

# Diverse Promising Electrode Materials for Advanced Sodium-Ion Batteries

Yuchen Zhang\*

Hefei No.8 High School, Hefei, Anhui, 230031, China

\* Corresponding Author Email: yuchen.zhang@hf.lyndoninstitute.org.cn

**Abstract.** Taking seriously gradually, along with the global environmental protection consciousness, the development of new energy rapidly, many countries in the world of renewable energy are accelerating the renewal of the energy system upgrade solar energy, oceanic energy, wind energy, geothermal energy and other renewable energy has been widely used, energy storage technology is the key to building energy Internet support technology, At present, electrochemical energy storage is one of the mainstream energy storage methods, with the advantages of small geographical restrictions and a short construction cycle. Lithium-ion battery (LIB) is the most mature development in energy-storage devices, but with the popularization of electric vehicles, the LIB may face the problem of a shortage of lithium resources. Due to its diverse advantages, the sodium-ion battery (SIB) has become a research hotspot of energy storage technology. This paper analyzes the feasibility and application principle of SIB energy storage technology and briefly introduces the application scenario and electrode materials of SIBs. It gives some suggestions for applying SIBs in energy storage power stations.

**Keywords:** Energy storage technology, sodium-ion battery, working principle, electrode material

## 1. Introduction

With social development, scientific progress and an accelerated pace of life, people's demand for energy continues to increase. Currently, global electricity consumption exceeds 25 trillion kWh, and the annual per capita electricity consumption is about 3,400 kWh/person [1]. Regarding fuel, electricity production relies on traditional power sources and renewable energy, etc. Among them, fossil fuels such as oil, coal and natural gas are non-renewable resources and will produce a large number of greenhouse gases, which have a bad impact on the environment in which human beings live, and then endanger the survival and development of human beings. Therefore, people need to seek more clean, safe and renewable energy; the energy is largely limited by factors such as time, space, season, climate change and energy storage access, which not only can decrease the rate of abandoned wind, discard, can slow a new energy fluctuation, tracking plan, and participate in the system load frequency control [2].

The so-called energy storage technology is a technology that converts the energy that is not easy to store into a more convenient or economical form of energy for storage and then releases the stored energy in a specific form when an energy supply is needed in the future [2]. At present, electrochemical energy storage is the most mature in the development of LIB technology. However, with the electric car popularity and large-scale energy storage applications, the LIB has gradually exposed the lithium resources bottleneck problem. By January 2022, the price of battery-grade lithium carbonate rose from 40,000 yuan/ton at the beginning of the year to 400,000 yuan/ton; In addition, China's dependence on lithium resource import is as high as 80%, once overseas lithium ore import is blocked, domestic LIB enterprises will face a severe test, can be said to have no buffer period at all; At present, NingDE Times, Ganfeng Lithium and other domestic leading enterprises have arranged lithium resources in the world. Sodium-ion batteries (SIBs) as a new type of secondary chemical power supply, not only are there no raw material resource constraints, and the low-temperature performance and high security, charge and discharge properties, resources advantage and cost advantage in large-scale electrochemical energy storage, low-speed electric cars, and other areas of the application, is expected to be complementary with a LIB and effective alternative.

## 2. Working Mechanism of SIB

The structure and working principle are shown in Figure 1. The composition of SIB mainly includes a positive electrode, negative electrode, diaphragm, electrolyte and fluid collector. A diaphragm separates the anode and cathode to prevent short circuits, the electrolyte infiltrates the anode and cathode to ensure ion conduction, and the collector serves to collect and transport electrons. When charging,  $\text{Na}^+$  comes out from cathode and is inserted in anode via electrolyte through the diaphragm so that cathode is in the poor sodium state with high potential and the negative electrode is in the sodium-rich state with low potential. In the opposite process,  $\text{Na}^+$  is released from anode and implanted in cathode via electrolyte, returning cathode to a sodium-rich state. In order to maintain the balance of charge, the same number of electrons are transferred in the process of charge and discharge and migrate between anode and cathode together with  $\text{Na}^+$  so that oxidation and reduction reactions occur at the positive and negative electrodes, respectively. Sodium ions can migrate reversibly between both side electrodes, composed of insertion-type materials that allow sodium ions to be inserted and removed. SIBs, like LIBs, are called "rocking chair batteries."

