

SPECIFICATION

A High Safety Sodium Ion Battery and Its Capacity Grading Method and Application

Technical Field

The present invention relates to a sodium-ion battery, in particular to a high safety sodium ion battery and its capacity grading method and application.

Background Technology

The batteries used as backup power sources are usually lead-acid batteries, but due to heavy metal pollution, lead-acid batteries are banned in many countries; meanwhile the lead-acid batteries must be replaced frequently for their short cycle life of 3-5 years. However, the large-scale use of lithium-ion batteries, with the long-term floating charge state, changes will be caused in the internal structure of the battery, mainly including the following:

(1) The irreversible reaction between the positive electrode material and the electrolyte. Such as lithium manganese oxide and lithium nickel oxide, which are prone to the collapse of the crystal structure. For example, during long-term charging, the positive electrode of lithium manganese oxide undergoes irreversible phase transformation;

(2) The irreversible reaction between the anode material and the electrolyte. The SEI film (solid electrolyte phase boundary film) formed during the formation is to protect the anode from the corrosion of the electrolyte. Since the anode is always in the full charging state during the floating charge, the possible reaction between the anode and the electrolyte: $\text{Li}_y\text{C}_6 \rightarrow \text{Li}_{y-x}\text{C}_6 + x\text{Li}^+ + x\text{e}^-$, etc., reference: Research review of lithium-ion battery floating charge, Energy Storage Science and Technology, January 2021, Vol. 10, Issue 1;

(3) During the cycle life of batteries, the SEI film of the battery is constantly damaged and rebuilt due to the volume effect of the electrodes. Similar reactions irreversibly

consume lithium ions in the electrolyte, resulting in a loss of battery capacity. Reference: Analysis of Float Charge Life and Ineffectiveness of Lithium Iron Phosphate/Graphite Batteries, Battery, October 2023, Volume 53, Issue 5.

It can be concluded that the unstable crystal structure of the active material and the damage of the SEI film will cause the irreversible capacity loss of the battery during floating charge.

Before assembling the energy storage system, traditional batteries will undergo battery formation and capacity grading process. The conventional process focuses on capacity and open circuit voltage, but batteries used as energy storage modules in backup systems do not have a positive correlation between floating charge performance and capacity / open circuit voltage. Using conventional formation and capacity grading method may lead to unqualified batteries introduce to the energy storage module in the backup power system , which will result in decrease of the system lifespan.

Summary of The Invention

The purpose of the present invention is to overcome the shortcomings of existing technology, provide a capacity grading method for battery application in the energy storage module of the backup system, which can improve the consistency of the batteries and the service life, thus be widely applied in UPS systems. At the same time, the invention provides a high safety sodium ion battery, using a highly stable polyanionic materials as the active substance. The battery does not produce a solid electrolyte interphase (SEI) during operation, which can meet the technical requirements of long-term floating charge.

The technical solution for achieving the above objectives is: a capacity grading method for a high safety sodium ion battery, characterized in that when the high safety sodium ion battery is used as an energy storage module, the following steps are used for capacity grading:

S1, Activation of the assembled high safety sodium ion battery in an environment of 40-50 °C;

S2, then charging and discharging of the high safety sodium ion battery between 0.3-

1.6V for capacity calibration by 0.1C, and determine whether the battery is qualified based on the rated capacity of the battery;

S3, a high safety sodium ion battery with qualified capacity, charged to 1.3V at a current of 0.1C, and then switched to constant voltage charging, with a constant voltage charging time of 40 hours;

S4, after the high safety sodium ion battery enters the constant voltage charging stage, take any 2-hour period from 30-40 hours, capacity grading is based on the ratio R. R is the ratio of average hourly capacity during constant voltage charging to the total battery capacity. $R < 0.2\%$ is classified as Class A, $R = 0.2-0.4\%$ is classified as Class B, and $R > 0.4\%$ is classified as Class C.

A capacity grading method for a high safety sodium ion battery as mentioned in above, characterized in that the selected Class A battery is applied for an energy storage module in a backup power system; The selected B-class batteries are used as energy storage modules in industrial and commercial energy storage systems; The selected Class B batteries are also can be used as energy storage modules in a small-scale energy storage system.

