

MOLDABLE ELECTRODE AND AQUEOUS SODIUM BATTERY AND PREPARATION METHODS THEREOF

FIELD OF THE INVENTION

[0001] The invention belongs to the field of aqueous battery materials, and specifically relates to a moldable electrode and its preparation method, and aqueous sodium battery and its preparation method.

BACKGROUND OF THE INVENTION

[0002] So far, resource-based fossil fuels are still the main source of power for mankind. Carbon emission resulting from extensive use of these fuels is the main cause of the current global greenhouse effect. Only through energy storage systems can intermittent renewable energy represented by solar and wind energy be stored and released into the electric grid. Therefore, large-scale energy storage technology is the foundation of new energy promotion and energy innovation. It is an important part of the national energy strategic plan, enabling improvement of the national energy infrastructure and safe and stable operation of the energy grid. Electrochemical batteries show great advantages due to their high conversion efficiency, flexible assembly, and freedom from geographical constraints, and are the focus of research on energy storage technology, gradually moving from prototype demonstration to commercial operation. Lithium batteries containing organic electrolytes are widely used in mobile electronic devices, electric vehicles, and various high specific energy applications. But large-scale (MWh level and above) energy storage requires big investment and long maintenance periods, and there are issues of battery uniformity and difficulty in operation. In recent years, a series of fire accidents in energy storage systems and power stations have occurred around the world, indicating that intrinsic safety of energy storage batteries is an urgent problem to be solved before such batteries can be popularized.

[0003] A water-based ion battery with a neutral salt solution as the electrolyte avoids the flammability of organic electrolytes. It overcomes the shortcomings of high pollution, short life span (such as lead-acid batteries) and high cost (such as nickel-metal hydride batteries). A new battery with the characteristics of safety, low-cost, long-life span, environmental friendliness and recyclability is an ideal system for large-scale energy storage. An aqueous

sodium battery is one of the energy storage batteries with the most investment potential. There are certain challenges, such as the relatively low specific energy, so that thick electrodes (thickness greater than 1.0 mm) must be used to increase the specific energy of the battery. Existing mature manufacturing processes, whether the coating technology of lithium batteries or the drawing process of nickel-metal hydride batteries, can only make thin electrodes, not suitable for aqueous sodium batteries.

[0004] Patent CN104871349A indicates that its aqueous sodium battery uses sheet-shaped square electrodes to be stacked and assembled in sequence, and the electrodes are formed by pressing a mixture of active material, conductive agent and binder. The aspect ratio (the ratio of length to thickness) limits the development of large-area electrodes, so that a single cell contains hundreds or thousands of electrodes, making the battery assembly process extremely complicated and difficult to ensure the consistency of the battery. and the arrangement of multiple electrodes, whereby affecting the electrochemical performance and life span of the battery, and limiting its engineering application.

[0005] Patent CN109351793A describes an electrode extrusion device and system. The active material is extruded and then coated on the current collector to form the electrodes. This system is composed of two parts: shaping of the active material and configuration of the electrode sheet. The system involves processes such as mixing, kneading, and conveying of active materials, uncoiling of current collector, and coating, drying, compacting, and winding of electrode sheet. Each process has a certain uncontrollable effect on the actual product performance, and the complicated and tedious preparation process will seriously reduce controllability, thereby affecting the performance of the battery.

SUMMARY OF THE INVENTION

[0006] The purpose of the present invention is to provide a moldable electrode for an aqueous sodium battery in order to address issues of complicated production and assembly of existing aqueous sodium batteries, poor process controllability, and poor battery performance consistency.

[0007] The technical scheme of the present invention is: moldable electrodes for aqueous sodium batteries, wherein the components and mass percentages are as follows:

positive/negative electrode active material 40-50%, conductive material 3-10%, binder 0 ~ 10%, crosslinking agent 0-5%, humectant 0-10%, surfactant 0-3%, electrolyte salt 0-30% and deionized water 10-30%.

[0008] Positive electrode active material is for a positive electrode, and negative electrode active material is for a negative electrode. The positive electrode active material includes, but is not limited to, transition metal oxides, phosphates, Prussian blue analogs, and organic electrode materials; the negative active material includes, but not limited to, activated carbon, Prussian blue analogs, sodium storage organics, and titanium phosphorus-based oxides.