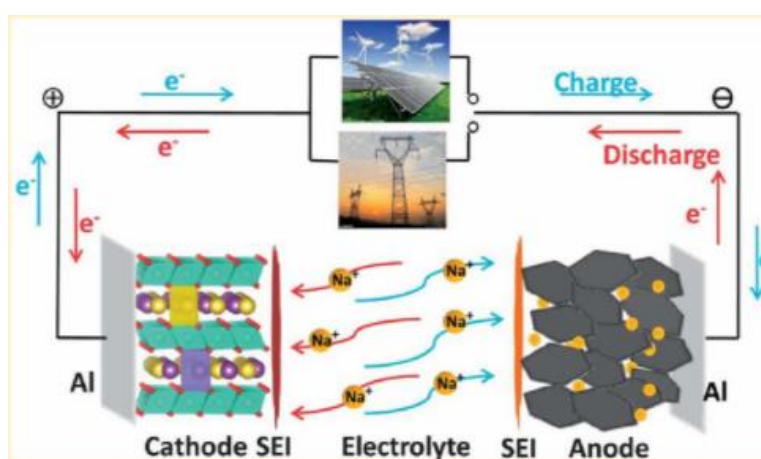


Figure 1. Scheme of how SIBs work [1].

## 3. Feasibility and Application Principle of SIB Technology

Research on SIBs dates back to the 1970s, even before research on LIBs. Although, after 1991, the successful commercialization of LIBs attracted the attention of most scientists, the development of SIBs has never stopped. A recent study found that many of the advantages of SIBs, in addition to the advantage of the resources, are abundant sodium, but also has high and low-temperature performance, high safety, and can use the advantages of low salt concentration of electrolyte. Some technical indicators are even better than LIBs, showing huge development potential.

### 3.1. Technical feasibility

Sodium resources are abundant, evenly distributed and low cost, sufficient to support the sustainable development of electrochemical energy storage. Like LIBs, most of the production equipment is compatible, with less short-term or long-term equipment and process investment, which is conducive to cost control. Cheap aluminum foil can function in positive and negative fluid collectors in SIBs, further reducing the cost of the battery system. Higher ion diffusion capacity and higher ion conductivity mean SIBs have better rate performance, stronger power output and acceptance capacity. The published SIBs have charge and discharge rates of 3C and above, which can be well applied in large-scale energy storage and frequency modulation applications. It can release more than 70% capacity at  $-40\text{ }^\circ\text{C}$  and can be used by cyclic charging and discharging at  $80\text{ }^\circ\text{C}$ . This will reduce the air conditioning system's power quota at the energy storage system's level and the temperature control system's online time. Thus, the primary input cost and operation cost of the energy storage system can be reduced. In addition, no fire was found in all the safety items tested,

and the safety performance was better. The internal resistance of SIB is slightly higher than that of the LIB, resulting in less heat and low-temperature rise in short circuits and other safety tests.

### **3.2. Application principle**

As a novel electrochemical energy-storage technology, the SIB can take advantages of low cost in widespread energy storage applications. At the same time, in application fields such as frequency modulation and power start-up, SIBs' high-power charging and discharging characteristics can well support system operation.

#### **3.2.1. Application on power supply**

With the large-scale distributed power supply connected to the grid, the problem of insufficient peak regulation and frequency modulation resources is becoming increasingly prominent. On the power generation side, the SIB energy storage system can be combined with the thermal power unit to give full play to its advantages, such as fast response speed and strong instantaneous power regulation ability and provide frequency and voltage regulation services. Under the AGC system scheduling, the SIB energy storage system can cooperate with the wind power, photovoltaic and other new energy systems to improve the power system regulation ability and reduce the wind and light abandonment rate. In addition, the energy storage device can provide emergency power support to enhance the power grid's high and low voltage crossing capability when the voltage of the new energy connection point drops instantaneously.

#### **3.2.2. Application in substation system**

The accelerated arrival of new power systems makes the role of energy storage technology increasingly apparent. The advantages of low cost and high efficiency of the SIB energy storage system will be reflected in the application scenarios, which can further reduce the energy loss and promote the perfection of the Chinese electric power market. Bidding mechanism in the auxiliary service market will be improved day by day, and the low-cost SIB energy storage system will have an advantage in the bidding system. At the same time, when a large-scale SIB energy storage system participates in the spot power market, it can also obtain electricity revenue through the spot market trading mode.