The high safety sodium ion battery classified by the capacity grading method as claimed above, used as the energy storage module in a backup system, comprising a positive electrode, a negative electrode, and the electrolyte. The positive electrode and negative electrode are both composed of active materials, conductive agents, and binders, characterized in that the active materials of the positive electrode and negative electrode are both made of highly stable polyanionic materials, and there is no interface reaction happens with the electrolyte and the active materials used in the electrodes.

A high safety sodium ion battery as mentioned in above, the active materials of the positive and negative electrodes are both phosphate compounds with the fast conduction structure of sodium ions.

A high safety sodium ion battery as mentioned in above, the active material of the positive electrode is selected from at least one of $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Fe}_{2.5}\text{Ti}_{0.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Fe}_{3-x}\text{Mn}_x(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, and $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$, wherein $0 < x < 3$;

The active material of the negative electrode is selected from at least one of $\text{NaTi}_2(\text{PO}_4)_3$, $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$, or $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$.

A high safety sodium ion battery as mentioned in above, which is characterized in that there is no solid electrolyte phase generated during the battery performance. and the interface between the positive electrode and the electrolyte does not generate an electrochemical boundary facial phase.

A high safety sodium ion battery as mentioned in above, characterized in that the electrolyte uses at least one of methyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, dimethyl carbonate, and diethylene glycol dimethyl ether as an organic solvent.

A high safety sodium ion battery as mentioned in above, characterized in that the electrolyte uses at least one of sodium perchlorate, sodium bis (oxalate) borate, sodium bis (salicylic acid) borate, and sodium tetraphenylborate as the electrolyte salt.

A high safety sodium ion battery as mentioned in above, characterized in that the individual battery capacity of the high safety sodium ion battery is 100-350Ah.

An application of a high safety sodium ion battery as an energy storage module in a backup power system, when the floating charge of the single high safety sodium ion battery for one hour is less than 0.2 % of the total battery capacity, it is used as an energy storage module in the backup power system.

The highly safe sodium ion battery of the present invention and its application and capacity grading method have the following beneficial effects:

- (1) The crystal structure of the negative electrode active material is stable, and for phosphate compounds crystal structure, the distance between P-O and Fe-O atoms does not change much during the charging and discharging process. The volume effect of the material is relatively small (about 6%), so it has extremely high structural stability and fatigue resistance; Even under overcharging, phosphate compounds do not produce free oxygen and have low reactivity with organic electrolytes, resulting in superior electrical safety performance; In addition, phosphate compounds have high P-O bond energy, remain unchanged below 400 °C, and exhibit excellent thermal stability;

(2) As both positive and negative electrodes being ion intercalation materials, the battery system is highly stable. a) Without the "generation-dissolution-reconstruction" process of SEI film, the sodium ions are not consumed; b) For ionic intercalation materials, it will not produce sodium-dendrites, and the current approaches zero during long-term floating charge. Unlike the traditional lithium-ion battery, when the battery was overcharging,, the excessive lithium ions are released from the cathode material, and the excess lithium ions are hard inserted into the carbon anode structure, which inducing deposition on the carbon surface to form lithium dendrites, causing the collapse of the positive electrode materials structure and permanent damage to the electrode.(see reference: Research on the Application of Float Charge Protected Lithium Iron Phosphate Battery, Cen Kai jia, Da Zhong Yong Dian 2016/9).

Description of the Drawings

Figure 1 shows the 0.1C charge/discharge curve of the high safety sodium ion battery of the present invention;

Figure 2 shows the current voltage curve of the battery during float charging in Example 1;

Figure 3 shows an enlarged current curve of the battery during float charging in Example 1;

Figure 4 shows the capacity curve of the battery during float charging in Example 1;

Figure 5 shows an enlarged current curve of a Comparative example during float charging;

Figure 6 Flow chart of high safety sodium ion battery capacity grading method;

Figure 7 Comparison of float charging performance of different types of batteries;

Figure 8 Comparison of cycling performance of different types of batteries .