[0009] The conductive material includes, but is not limited to, artificial graphite, natural graphite, activated carbon, graphene, carbon black, carbon fiber, and mesoporous carbon.

[0010] The binder includes, but is not limited to, polyacrylic acid, polyvinyl alcohol, staghorn pectin, hydroxyethyl cellulose, xanthan gum, polytetrafluoroethylene, and PVDF.

[0011] The crosslinking agent includes, but is not limited to, silane crosslinking agents, polyvinyl alcohol, and boric acid; and the humectant includes, but is not limited to, glycerin, sorbitol, propylene glycol, and polyethylene glycol.

[0012] The surfactant includes, but is not limited to, sodium dodecylbenzene sulfonate and stearic acid.

[0013] The electrolyte salt includes, but is not limited to, sodium sulfate, sodium nitrate, sodium hypochlorite, sodium sulfite, sodium chloride, sodium sulfonate, and sodium phosphate.

[0014] The second objective of the present invention is to provide a method for preparing moldable electrodes for an aqueous sodium battery, including the following steps:

S1: Uniformly mixing an electrolyte salt and deionized water to form an electrolyte solution;

S2: Adding a surfactant and humectant to the electrolyte solution and mixing them to give a uniform solvent matrix;

S3: Adding a conductive material into the solvent matrix, and making the conductive material uniformly dispersed in the solvent matrix through high-speed stirring;

S4: If a positive electrode is to be prepared, adding a positive electrode active material and a binder; if a negative electrode is to be prepared, adding a negative electrode active

material and a binder, and then mixing evenly at high speed; and

S5: Adding a cross-linking agent to cross-link with the binder under low speed stirring to form a three-dimensional network structure of a moldable electrode as a paste for use in an aqueous sodium battery.

[0015] In the above preparation steps, the weight percentages of the components are: positive/negative electrode active material 40-50%, conductive material 3-10%, binder 0-10%, cross-linking agent 0-5%, humectant. 0-10%, surfactant 0-3%, electrolyte salt 0-30%, and deionized water 10-30%.

[0016] A third objective of the present invention is to provide a method for preparing an aqueous sodium battery, comprising the following steps:

Z1: Placing a bottom pressure plate and, on top of it, a bottom current collector ;

Z2: Placing a conductive plate on the current collector, and adding an appropriate amount of negative moldable electrode paste on the conductive plate;

Z3: Placing a separator over the negative moldable electrode paste, and pressing the negative moldable electrode paste into shape;

Z4: Adding an appropriate amount of positive moldable electrode paste on the separator;

Z5: Repeating the above steps Z2-Z4 a number of times until the number of electrode layers required for a specific battery capacity is completed; pressing each positive moldable electrode paste into shape every time a conductive plate is put over a positive moldable electrode paste; and

Z6: Placing a top conductive plate, top current collector and top pressure plate in sequence to make an aqueous sodium battery with moldable electrodes.

[0017] A fourth objective of the present invention to provide an aqueous sodium battery, which includes a bottom pressure plate, a bottom current collector, a conductive plate, a negative moldable electrode, a separator, a positive moldable electrode, a top conductive plate, a top current collector and top pressure plate. Between the bottom and top pressure plates, there are several battery cells composed of conductive plates, negative moldable electrodes, separators, and positive moldable electrodes. Both sides of each conductive plate and each separator have upward protruding edges. The height of the protruding edges on each conductive

plate is the same as the thickness of the negative moldable electrode. Correspondingly, the height of the protruding edges of each separator corresponds to the thickness of the positive moldable electrode. The bottom pressure plate, the bottom current collector, the top conductive plate, the top current collector and the top pressure plate are all plate-shaped.

