Rolled battery cell, preparation process, and high-capacity aqueous sodium salt battery

Technical field

[0001] This invention relates to the technical field of battery for energy storage, in particular, a rolled battery cell, its preparation process, and a high-capacity aqueous sodium salt battery

Background of the invention

[0002] In the context of China's realization of the goal of "carbon peaking and carbon neutrality", power demand is growing, and large-capacity energy storage technology is a key part of new energy, which has attracted widespread attention in recent years. At present, the mainstream energy storage battery cells can be categorized according to their production processes: winding process and stacking process. The winding process is widely used because of its easy production and high production efficiency. However, due to safety requirements of lithium-ion battery, the size and capacity of the cells are generally small. For example, the size of the largest cylindrical lithium-ion battery is 46 mm in diameter and 80 mm in height (Model 46800). Aqueous sodium-salt batteries use neutral sodium-salt solution as electrolyte, which inherently has the advantages of safety, environmental friendliness, long life, etc. This battery system not only avoids the flammability problem of organic electrolytes, but also overcomes some issues of conventional aqueous batteries including high pollution, short life (such as lead-acid battery) and high price (lithium-ion battery), The system is an ideal system that can meet the requirements of large-scale energy storage technology. If the winding process can be applied to the preparation of aqueous sodium-salt battery, there is no need to be limited by the size and safety of the battery. In theory, large-size, high-capacity, safe and environmentally friendly aqueous sodium-salt battery can be prepared, with greatly improved assembly efficiency

[0003] Chinese Invention Patent Application Publication No. CN109755473A (Application No.201811630834.5) discloses a dry preparation method of lithium battery electrode. The thickness of the electrode film band obtained by the dry method is 50-100 microns, and the electrode film band is complexed to the electrode current collector through hot pressing to

obtain a rolled lithium battery electrode. Chinese Invention Patent Application Publication No. CN112687833A (Application No.202011553241.0) discloses a method of preparing dry electrode sheet, electrode sheet prepared by said method and the use thereof, After the raw material powders are mixed, they are heated and caused to become fibrous, resulting in an electrode powder. The electrode powder is successively rolled vertically and horizontally to obtain a film sheet, The film sheet and a foil are put into a fitting roller together and, after roller pressure is applied, an electrode sheet is obtained. Chinese Utility Model Patent No. CN213660479U discloses a Multiple tab rolled battery. In this multi-tab design, two tabs and a current collector are integrally formed. There are tab weldings and protective tape, so that not all the tabs and the current collector are integrated.

[0004] Conventional preparation method has the following problems:1) At present, electrode preparation adopts a wet process, involving slurry preparation, coating, drying and roll pressing. The process uses a large amount of organic solvent or deionized water, making it difficult to recover the solvent, and the drying process consumes a lot of energy, so that the electrode is easy to crack and the electrode density is low. 2) The existing winding technology is to put an active material on an aluminum foil (copper foil) current collector by coating or hot pressure. Although the product shows high efficiency and good consistency, the winding process is difficult to use for thick electrodes due to a differences in internal and external curvatures, so that the process is mainly used for making batteries with thin electrodes. Stacking process is low in production efficiency, wherein the production control is more cumbersome, with each cell containing at least dozens of electrodes, so that it is difficult to perform tests, operation, and statistics, resulting in difficulty in controlling product consistency;3) The current collector of an aqueous sodium salt battery is presently made of stainless steel. Aluminum foil requires corrosion protection. Stacked electrodes have multiple cut edges, especially the cut surfaces of a current collector that are prone to salt solution corrosion. Eliminating the impact of current collector corrosion requires more process and equipment, further complicating the process.

Summary of the invention

[0005] This invention relates to the structure of an aqueous sodium salt battery prepared by winding self-supporting flexible thick electrodes, The main features and advantages include: a) The self-supporting flexible thick electrodes are in the form of a continuous sheet and capable of being wound into a roll, They are produced by a continuous winding process, with high production efficiency; b) The length of the electrode and the current collector can be adjusted freely, according to the battery design specifications. Control is easy, and products of different specifications can be made; c) The current collector is protected against corrosion, The positive and negative electrodes only need to be cut once, and the entire battery cell structure only has two cut surfaces at the positive and negative current collectors, greatly reducing the risk of corrosion of the current collector, d) Since the electrode tab and current collector are integrated in structure, there is no need to weld the tab within the electrode, facilitating formation of a battery and effectively reducing battery impedance.

Brief description of the drawings

[0006] Figure 1 illustrates a winding process, wherein: 1-flexible thick positive electrode sheet; 2-flexible thick negative electrode sheet; 3-composite current collector; 4-separator; 5-core

[0007] Figure 2 shows structure 1 of a composite current collector wherein: 6-conductive film; 7-aluminum foil (tab).

[0008] Figure 3 shows structure 2 of a composite current collector wherein : 6-conductive film; 7-aluminum foil (tab).

[0009] Figure 4 is a cross-sectional view of a rolled battery cell.

[0010] Figure 5A is a graph showing the cycle life of a battery assembled with structure 2 of the composite current collector.

[0011] Figure 5B is a graph showing the discharge rate of a battery assembled with structure 2 of the composite current collector.

