( $\text{NaPF}_6$ ), sodium perchlorate ( $\text{NaClO}_4$ ), sodium (NaTFSI), sodium fluoride sulfonyl (trifluoromethane sulfonyl) imide (NaFTFSI), sodium sodium (fluoride sulfonyl) imide (NaFSI), etc. The main sodium salt of transition metal oxides and polyanionic compounds is sodium hexafluorophosphate, which has the same preparation process as lithium hexafluorophosphate, and the production line can be reused basically. According to a patent on sodium ions from the Ningde era, one of the Prussian blue electrolytes is composed of a mixture of vinyl carbonate (EC), dimethyl carbonate (DMC), and sodium salt  $\text{NaClO}_4$ . Existing lithium hexafluorophosphate enterprises have layout in sodium hexafluorophosphate. Compared with lithium-ion battery electrolyte, the most important material change in sodium-ion battery is sodium salt, which changes from lithium

hexafluorophosphate to sodium hexafluorophosphate. The preparation process of the two is basically the same. It is expected that enterprises with the production capacity of lithium hexafluorophosphate will maintain their advantages in sodium hexafluorophosphate products.

The following figure shows the battery cycle life under different electrolyte systems:



## 7. Summary

After comparative analysis, it can be found that due to the limitations of sodium ion batteries, the power batteries used in mainstream vehicles cannot be comparable to lithium-ion batteries. But in the small power battery industry such as electric

bicycles, the future is bound to be the sodium-ion battery rapid development of applications. In the field of large vehicles, the development direction of sodium-ion batteries should be as a supplement, rather than a substitute, instead of lithium-ion batteries. Since sodium-ion batteries and Li-ion batteries have their respective strengths, the market prospects are likely to be broader together, and more attention is paid to the development of compatibility between the two batteries. Absorbing the advantages of the two batteries, developing new batteries is a more long-term development line in the future.