[0018] The beneficial effects of the present invention are:

1) The moldable electrode for an aqueous sodium battery of the present invention is a stable mixture of active material and electrolyte. The ionic and electronic impedance are greatly reduced, conducive to high output rate;

2) The design of the moldable electrode of the present invention overcomes the limitation of electrode size and shape so that batteries of different shapes and modules can be prepared to meet the requirements of different customers' demand, or product customization;

3) In a preparation method of the aqueous sodium battery of the present invention, the preparation of the electrodes and the assembly of the battery are completed simultaneously, and liquid injection is unnecessary during the assembly process, thereby greatly simplifying the battery assembly process and increasing the production efficiency;

4) Since an aqueous sodium battery made by this preparation method has no metal current collector that would corrode, the battery can be cycled for a long period of time;

4) The production flexibility of the aqueous sodium battery of the present invention has been significantly improved, allowing the battery to be deployed in a variety of products requiring different sizes, different charge and discharge rates, and different energy capacities.

BRIEF DESCRIPTION OF THE FIGURES

[0019] FIG. 1 is a flowchart illustrating the preparation process of the aqueous sodium battery of the present invention.

[0020] FIG. 2 shows an aqueous sodium battery of the present invention.

[0021] FIG. 3 is a graph showing the cycle performance of an aqueous sodium battery made in the following example.

[0022] FIG. 4 is an outline view of an aqueous sodium battery made in the following example.

[0023] FIG. 5 is a structural diagram of a battery installed within wall layers.

[0024] The labels in the figure are: bottom pressure plate 1, bottom current collector 2,

conductive plate 3, negative moldable electrode 4, separator 5, positive moldable electrode 6, top conductive plate 7, top current collector 8, top splint 9, wall layers 10, battery 11.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The present invention will be further described below in conjunction with the accompanying drawings and examples.

[0026] A moldable electrode for aqueous sodium batteries, wherein the electrode includes components and mass percentages as follows: positive/negative electrode active material 40-50%, conductive material 3-10%, binder 0-10%, crosslinking agent 0-5%, humectant 0-10%, surfactant 0-3%, electrolyte salt 0-30% and deionized water 10-30%.

[0027] The positive electrode active material includes, but is not limited to, transition metal oxides, phosphate polyanionic compounds, Prussian blue analogs, and organic electrode materials. Transition metal oxides include, but are not limited to, MnO_2 , Na_xMnO_2 ; phosphate polyanion compounds including but not limited to $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, NaFePO_4 and NaVPO_4F ; Prussian blue analogs including but not limited to $\text{Na}_2\text{NiFe}(\text{CN})_6$ and $\text{KCo}_{0.5}\text{Cu}_{0.5}\text{Fe}(\text{CN})_6$; organic electrode materials including but not limited to poly(2, 2, 6, 6)-tetramethylpiperidinyloxy-4-vinyl ether (PTVE).

[0028] The negative electrode active material includes, but is not limited to, activated carbon, Prussian blue analogs, sodium storage organics, and titanium phosphorus-based oxides. Prussian blue analogs include, but are not limited to, $\text{K}_{0.11}\text{Mn}[\text{Mn}(\text{CN})_6]_{0.83} \cdot 3.64\text{H}_2\text{O}$; sodium storage organics include, but are not limited to, polyimide, anthraquinone structure polymer, and disodium naphtholate. Titanium phosphorus-based oxides include, but are not limited to, $\text{NaTi}_2(\text{PO}_4)_3$, $\text{NaV}_3(\text{PO}_4)_3$, and $\text{Na}_2\text{VTi}(\text{PO}_4)_3$.

[0029] The conductive material includes, but is not limited to, artificial graphite, natural graphite, activated carbon, graphene, carbon black, carbon fiber, and mesoporous carbon.

[0030] A binder includes, but is not limited to, polyacrylic acid, polyvinyl alcohol, staghorn pectin, hydroxyethyl cellulose, xanthan gum, polytetrafluoroethylene and PVDF.

[0031] The crosslinking agent includes, but is not limited to, a silane crosslinking agent, polyvinyl alcohol, and boric acid.

[0032] The humectant includes, but is not limited to, glycerin, sorbitol, propylene glycol, and

polyethylene glycol.

[0033] A surfactant includes, but is not limited to, sodium dodecylbenzene sulfonate and stearic acid.

[0034] The electrolyte salt includes, but is not limited to, sodium sulfate, sodium nitrate, sodium hypochlorite, sodium sulfite, sodium chloride, sodium sulfonate, and sodium phosphate.

[0035] A method for preparing a moldable electrode of an aqueous sodium battery includes the following steps.