#### **3.2.3. Application on the load side**

In power distribution, the complexity of the distribution network is higher and higher, and temperature, humidity and other environmental conditions are challenging for standardized energy storage products. Because of its wide temperature region characteristics, the SIB energy storage system can adapt to the conditions of different latitude regions, improve the permeability of distributed power supply, and enhance distribution network operation stability and economy. In addition, the energy storage system is used to store energy when the load is low, generate electricity when the load is high, smooth the load curve, reduce the basic electricity bill through the energy storage system, delay equipment expansion, improve power quality, and improve the operation economy of the power grid. Through the above analysis, the application of SIB pack technology is feasible in terms of technology and economy, and the purchase cost and cycle number of batteries are the main factors affecting the energy storage system of SIBs. Combined with the performance characteristics of SIBs, the following suggestions are put forward:

i) In terms of system integration design before the SIB is industrialized, it is recommended to adopt the system scheme of group series multi-converter parallel integration to design an independent energy storage unit for the SIB and then integrate multiple independent energy storage units to form an energy storage system, to maximize the capacity of the SIB.

ii) In terms of charge and discharge management, it is suggested that, on the one hand, the advantages of SIBs in different application scenarios should be taken advantage of their excellent rate performance. On the other hand, a more appropriate battery management system is developed according to the actual situation of SIBs, and targeted and refined control strategies are studied.

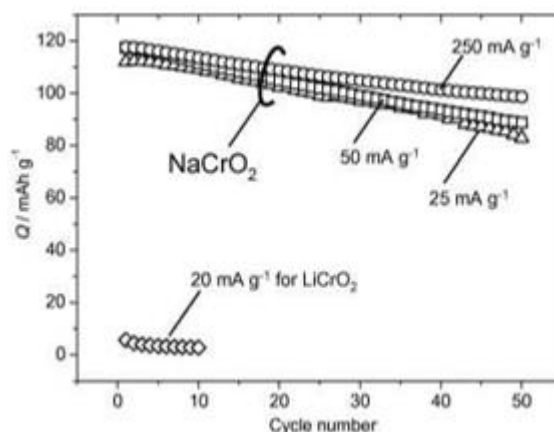
iii) Improve the top-level design, promote the deep integration of SIB energy storage policies, regulations and guidelines with the industry, carry out comprehensive evaluation studies on the safety, scene adaptability and economy of SIB energy storage, promote the construction of large-scale demonstration projects of SIB energy storage, and accelerate the large-scale application process of SIBs [2].

## 4. Electrode Materials for SIBs

### 4.1. Anode materials

#### 4.1.1. Layered transition metal oxides

According to the different dense packing modes of sodium ion layered oxide and general oxide layer, Delmas divides the layered transition metal oxide into three categories: O3 (ABCABC), P2 (ABBA) and P3 (ABBCCA). The sodium ions are in different dense accumulation modes in coordination environments (P= prism, O= octaheon) [3].