Detailed Description of the Invention

In order to enable technical person in this field to better understand the technical solution of the present invention, the following is a detailed explanation of its specific

implementation method in conjunction with the accompanying drawings:

An embodiment of the present invention relates to a high safety sodium ion battery, comprising a positive electrode, a negative electrode, and an electrolyte. The positive electrode and negative electrode are both composed of active materials, conductive agents, and binders. The active materials of the positive electrode and negative electrode are both made of highly stable polyanionic materials. The active materials used in the positive electrode and negative electrode will not undergo interfacial reactions with the electrolyte; The capacity of a single battery floating charge for one hour is less than 0.4 ‰ of the total battery capacity.

Table 1 Positive and Negative Active Materials of examples:

Number	Positive electrode active material	Negative electrode active material	Battery capacity/mAh	Float stable current/mA	The ratio R
Example 1	$\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	$\text{NaTi}_2(\text{PO}_4)_3$	520	0.1	0.19 ‰
Example 2	$\text{Na}_4\text{Fe}_{2.5}\text{Ti}_{0.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	$\text{NaTi}_2(\text{PO}_4)_3$	530	0.09	0.16 ‰
Example 3	$\text{Na}_4\text{Fe}_{2.5}\text{Mn}_{0.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	$\text{Na}_3\text{MnTi}(\text{PO}_4)_3$	515	0.12	0.23 ‰
Comparative example	$\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	Hard carbon	550	2	3.6 ‰

Example 1:

A high safety sodium ion battery, referring to the positive and negative electrode active materials in Table 1, using $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ as the positive electrode active material, $\text{NaTi}_2(\text{PO}_4)_3$ as the negative electrode active material, acetylene black as the conductive agent, and 5 wt.% PVDF (polyvinylidene fluoride) NMP (N-methylpyrrolidone) solution as the adhesive. The electrode were prepared by slurry-coating according to the ratio of active material: conductive agent: adhesive: 90:5:5, and assembled in pouch cell see Example 1 Test . The electrolyte salt in the electrolyte is sodium perchlorate, with a concentration of 1mol/Kg, and the solvent is propylene carbonate.

Please refer to Figure 1. The battery in Example 1 was calibrated for capacity by

charging and discharging at 0.1C between 0.3-1.6V. The charging and discharging curve is shown in Figure 1, and it can be seen that the capacity of the battery cell is 520mAh.

Please refer to Figures 2 and 3. The battery in Example 1 adopts a constant current constant voltage floating charge mode, with a current of 50 milliamperes (0.1C) at constant current and a voltage of 1.3V at constant voltage for 168 hours. The current voltage curve during the floating charge stage is shown in Figure 2. It can be seen that after switching to constant voltage charge mode, the charging current starts to decrease from 50mA, and after 20 hours of constant voltage charging (total charging time of 30 hours), the current basically stabilizes. The current during the floating charge stage is mostly less than 0.1 milliamperes for most of the floating charging time (>98%), as shown in Figure 3. The calibrated capacity of the entire battery is 520 milliamperes, and the ratio R was calculated as 0.19‰.

Please refer to Figure 4. The battery in Example 1 is normally tested (0.1C charge and discharge) for 10-20 times after the activation. The capacity of the battery did not change during the floating charge stage. This phenomenon confirms that the battery system does not have any electrolyte reactions, dissolution of active substances or other side reactions, and no additional capacity needs to be supplied during the floating charge process.

Example 2:

A high safety sodium ion battery, referring to the positive electrode active material and negative electrode active material in Table 1, using $\text{Na}_4\text{Fe}_{2.5}\text{Ti}_{0.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ as the positive electrode active material and $\text{NaTi}_2(\text{PO}_4)_3$ as the negative electrode active material. The electrode were prepared by manual slurry-coating according to the method in Example 1, and the pouch cell in Example 2 was assembled for testing. The capacity of the battery cell was 530mAh, and the ratio R was 0.16 ‰.

Example 3:

A high safety sodium ion battery, referring to the positive and negative electrode active materials in Table 1, using $\text{Na}_4\text{Fe}_{2.5}\text{Mn}_{0.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ as the positive electrode active material and $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$ as the negative electrode active material. According to the method described in Example 1, the electrode are prepared by manual slurry coating, and

the pouch cell of Example 3 is assembled for testing. The capacity of the battery cell is 515mAh, and the ratio R was 0.23 ‰.