S1: Uniformly mixing an electrolyte salt and deionized water to form an electrolyte solution;

S2: Adding a surfactant and humectant to the electrolyte solution mixing them to give a uniform solvent matrix;

S3: Adding a conductive material into the solvent matrix, and making the conductive material uniformly dispersed in the solvent matrix through high-speed stirring;

S4: If a positive electrode is to be prepared, adding a positive electrode active material and a binder; if a negative electrode is to be prepared, adding a negative electrode active material and a binder, and then mixing evenly at high speed; and

S5: Adding a cross-linking agent to cross-link with the binder under low speed stirring to form a three-dimensional network structure of a moldable electrode as a paste for use in an aqueous sodium battery;

[0036] In the above preparation steps, the weight percentages of the components are: 40-50% of the positive/negative electrode active material, 3-10% of the conductive material, 0-10% of the binder, 0-5% of the cross-linking agent, 0-10% of the humectant, 0-3% of surfactant, 0-30% of electrolyte salt, and 10-30% of deionized water.

[0037] A method for preparing an aqueous sodium battery includes the following steps.

Z1: Placing a bottom pressure plate and, on top of it, a bottom current collector;

Z2: Placing a conductive plate on the current collector, and adding an appropriate amount of negative moldable electrode paste on the conductive plate;

Z3: Placing a separator over the negative moldable electrode paste, and pressing the negative moldable electrode paste into shape;

Z4: Adding an appropriate amount of positive moldable electrode paste on the separator;

Z5: Repeating the above steps Z2-Z4 a number of times until the number of electrode layers required for a specific battery capacity is completed; pressing each positive moldable electrode paste into shape every time a conductive plate is put over a positive moldable electrode paste; and

Z6: Placing a top conductive plate, top current collector and top pressure plate in sequence to make an aqueous sodium battery with moldable electrodes.

[0038] An aqueous sodium battery includes from bottom to top a bottom pressure plate, a bottom current collector, a conductive plate, negative moldable electrode, separator, positive moldable electrode, top conductive plate, top current collector and top pressure plate. Between the bottom and top pressure plates, there are a number of battery cells composed of conductive plates, negative moldable electrodes, separators, and positive moldable electrodes. Both sides of each conductive plate and each separator have upward protruding edges. The height of the protruding edges on each conductive plate is the same as the thickness of the negative moldable electrode. Correspondingly, the height of the protruding edges of each separator corresponds to the thickness of the positive moldable electrode. The bottom pressure plate, the bottom current collector, the top conductive plate, the top current collector and the top pressure plate are all plate-shaped.

[0039] The bottom and top pressure plates are made of any pressure-resistant materials, such as stainless steel, plastic, etc. The top current collector and the bottom current collector are made of Cu, Al or stainless steel. The separator is a porous non-woven fabric such as PP and PC. The conductive plate uses non-porous and water-impermeable conductive materials. In one embodiment, conductive carbon materials (graphite, carbon black, acetylene black, etc.) together with plastic substrates (PE, PP, etc.) are converted into diaphragms of 0.3 – 2 mm thickness by way of mixing, extrusion and blow molding. In another embodiment, non-porous and water-impermeable impregnated graphite paper/board is obtained from porous graphite paper/board by impregnation. In a third embodiment, low molecular weight polyethylene (LDPE) is used to seal the cavities of graphite paper by hot pressing to obtain impermeable graphite paper.

[0040] The positive moldable electrode and the negative moldable electrode are paste-like moldable electrodes made according to the above-mentioned materials and processes.

[0041] Example. A moldable electrode for aqueous sodium batteries: $\text{Na}_{0.44}\text{MnO}_2$ is used as the positive electrode active material, sodium titanium phosphate is used as the negative electrode active material, and a mixture of graphite and acetylene black is used as the conductive material. The mass ratio of graphite to acetylene black is 1:1. The binder is polyvinyl alcohol, the cross-linking agent is borax, the humectant is polyethylene glycol, the surfactant is sodium dodecylbenzene sulfonate, and the electrolyte salt is sodium sulfate.