**Figure 2.** Na || NaCrO<sub>2</sub>, Li || LiCrO<sub>2</sub> Comparison of battery cycle performance [4].

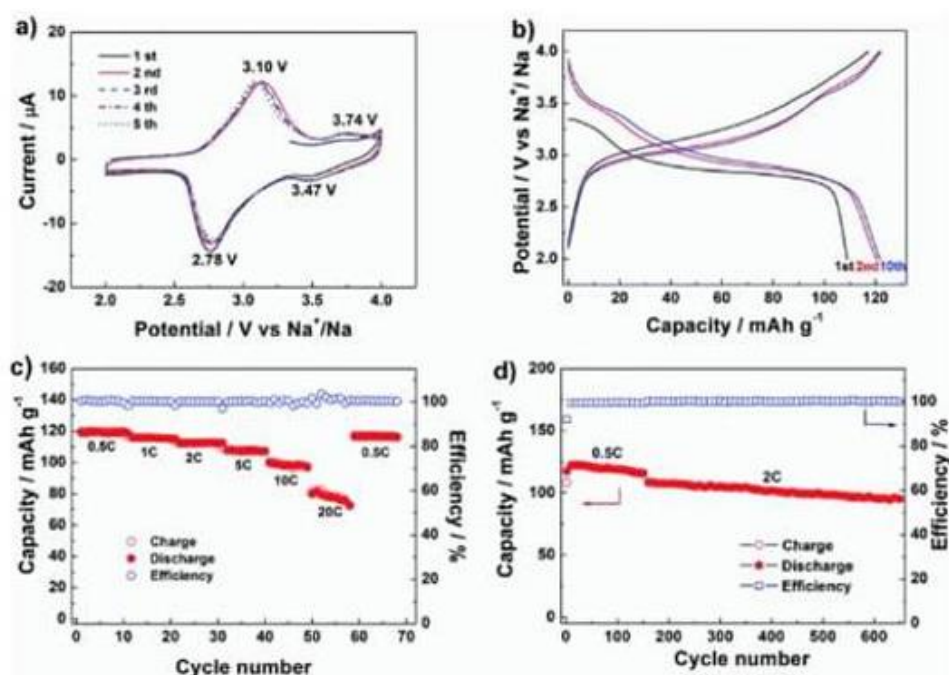
Manganese oxides and iron oxides have been widely studied. As single metal oxides, they show good electrochemical performance. However,  $\alpha$ -NaFeO<sub>2</sub> is sensitive to water and easy to produce FeOOH and NaOH, affecting the battery's capacity. Other transition metals can be substituted or doped in monomial oxides. For example, Fe substituted for Mn can inhibit the phase transition after sodium removal of NaMnO<sub>2</sub> materials, thus improving the stability of materials. For layered NaCrO<sub>2</sub>, when used for SIBs, the discharge capacity is 90-120 mAhg<sup>-1</sup> (Figure 2) [3]. When the discharge capacity is increased, the capacity retention rate is also improved, and the electrochemical performance is good. Although layered transition metal oxides show good electrochemical performance, they are difficult to prepare.

#### 4.1.2. Polyanionic compounds

Polyanionic materials are characterized by structural diversity, structural stability, low sodium ion migration energy and stable voltage plateau. Its stable covalent structure makes it have high thermodynamic stability and high voltage oxidation stability. Because of the above advantages, polyanionic compounds are popular in researching cathode materials for SIBs. However, its large polyanion group makes its theoretical capacity generally low.

Polyanionic compounds mainly include phosphate, fluorophosphate, pyrophosphate, sulfate, etc. Fluorine atoms with high electronegativity are introduced into the structure of fluorinated polyanionic materials. The introduction of fluorine atoms can improve the REDOX pair voltage of the materials, thus increasing the energy density. Sulfate in sulfate is more electronegative, which makes it have a higher voltage platform as the anode material of SIB.

### 4.1.3. Prussian blue compounds



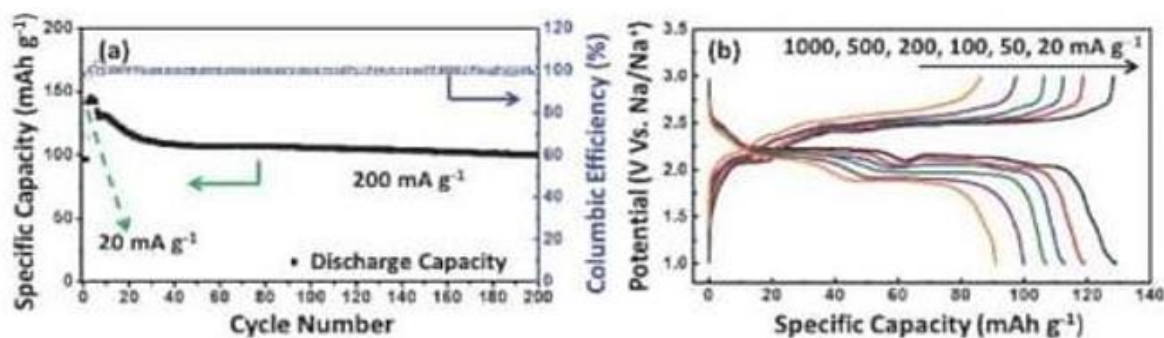
**Figure 3.** Properties of FeFe(CN)<sub>6</sub> [5].

