

A sodium ion battery

Technical field

[1] The present invention relates to the field of secondary energy storage batteries, specifically to an electrochemical energy storage battery using polyanion material.

Background technology

[2] In large-scale electrochemical energy storage systems, rechargeable batteries with long lifespan, low cost, and environmental friendliness are important directions for development. However, existing energy storage technologies, such as lithium-ion batteries, are unable to meet the requirements of large-scale energy storage due to their scarcity of lithium resources and high prices. Therefore, in recent years, researchers have expanded their horizons to some resource rich and low-cost alkali metals or high valence metal elements, such as Na^+ , Mg^{2+} , Zn^{2+} , Al^{3+} , etc., in order to utilize the embedding reactions of these ions to construct low-cost and high-performance new secondary battery systems. Among numerous battery systems, sodium ion batteries have attracted great attention due to their abundant reserves and similar preparation processes to large-scale production of lithium-ion batteries.

[3] The existing sodium ion battery energy storage system mainly consists of layered oxides, Prussian blue analogues, and polyanions as cathode electrode materials, and hard carbon as anode electrode materials. The layered oxide in the cathode electrode material has the characteristics of high specific capacity and rate performance, but its stability in air is poor. Due to the involvement of multiple phase transitions and large volume strain during charging and discharging, it leads to poor cycling stability; Prussian blue analogues have the characteristics of low cost, high specific capacity, and high magnification, but there is difficulty in removing crystalline water, which leads to gas evolution and swelling during the battery cycling, resulting in instability; Polyanionic compounds are three-dimensional framework structures composed of strong covalent bonds, thus possessing high structural stability. Its chemical formula is $\text{Na}_x\text{M}_y(\text{X}_a\text{O}_b)_z$, where M is a transition metal, x is phosphorus, sulfur, silicon, tungsten, etc., and z is F, OH, etc. The strong induction effect of polyanions can regulate the energy of transition metal oxidation-reduction pairs, resulting in higher working voltage. Its stable

framework structure induce a fast sodium ion diffusion rate and minimal volume change and phase transition during ion deintercalation, ensuring good cycling stability, thermal stability, and excellent safety in sodium ion batteries.

[4] The existing anode electrode materials for sodium ion batteries are mainly amorphous soft carbon and hard carbon materials. Hard carbon with superior capacity performance is potential for developing high-energy density sodium batteries. However, the current cost remains high. The precursor source, batch consistency, and process adaptability of hard carbon in anode electrode materials need to be broken through, which is a key factor restricting their industrialization. In addition, the embedding mechanism of sodium ions in hard carbon is currently unclear, making it difficult to provide guidance for the synthesis path.

[5] In addition to carbon materials, titanium-based anode electrode materials have also received widespread attention from researchers. Due to its low oxidation-reduction potential, titanium is a suitable anode electrode material choice among variable valence transition metals, and the tetravalent titanium element can stably exist in air, ensuring the crystal structure stability of the prepared material. Among them, polyanionic titanium-based materials sodium titanium phosphate and sodium titanium manganese phosphate have NASICON type three-dimensional skeleton structures, and sodium ions can quickly diffuse in the three-dimensional channels in their crystal structures. Although the voltage of titanium-based materials is relatively high, their lattice structure is stable, the volume strain is small, which can achieve long-life cycling.

[6] Among polyanionic materials, vanadium based materials weaken the cost advantage due to their high price and toxicity, and are constrained in large-scale applications. Sulfate based materials are sensitive to air, which increases the difficulty of material preparation and battery assembly processes; Phosphates and mixed phosphate systems are the best choices for large-scale energy storage electrochemical systems due to their stable materials and ease of mass production. Low-cost element of Fe, Mn, and Ti ions are chosen for variable valence metal ions, ensuring the low price principle of raw materials. They are also bulk products suitable for mass production.

[7] In different electrolyte systems, the capacity of the battery is controlled by different electrodes. In aqueous electrolytes, when metal ions are removed from the electrolyte, some

cathode electrode materials will react with water under strong coupling of water molecules, making it difficult to achieve complete insertion. Additionally, materials containing Mn ions will experience capacity decay due to the disproportionation reaction of trivalent manganese. Therefore, a chemically stable anode electrode is used to control the capacity in aqueous electrolytes; In organic electrolyte systems, in order to improve energy density, the electrochemical stability of the cathode electrode is greatly improved, but the load is low. Therefore, using the cathode electrode to control capacity can increase the volume energy density of the battery.

[8] To achieve the requirements of low cost and long-life span for energy storage batteries, it is necessary to start from the essential crystal structure of the cathode and anode electrode materials themselves, choosing materials with high-strength lattice structure, small volume strain, and abundant sources. The present invention proposes a battery with both cathode and anode electrode materials made of polyanionic compounds, which can fully utilize the advantages of stable lattice structure of polyanionic materials and achieve long-term application.