Comparative example:

Please refer to Figure 5. Referring to the positive and negative electrode active materials in Table 1, $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ is used as the positive electrode active material, hard carbon is used as the negative electrode active material, and the electrodes are prepared by manual coating according to the method in Example 1. When the rated capacity of the battery is 550mA, the current in the floating charge stage is shown in Figure 5. It can be seen that the current in the stable floating charge stage is relatively high, always higher than 2mA, and the ratio R is greater than 3.6 ‰. This is mainly because the solvent undergoes a reduction reaction on the surface of the hard carbon negative electrode, while the SEI film undergoes continuous reforming and repair reactions. However, when $\text{NaTi}_2(\text{PO}_4)_3$ is used as the negative electrode, due to its sodium insertion potential (2.1V) being much higher than the sodium evolution potential (0V), there will be no SEI generated (reference: Analysis and Improvement of Bulging Causes in Lithium ion Battery Float Charging Test, Li Huifang, Gao Junkui, Li Fei, Huang Jiajian, Power Technology, 2023/12), which can meet the technical requirements of long-term floating charge and be widely applied in UPS systems.

Please refer to Figure 6, 200 batteries with rated capacity of 260Ah were assembled according to the active materials and electrolyte in Example 1, and divide them into different classes according to the following method:

S1, the assembled battery is charged and activated in an environment of 40-50 °C;

S2, perform 0.1C charging and discharging for capacity calibration of batteries between 0.3-1.6V. If the capacity is greater than 260Ah, it is considered qualified. The number of qualified batteries is 193;

S3, charge the qualified battery with a current of 0.1C to 1.3V, and then switch to constant voltage charging. The constant voltage charging time is 40 hours;

S4, take any 2-hour period from 30-40 hours, capacity grading is based on the ratio R. R is the ratio of average hourly capacity during constant voltage charging to the total

battery capacity. Divide the batteries into different classes depending the ratio R.

Please refer to Figures 7 and 8. According to $R < 0.2\%$ for Class A, $R = 0.2-0.4\%$ for Class B, and $R > 0.4\%$ for Class C, a total of 142 Class A products, 27 Class B products, and 24 Class C products were classified. In order to verify the effectiveness of classification, 12 batteries from Class A, Class B, and Class C products were randomly selected and assembled in series into a small module with a rated voltage of 12V respectively to simulate "UPS" for performance testing. The testing method is as follows: the 12V small module are charged at a voltage of 1.3V for 14 days, and then charged and discharged at 0.1C for 2 cycles of capacity calibration, and then repeat the above steps for testing. From Figure 7, it can be seen that during a total of 15 cycles conducted over 8 months, the rated capacity of Class A batteries show no decay, while the capacity retention rate of Class B batteries is 91.5%, and the capacity retention rate of Class C batteries is the worst at 87.4%. This is because the differences between individual batteries during the preparation process can be amplified during long-term floating charge under high voltage, such as micro short circuits causing a decrease in individual battery capacity and affecting module capacity.

In order to compare the differences between cycling and floating charge, at the same time, 12 batteries of Class A, Class B, and Class C were randomly selected and assembled into a small module with a rated voltage of 12V for cycling testing. The testing method is as follows: after the battery is divided, 1C charging and discharging cycles are carried out at a voltage of 0.3-1.6V, 0.1C charging and discharging cycles are carried out every 500 cycles for capacity calibration, and repeat the above steps for testing. From Figure 8, it can be seen that the order of decay is still the best for Class A, followed by Class B, and the worst for Class C. However, the capacity retention rate of Class B batteries (with the same capacity retention rates of 1C and 0.1C) is 96.5%, and the capacity retention rate of Class C batteries (with the same capacity retention rates of 1C and 0.1C) is 90.3%. Therefore, Class B and C batteries are not suitable for assembling energy storage modules as UPS, but can be used as energy storage systems. According to the decay rate of Class B and C batteries, the capacity decays to 70%, with 20000 and 7000 cycles, respectively. Class B batteries can be fully used as energy storage modules in industrial and commercial energy

storage systems. Class C batteries can be used in small energy storage systems (<20KWh), such as electric bicycle or street lights.