Prussian blue compounds are complexes formed by coordinating CN<sup>-</sup> and transition metal ions. They have a 3D open structure. FeFe(CN)<sub>6</sub> single crystal nanoparticles showed excellent Na-storage performance. The Coulomb efficiency is about 100%. At 20 °C, it still has good rate performance, and the capacity retention rate reaches 87% after 500 cycles (Figure 3). It has excellent cycle stability and can be low-cost and pollution-free for SIBs.

### 4.1.4. Organic electrode materials

Organic electrode materials have attracted increased attention due to their environmental friendliness, abundant reserves and diverse structures, which may become ideal substitutes for traditional inorganic materials. Among them, conjugated carbonyl compounds have been widely studied due to their good REDOX reversibility and structural stability.

PTCDA, an organic dye with an aromatic ring center and two anhydride groups, exhibits high electrochemical reversibility when used for high-performance SIBs (Figure 4) [3]. When the current density is 10 mAh g<sup>-1</sup>, the capacity manages to reach 140 mAh g<sup>-1</sup>. After 200 cycles (initial 5 cycles of 20 mAh g<sup>-1</sup>, followed by 195 cycles of 200 mAh g<sup>-1</sup>), it was still 100 mAh g<sup>-1</sup>, and the Coulomb efficiency was almost 100%, showing excellent rate performance. In addition, Na<sub>2</sub>C<sub>6</sub>O<sub>6</sub> was also used as sodium ion cathode material. Although organic electrode materials have many advantages, they are not conductive and are likely to be dissolved. Therefore, it is necessary to improve the electrochemical stability and cycling performance.



**Figure 4.** Study on cyclic performance of PTCDA [5].

## 4.2. Cathode materials

### 4.2.1. Embedded materials

Hollow carbon nanowires can play a crucial role in SIBs. After 400 cycles of  $50\text{mAh g}^{-1}$  ( $0.2\text{C}$ ) and  $0.01\text{-}1.2\text{V}$ , the reversible capacity is  $251\text{mAh g}^{-1}$  with capacity retention rate of  $82.2\%$  [6]. At  $500\text{mAh g}^{-1}$  ( $2\text{C}$ ), the reversible capacity is still  $149\text{mAh g}^{-1}$ , showing good rate performance (Figure 5).

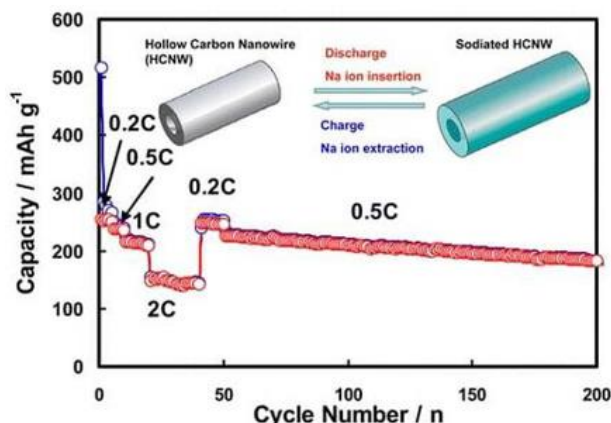


Figure 5. Magnification properties of hollow carbon nanowires [5].

### 4.2.2. Alloy materials

When alloy materials are used for SIBs, they have a high theoretical capacity, low sodium storage potential and good conductivity. Sn and Na can be alloyed, and NA-Sn alloy can be used as sodium anode material. A Sn atom can bind up to 3.75 sodium atoms, so Sn will inevitably undergo a huge expansion/contraction during sodium entrapment/removal. This repeatable structural change due to large volume change. The key to solving this problem is to develop nanocomposites or modify their structures. When  $\text{Sn}_{0.9}\text{Cu}_{0.1}$  nanoparticles were used as sodium anode materials, the reversible capacity of the battery was  $420\text{mAh g}^{-1}$  with a high capacity retention rate of  $97\%$  after 100 weeks of cycle charging and discharging at a rate of  $0.2\text{C}$ , showing a good electrochemical performance (Figure 6) [7].