Content of the invention

[9] The present invention provides a sodium ion battery. In one embodiment, the sodium ion battery comprises a cathode electrode, an anode electrode, and an electrolyte, characterized in that: both the cathode electrode and the anode electrode are selected phosphate compounds with sodium ion fast conductivity structures; The cathode electrode is selected from at least one of $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Fe}_{3-x}\text{Mn}_x(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, and $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$; Among them, $0 < x < 3$; And the anode 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 $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$.

Figure Description

[10] Figure 1 shows the charging and discharging curve of the battery in Example 1 of the present invention.

[11] Figure 2 shows the cycling performance of the battery of Figure 1 at 1C.

[12] Figure 3 shows the Coulombic efficiency of the first 3700 cycles of the battery in Figure 1.

[13] Figure 4 shows the EIS spectrum of the 6*6cm electrode in Example 2 of the present invention.

Examples

[14] The present invention provides a sodium ion battery. In one embodiment, the sodium ion battery comprises a cathode electrode, an anode electrode, and an electrolyte, characterized in that: both the cathode electrode and the anode electrode are selected from phosphate compounds with sodium ion fast conductivity structures; The cathode electrode is selected from at least one of $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Fe}_{3-x}\text{Mn}_x(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, and $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$, where $0 < x < 3$; And the anode 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 $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$.

[15] In one embodiment, the electrolyte is selected from an organic electrolyte, an inorganic aqueous solution, or a mixture of both.

[16] In one embodiment, the organic electrolyte comprises at least one of methyl ethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, dimethyl carbonate, trimethyl phosphate, triethyl phosphate, or diethylene glycol dimethyl ether.

[17] In one embodiment, the inorganic aqueous solution comprises at least one of sodium hexafluorophosphate, sodium difluorosulfonamide, sodium perchlorate, or sodium difluorophosphate.

[18] In one embodiment, the electrolyte is an organic electrolyte, and the battery capacity of the sodium ion battery is controlled by the cathode electrode, with a cathode and anode electrode capacity ratio of 1: (1.02-1.10).

[19] In one embodiment, the electrolyte is an inorganic aqueous solution or a mixture of organic electrolytes and inorganic aqueous solution, and the battery capacity of the sodium ion battery is controlled by the anode electrode, with a cathode anode electrode capacity ratio of (1.05-1.50): 1.

[20] In one embodiment, the cathode or anode electrode is coated with organic and inorganic carbon.

[21] In one embodiment, the cathode electrode is $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, the anode electrode is $\text{NaTi}_2(\text{PO}_4)_3$, and the electrolyte is propylene carbonate and sodium perchlorate

[22] In one embodiment, the cathode electrode is $\text{Na}_4\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, the anode electrode is $\text{NaTi}_2(\text{PO}_4)_3$, and the electrolyte is propylene carbonate and sodium perchlorate.

[23] In one embodiment, the cathode electrode is $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, the anode electrode is $\text{NaTi}_2(\text{PO}_4)_3$ or $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$, and the electrolyte is a Na_2SO_4 aqueous solution.

[24] In one embodiment, the cathode electrode is $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$, the anode electrode is $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$, and the electrolyte is Na_2SO_4 aqueous solution.

[25] In one embodiment, the design ratio of the cathode and anode electrode capacity of the sodium ion battery is 1:1.05.

[26] In one embodiment, the design ratio of the cathode and anode electrode capacity of the sodium ion battery is 1.3:1.

[27] In one embodiment, the concentration of the electrolyte is 0.5-3mol/kg.

[28] In one embodiment, the discharge medium voltage of the sodium ion battery is 1.0 to 1.8V.

[29] Example 1

[30] The cathode electrode material uses sodium iron pyrophosphate sodium $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, the anode electrode material uses sodium titanium phosphate sodium $\text{NaTi}_2(\text{PO}_4)_3$, and the electrolyte uses organic electrolyte (propylene carbonate + sodium perchlorate, concentration 1mol/kg). The design ratio of cathode and anode electrode capacity is 1:1.05. The charge discharge curve of the battery is shown in **Figure 1**. At a 1C rate, the actual cycle number is 3700, and the estimated cycle life (greater than 80% of the initial capacity) is greater than 30000 cycles. Please refer to **Figure 2**, The average coulombic efficiency of the first 3700 cycles is 99.95%, as shown in **Figure 3**.