According to the capacity grading method of the high safety sodium ion battery of the present invention, when the high safety sodium ion battery is used as an energy storage module in the backup system, a Class A battery with $R < 0.2\text{‰}$ is selected for assembly; When using high safety sodium ion batteries as energy storage modules in industrial and commercial energy storage systems, B-class batteries with $R = 0.2\text{‰} - 0.4\text{‰}$ can be selected for assembly; As an electric vehicle or a small power supply system such as street lights (<20KWh), Class C batteries with $R > 0.4\text{‰}$ can be selected for assembly.

In summary, the high safety sodium ion battery and its application and capacity grading method of the present invention use highly stable lattice structure materials as active substances, and there is no solid electrolyte interphase film generated during the operation of the battery, which can meet the technical requirements of long-term float charging and be widely applied in UPS systems.

Ordinary technical personnel in this field should recognize that the above embodiments are only used to illustrate the present invention and not as a limitation of the present invention. As long as they fall within the substantive scope of the present invention, any changes or variations to the above embodiments will fall within the scope of the claims of the present invention.

Claims

1. A capacity grading method for a sodium ion battery for use as an energy storage module, the method comprising:

S1, activating the sodium ion battery in an environment of 40-50 °C;

S2, then charging and discharging the sodium ion battery between 0.3-1.6V for capacity calibration by 0.1C, and determining whether the sodium ion battery is qualified based on a rated capacity of the sodium ion battery;

S3, if the sodium ion battery is determined to be qualified, charging the sodium ion battery to 1.3V at a current of 0.1C, and then switching to constant voltage charging, with a constant voltage charging time of 40 hours;

S4, after the sodium ion battery enters the constant voltage charging, take any 2-hour period from a period starting from the 30th hour to the 40th hour of the constant voltage charging, capacity grading the sodium ion battery based on R, wherein R is a ratio of average hourly capacity during constant voltage charging to a total capacity of the sodium ion battery, if $R < 0.2\%$ the sodium ion battery is classified as Class A, if $R = 0.2\% - 0.4\%$ the sodium ion battery is classified as Class B, if $R > 0.4\%$ the sodium ion battery is classified as Class C.

2. The capacity grading method for a sodium ion battery according to claim 1, characterized in that the sodium ion battery classified as Class A is applied for an energy storage module in a backup power system; the battery classified as Class B is used as an energy storage module in industrial and commercial energy storage systems; the sodium ion battery classified as Class B can also be used as an energy storage module in a small-scale energy storage system.

3. The capacity grading method for a sodium ion battery according to claim 1, characterized in that the sodium ion battery comprises a positive electrode, a negative electrode, and an electrolyte; the positive electrode and the negative electrode are both composed of active materials, conductive agents, and binders, wherein the active materials of the positive electrode and the negative electrode are both made of polyanionic materials, and no interface reaction happens

between the electrolyte and the active materials used in the positive and negative electrodes.

4. The capacity grading method for a sodium ion battery according to claim 3, characterized in that the active materials of the positive and negative electrodes are both phosphate compounds with a fast conduction structure of sodium ions.

5. The capacity grading method for a sodium ion battery according to claim 4, characterized in that the active material of the positive electrode is selected from at least one of $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Fe}_{2.5}\text{Ti}_{0.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Fe}_{3-x}\text{Mn}_x(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, and $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$, wherein $0 < X < 3$;

the active material of the negative electrode is selected from at least one of $\text{NaTi}_2(\text{PO}_4)_3$, $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$, and $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$.

6. The capacity grading method for a sodium ion battery according to claim 5, characterized in that there is no solid electrolyte phase generated during the battery performance, and an interface between the positive electrode and the electrolyte does not generate an electrochemical boundary facial phase.

7. The capacity grading method for a sodium ion battery according to claim 3, characterized in that the electrolyte uses at least one of methyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, dimethyl carbonate, and diethylene glycol dimethyl ether as an organic solvent.

8. The capacity grading method for a sodium ion battery according to claim 3, characterized in that the electrolyte uses at least one of sodium perchlorate, sodium bis (oxalate) borate, sodium bis (salicylic acid) borate, and sodium tetraphenylborate as electrolyte salt.

9. The capacity grading method for a sodium ion battery according to claim 3, characterized in that an individual battery capacity of the sodium ion battery is 100-350Ah.