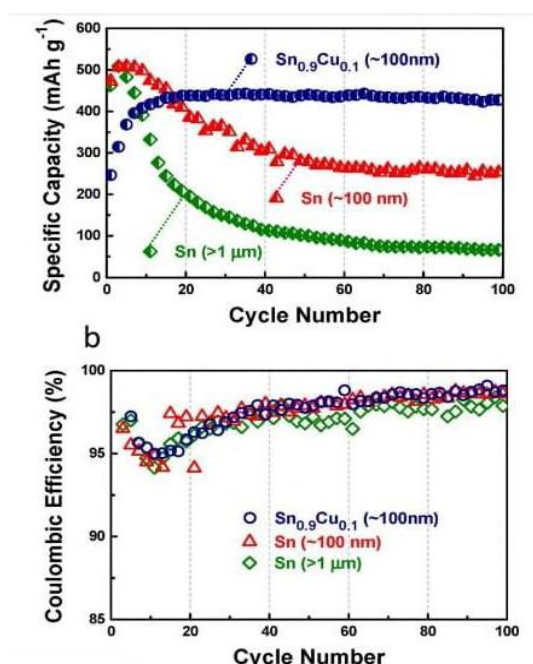
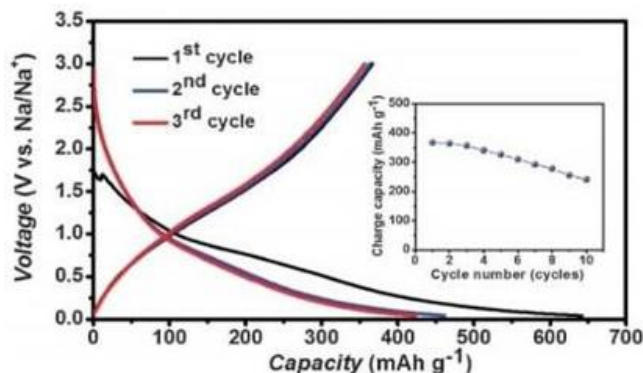


Figure 6. (a) Discharge capacity and (b) Coulomb efficiency of  $\text{Sn}_{0.9}\text{Cu}_{0.1}$  nanoparticle, Sn nanoparticle and Sn particle electrodes at  $0.2\text{C}$  ( $169\text{mAh g}^{-1}$ ) cycle [5].

### 4.2.3. Conversion materials

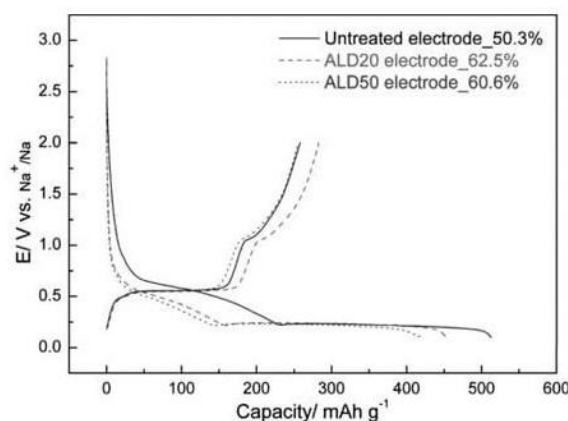
Metal oxides, such as  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{CoO}$ ,  $\text{MoO}_3$ , and  $\text{NiCo}_2\text{O}_4$ , are also exceptional negative materials.  $\text{Fe}_3\text{O}_4$ , with a theoretical capacity of  $926 \text{ mAh g}^{-1}$ , is an anode material for SIBs. In the process of transformation reaction, sodium ions embedded in  $\text{Fe}_3\text{O}_4$  will generate metal Fe and  $\text{Na}_2\text{O}$  (Figure 7) [8]. Its coulomb efficiency is high, can reach 57%, 10 cycles after its capacity is still 65% of the initial charging capacity. However, metal oxide anode materials will destroy the integrity of electrode materials due to their poor conductivity and large volume expansion in the cycling.



**Figure 7.**  $\text{Fe}_3\text{O}_4$  in 0.04-3.0 V vs.  $\text{Na}/\text{Na}^+$ , with 0.06C constant current loop voltage curve [5].