[31] Example 2

[32] The cathode electrode material is manganese sodium pyrophosphate phosphate, and the anode electrode material is titanium sodium phosphate. The electrolyte is a water-based electrolyte (Na_2SO_4 aqueous solution, 1mol/Kg), with a designed cathode and anode electrode capacity ratio of 1.3:1. During the preparation process, the electrode material is coated with organic and inorganic carbon, greatly improving the electronic conductivity of the active material. The EIS spectrum of the 6*6cm electrode is shown in **Figure 4**.

[33] Example 3

[34] We designed and prepared different cathode and anode electrode materials, assembled the entire battery, and tested the electrochemical performance in different electrolyte systems. The discharge voltage of the battery under different cathode and anode electrode material matching is shown in **Table 1**.

Table 1: Discharge medium voltage of the sodium ion battery of the present invention

Number	cathode electrode	anode electrode	electrolyte	Discharge medium voltage
1	$\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	$\text{NaTi}_2(\text{PO}_4)_3$	$\text{PC}+\text{NaClO}_4$	1.1
2	$\text{Na}_4\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	$\text{NaTi}_2(\text{PO}_4)_3$	$\text{PC}+\text{NaClO}_4$	1.5
3	$\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	$\text{NaTi}_2(\text{PO}_4)_3$	$\text{H}_2\text{O}+\text{Na}_2\text{SO}_4$	1.8
4	$\text{Na}_3\text{MnTi}(\text{PO}_4)_3$	$\text{Na}_3\text{MnTi}(\text{PO}_4)_3$	$\text{H}_2\text{O}+\text{Na}_2\text{SO}_4$	1.3
5	$\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$	$\text{H}_2\text{O}+\text{Na}_2\text{SO}_4$	1.3

Claims

1. A sodium ion battery comprising a cathode electrode, an anode electrode, and an electrolyte, characterized in that:

The cathode and anode electrodes both use phosphate compounds with sodium ion fast conductivity structures,

The cathode electrode is selected from at least one of $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Fe}_{3-x}\text{Mn}_x(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ and $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$, among them, $0 < x < 3$; and

The anode electrode is selected from at least one of $\text{NaTi}_2(\text{PO}_4)_3$, $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$, $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$.
2. The sodium ion battery according to claim 1, characterized in that the electrolyte is selected from an organic electrolyte, an inorganic aqueous solution, or a mixture of both.
3. The sodium ion battery according to claim 2, characterized in that the organic electrolyte comprises at least one of methyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, dimethyl carbonate, trimethyl phosphate, triethyl phosphate, or diethylene glycol dimethyl ether.
4. The sodium ion battery according to claim 2, characterized in that the inorganic aqueous solution comprises at least one of sodium hexafluorophosphate, sodium difluorosulfonamide, sodium perchlorate, or sodium difluorophosphate.
5. The sodium ion battery according to claim 2, characterized in that the electrolyte is an organic electrolyte, and the battery capacity of the sodium ion battery is controlled by the cathode electrode, with a cathode and anode electrode capacity ratio of 1: (1.02-1.10).
6. The sodium ion battery according to claim 2, characterized in that the electrolyte is an inorganic aqueous solution or a mixture of organic electrolyte and inorganic aqueous solution, and the battery capacity of the sodium ion battery is controlled by the anode electrode, with a cathode :anode electrode capacity ratio of (1.05-1.50): 1.
7. The sodium ion battery according to claim 1, characterized in that the cathode or anode electrode is coated with organic and inorganic carbon.

8. The sodium ion battery according to claim 1, characterized in that: the cathode electrode is $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, the anode electrode is $\text{NaTi}_2(\text{PO}_4)_3$, and the electrolyte is propylene carbonate and sodium perchlorate.
9. The sodium ion battery according to claim 1, characterized in that: the cathode electrode is $\text{Na}_4\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, the anode electrode is $\text{NaTi}_2(\text{PO}_4)_3$, and the electrolyte is propylene carbonate and sodium perchlorate.
10. The sodium ion battery according to claim 1, characterized in that: the cathode electrode is $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, the anode electrode is $\text{NaTi}_2(\text{PO}_4)_3$ or $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$, and the electrolyte is a Na_2SO_4 aqueous solution.
11. The sodium ion battery according to claim 1, characterized in that: the cathode electrode is $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$, the anode electrode is $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$, and the electrolyte is Na_2SO_4 aqueous solution.
12. The sodium ion battery according to claim 8, characterized in that the design ratio of the cathode and anode electrode capacities of the sodium ion battery is 1:1.05.
13. The sodium ion battery according to claim 10, characterized in that the design ratio of the cathode and anode electrode capacities of the sodium ion battery is 1.3:1.
14. A sodium ion battery according to any one of claims 8 to 13, characterized in that the concentration of the electrolyte is 0.5-3mol/kg.
15. A sodium ion battery according to any one of claims 8 to 13, characterized in that the discharge medium voltage of the sodium ion battery is 1.0 to 1.8 V.