[0042] The preparation method of a moldable electrode includes the following steps:

S1: sodium sulfate and deionized water are mixed to form a 1M/L electrolyte solution;

S2: sodium dodecylbenzene sulfonate (the mass ratio to the electrolyte solution is 1%) and polyethylene glycol (the mass ratio to the electrolyte solution is 2%) are added to the electrolyte solution to make a uniform solvent matrix;

S3: conductive carbon material (the mass ratio of the active material is 5:85) is added to the uniformly mixed solvent matrix, through high-speed stirring (1000 RMP) to make the carbon material uniformly dispersed in the solvent matrix;

S4: positive/negative active material and binder (the mass ratio to the active material is 5:85), are added and mixed evenly at high speed;

S5: a cross-linking agent (the mass ratio to the active material is 2:85) is added and mixed at low speed (100 RMP) to cross-link with the binder, forming a three-dimensional network structure;

wherein, the ratio of the mass of the positive/negative electrode active material, the binder and the cross-linking agent to the mass of the solvent matrix is 70:30.

[0043] The above-mentioned moldable electrode is used to prepare aqueous sodium batteries.

[0044] As shown in Figure 5, the battery can be designed as indoor-sandwich-type energy storage module, placed within the wall layers. The battery is a long strip in shape, wherein the ratio of length: width: height is 10:1:5.

[0045] Using the above-mentioned moldable electrode, an aqueous sodium battery was prepared according to the process steps of FIG.1. Z1: placing a bottom current collector on top

of a bottom pressure plate; Z2: Placing a conductive plate on the current collector, and adding an appropriate amount of negative moldable electrode paste on the conductive plate; Z3: Placing a separator on the negative moldable electrode paste, and pressing the negative moldable electrode paste into shape; Z4: Adding an appropriate amount of positive moldable electrode paste on the separator; Z5: Repeating the above steps Z2-Z4 a number of times until the number of electrode layers required for the specific battery capacity is completed, pressing each positive moldable electrode paste into shape every time a conductive plate is put over a positive moldable electrode paste; Z6: placing a top conductive plate, top current collector and top pressure plate in sequence to make an aqueous sodium battery with moldable electrodes.

[0046] In the above scheme, the pressure plates can be made of ABS plastic, the current collector can be made of stainless steel, the conductive plate can be made of impregnated graphite plate, and the separator can be made of PP porous non-woven fabric.

[0047] Figure 2 is a diagram of an aqueous sodium battery of the present invention, which includes a bottom pressure plate, a bottom current collector, a conductive plate, a negative moldable electrode, a separator, a positive moldable electrode, a top conductive plate, a top current collector and a top pressure plate. Between the bottom and top pressure plates are a number of battery cells composed of conductive plates, negative moldable electrodes, separators, and positive moldable electrodes. Both sides of each conductive plate and each separator have upward protruding edges, The height of the protruding edges on a conductive plate is the same as the thickness of the negative moldable electrode, and the height of the protruding edges of a separator corresponds to the thickness of the positive moldable electrode. The bottom pressure plate, bottom current collector, top conductive plate, top current collector and top pressure plate are all plate-shaped.

[0048] The cycling performance of the above aqueous sodium battery is shown in FIG.3 which shows that the aqueous sodium battery is cycled more than 6000 times, and the battery capacity stays as high as 85%.

[0049] The aqueous sodium battery of the present invention can be mass-produced on an automatic assembly line, wherein the production flexibility is greatly improved, and the battery can be deployed in various products with different sizes, different charge and discharge rates

and different energy capacities wherein the shape of the battery can be designed according to the application environment.

[0050] The above are only a few preferred embodiments of the present invention, but the scope of protection of the present invention is not limited thereto. In view of the present disclosure, any person skilled in the art can easily contemplate changes and replacements of the invention that should be covered by the protection scope of the present invention. Therefore, the protection scope of the present invention should be defined by the protection scope of the claims.