### 4.2.4. Organic electrode materials

$\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$  was introduced for SIBs, showing good electrochemical performance, with a low sodium embedding voltage at 0.29 V vs.  $\text{Na}^+/\text{Na}$  (Figure 8) [9]. With the transfer of two charges, the reversible capacity is  $250 \text{ mAh g}^{-1}$ , with good cycle performance. Although carboxylic acid organic molecules can provide relatively good electrochemical performance in capacity and operating voltage, the problems of rate performance and cycle performance remain to be solved. Through changing the molecular structure, surface coating and polymerization, the performance of organic anode materials for SIBs can be improved [10].



**Figure 8.** Untreated  $\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$  electrode and atomic layer deposition technology processed  $\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$  charge-discharge curves of two kinds of the electrode [5].

## 5. Conclusions

SIB is an important energy storage technology with low cost, rich resources and good comprehensive performance, with great development potential, sodium element has similar electrochemical properties to lithium, and its resources are rich, so in future development, the SIB has a very broad prospect. It can be applied in many fields of life and production and will promote the construction of the energy Internet. As electrode materials research and development, through the design of micro-/nanostructure or the preparation of carbon composite material, such as optimization

of electrolyte, will make SIB capacity and voltage stability and further improve SIB to face the challenge of future, possible solutions and future development prospect is looking for cathode materials possessing extraordinary energy density and decent function density; Looking for loop small volume change of the anode materials, through to the electrode material, electrolyte, manufacturing and group technology and battery management optimization, is expected to enhance the comprehensive performance of the SIBs further, as soon as possible in the center of electric cars, data backup power supply, communication station, family/industrial areas such as energy storage, large-scale energy storage applications.

## References

- [1] Li, Y., Lu, Y., Zhao, C., Hu, Y.S., Titirici, M.M., Li, H., Huang, X. and Chen, L., "Research advances of electrode materials for low-cost sodium-ion batteries towards practical application for grid energy storage," *Energy Storage Materials*, 7, 130-151 (2017).
- [2] Zhang P., Kang L., Wang M., "Energy storage technology and economic analysis of sodium-ion battery," *Energy Storage Science and Technology*, 11(6), 1892-1901 (2022).
- [3] Komaba, S., Takei, C., Nakayama, T., Ogata, A. and Yabuuchi, N., "Electrochemical intercalation activity of layered NaCrO<sub>2</sub> vs. LiCrO<sub>2</sub>," *Electrochemistry Communications*, 12(3) 358-355, (2010).
- [4] Oh, S.M., Myung, S.T., Hassoun, J., Scrosati, B. and Sun, Y.K., "Reversible NaFePO<sub>4</sub> electrode for sodium secondary batteries," *Electrochemistry communications*, 22, 149-152 (2012).
- [5] China energy Storage network news center, sodium ion battery electrode materials are what? China Energy Storage Network, August 31, 2016.
- [6] Cao, Y., Xiao, L., Sushko, M.L., Wang, W., Schwenzer, B., Xiao, J., Nie, Z., Saraf, L.V., Yang, Z. and Liu, J., "Sodium ion insertion in hollow carbon nanowires for battery applications," *Nano letters*, 12(7), 3783-3787 (2012).
- [7] Lin, Y.M., Abel, P.R., Gupta, A., Goodenough, J.B., Heller, A. and Mullins, C.B., "Sn-Cu nanocomposite anodes for rechargeable sodium-ion batteries," *ACS applied materials & interfaces*, 5(17), 8273-8277 (2013).
- [8] Hariharan, S., Saravanan, K., Ramar, V. and Balaya, P., "A rationally designed dual role anode material for lithium-ion and sodium-ion batteries: case study of eco-friendly Fe<sub>3</sub>O<sub>4</sub>," *Physical Chemistry Chemical Physics*, 15(8), 2945-2953 (2013).
- [9] Zhao, L., Zhao, J., Hu, Y.S., Li, H., Zhou, Z., Armand, M. and Chen, L., "Disodium terephthalate (Na<sub>2</sub>C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) as high performance anode material for low-cost room-temperature sodium-ion battery," *Advanced energy materials*, 2(8), 962-965 (2012).
- [10] Wu, X., Deng, W., Qian, J., Cao, Y., Ai, X. and Yang, H., "Single-crystal FeFe(CN)<sub>6</sub> nanoparticles: a high capacity and high rate cathode for Na-ion batteries," *Journal of Materials Chemistry A*, 1(35), 10130-10134 (2013).