WHAT IS CLAIMED IS:

1. A moldable electrode for an aqueous sodium battery, wherein the components of said electrode and their mass percentages are: Positive/negative electrode active material 40-50%, conductive material 3-10%, binder 0-10%, cross-linking agent 0-5%, humectant 0-10%, surfactant 0-3%, electrolyte salt up to 30% and deionized water 10-30%.
2. The moldable electrode of claim 1, wherein the positive electrode active material is for a positive electrode, and the negative electrode active material is for a negative electrode, wherein the positive electrode active material is at least one of the following: a transition metal oxide, a phosphate polyanionic compound, a Prussian blue analog, and an organic electrode material; and wherein the negative electrode active material is at least one of the following: activated carbon, a Prussian blue analog, a sodium storage organic material and a titanium-phosphorus-based oxide.
3. The moldable electrode of claim 1, wherein the conductive material is one or more of the following: artificial graphite, natural graphite, activated carbon, graphene, carbon black, carbon fiber and mesoporous carbon.
4. The moldable electrode of claim 1, wherein the binder is one or more of the following: polyacrylic acid, polyvinyl alcohol, staghorn pectin, hydroxyethyl cellulose, xanthan gum, polytetrafluoroethylene and PVDF.
5. The moldable electrode of claim 1, wherein: the crosslinking agent is selected from a silane crosslinking agent, polyvinyl alcohol, and boric acid; and the moisturizing agent is one or more of the following: glycerin, sorbitol, propylene glycol, and polyethylene glycol.
6. The moldable electrode of claim 1, wherein: the surfactant is one or more of the following: sodium dodecylbenzene sulfonate and stearic acid.

7. The moldable electrode of claim 1, wherein the electrolyte salt is one or more of the following: sodium sulfate, sodium nitrate, sodium hypochlorite, sodium sulfite, sodium chloride, sodium sulfonate, and sodium phosphate.

8. A method for preparing a moldable electrode for an aqueous sodium battery, comprising the following steps:

S1: Mixing an electrolyte salt with deionized water to form a uniform electrolyte solution;

S2: Adding a surfactant and humectant to the electrolyte solution to obtain a uniform solvent matrix;

S3: Adding a conductive material into the solvent matrix, and making the conductive material uniformly dispersed in the solvent matrix through high-speed stirring;

S4: If a positive electrode is to be prepared, adding a positive electrode active material and binder; if a negative electrode is to be prepared, adding a negative electrode active material and binder; and then mixing evenly by high-speed stirring; and

S5: Adding a cross-linking agent to cross-link with the binder under low-speed stirring to form a three-dimensional network structure of a moldable electrode as a paste for use in an aqueous sodium battery.;

wherein the weight percentage of each component in the above steps is as follows: positive/negative electrode active material 40-50%, conductive material 3-10%, binder 0-10%, crosslinking agent 0-5%, humectant 0-10%, surfactant 0-3%, electrolyte salt up to 30%, and deionized water 10-30%.

9. A method for preparing an aqueous sodium battery using the moldable electrode of claim 1, comprising the following steps:

Z1: Using a bottom pressure plate as the bottom of said battery, placing a bottom current collector on top of said bottom pressure plate:

Z2: Placing a conductive plate on top of the current collector, and adding an appropriate amount of negative moldable electrode paste on the conductive plate;

Z3: Placing a separator on top of the negative moldable electrode paste, and pressing the

negative moldable electrode paste into shape:

Z4: Adding an appropriate amount of positive moldable electrode paste on the separator; then placing a conductive plate on top of the positive moldable electrode paste, and pressing said paste into shape; followed by adding an appropriate amount of negative moldable electrode paste on the conductive plate;

Z5: Repeating steps Z3-Z4 a number of times until the number of electrodes required for a specific battery capacity is reached, and the top electrode paste is a positive electrode paste; and

Z6: Placing a top conductive plate, a top current collector and a top pressure plate in sequence on top of the positive electrode paste in Z5, and compressing it to make said aqueous sodium battery.

10. An aqueous sodium battery comprising, from bottom to top, a bottom pressure plate, a bottom current collector, a conductive plate, negative moldable electrode, separator, positive moldable electrode, top conductive plate, top current collector and top pressure plate; wherein between the bottom and top pressure plates, there are a number of battery cells composed of conductive plates, negative moldable electrodes, separators, and positive moldable electrodes; wherein both sides of each conductive plate and each separator have upward protruding edges, such that the height of the protruding edges on each conductive plate is the same as the thickness of the negative moldable electrode, and the height of the protruding edges of each separator corresponds to the thickness of the positive moldable electrode; wherein the bottom pressure plate, the bottom current collector, the top conductive plate, the top current collector and the top pressure plate are plate-shaped.