Detailed description of the invention

[0012] This invention relates to the structure of an aqueous sodium salt battery prepared by a winding process using self-supporting flexible thick electrodes, The main features and advantages include: a) The self-supporting flexible thick electrodes are in the form of a continuous sheet and capable of being wound into a roll, They are produced by a continuous winding process, with high production efficiency; b) The length of the electrode and the current collector can be adjusted freely, according to the battery design specifications, Control is easy, and products of different specifications can be made; c) The current collector is protected against corrosion, Only the positive and negative electrodes need to be cut once, and the entire battery cell structure only has two cut surfaces at the positive and negative current collectors, greatly reducing the risk of corrosion of the current collector, d) The electrode tab and current collector are integrated in structure, and there is no need to weld the tab within the electrodes, facilitating formation of a battery cell and effectively reducing battery impedance..

[0013] The technical solution in this invention is a type of rolled battery cell, comprising a positive electrode group, a negative electrode group, a separator and a core, The positive electrode group is composed of a layer of composite current collector sandwiched between two layers of thick flexible positive electrode sheets, and the negative electrode group is composed of a layer of composite current collector sandwiched between two layers of thick flexible negative electrode sheets, A stack is formed by stacking the negative electrode group on top of a separator, which is stacked on top of the positive electrode group, which is in turn stacked on top of another separator. The stack is then wound around a core with the positive electrode group on top of the negative electrode group. The positive electrode group is the same substance as the composite current collector in the negative electrode group, The composite current collector in the positive and negative electrode group can use the whole aluminum foil directly as the whole tab. Alternatively, the composite current collector in the positive and negative electrode group can be cut into multiple aluminum foil tabs, wherein the tab spacing is calculated according to the intended diameter of the battery cell, so that the inner and outer sides of the tabs would overlap when the composite current collector is being wound. A method

to prepare an aqueous sodium salt battery involves stacking raw materials together in the order of a negative electrode group, a separator, a positive electrode group, and another separator, rolling the raw materials into the shape of a cylinder or elliptical cylinder, which is placed into a plastic cylindrical or square shell, and then injecting aqueous electrolyte into the shell to produce an aqueous sodium salt battery.

[0014] The flexible positive electrode or negative electrode of the invention uses positive or negative electrode active material, carbon black as a conductive agent, and polytetrafluoroethylene emulsion (PTFE emulsion) as a main adhesive, wherein the PTFE in the mixture is caused to become fibrous by a high shear process and pressed into a self-supporting electrode sheet by a roller pressing process. The thickness of the electrode is uniform, and continuous preparation is possible. The thickness of the electrode is 0.1 mm - 5 mm, preferably 1 - 2.5 mm; the active material loading is 0.1 - 5 g/cm^2, preferably 0.15 - 2 g/cm^2; the porosity is 30% - 50%, preferably 35% - 45% %.

[0015] The positive electrode active material of the invention is selected from but not limited to MnO_2, $NaMnO_2$, $KMnO_2$, a compound containing a tetrahedron or octahedral anionic structure unit, Prussian blue analogs, and $NaMFe(CN)_6$ (M = Ni, Co, Fe, Cu).

[0016] The negative electrode active material of the invention is selected from but not limited to phosphate compounds, $NaTi_2(PO_4)_3$, $Na_3V_2(PO_4)_3$, metal oxide, MoO_3, $Na_2V_6O_{16}$, activated carbon, and Prussian blue analogs.

[0017] The battery core of the invention is a plastic round tube, and the plastic can be polyethylene, polypropylene, and polyvinyl chloride, etc., and the outer diameter of the round tube is 10 mm - 60 mm.

[0018] The aqueous electrolyte of the invention is a sodium salt aqueous solution, and the sodium salt can be one or more of sodium sulfate, sodium chloride, and sodium acetate.

[0019] The winding process of the invention is specifically as follows: stacking a negative electrode group, a separator, a positive electrode group, and another separator in sequence, rolling the stack into a cylindrical or elliptical cylindrical shape by winding around a core, and

then putting the roll into a plastic cylindrical or square shell, and injecting into the shell an aqueous electrolyte.

[0020] This invention has the following advantages:1) no solvent is used in the electrode manufacturing process, the binder exists in a fibrous state, contact between the activated carbon particles and the conductive agent particles is tight, electrode density is high, conductivity is good, electrode toughness is good, and density is high, capacity is high, carbon powder is not easy to fall off, and cycle life is long. 2) The positive and negative electrode groups use the same composite current collector, wherein the aluminum foil is cut or die-cut to obtain multiple aluminum foil tabs, or the entire aluminum foil is used as a full tab without welding the tabs within the electrodes, facilitating formation of a battery cell and effectively reducing battery impedance.3) The stacking method requires continuous precise control of the cutting process. Each composite current collector and flexible large electrode must be cut all around, so that issues such as cut surfaces, material loss, and burr need to be addressed, and the electrode consistency requirement becomes higher. The winding method requires a cut mainly at the two points where winding starts and ends, greatly reducing the risk of the current collector being corroded by an electrolyte.4) The active material and the current collector have not undergone a coating process or pressed together, and the flexible large electrode and the composite current collector are separate rolls to avoid wrinkling and deformation of the separator and the large electrode during a winding process, as a result of a difference in internal and external curvatures. The length of the roll can be flexibly cut, so that the size of the battery cell can be flexibly adjusted according to the capacity needs.

[0021] In one embodiment, the cell size and capacity of an aqueous sodium salt battery made by winding the green high-safety electrode structure of this invention can be flexibly adjusted as required: The diameter is 7 – 500 cm, the height is 14 – 200 cm, the aspect ratio is 2:1 – 20:1, the capacity is 1Ah - tens of thousands Ah, energy efficiency is > 80%. There are no hidden dangers such as thermal runaway, fire, explosion, etc. under high magnification and extreme use conditions.。

[0022] In one embodiment, the battery cell of this invention uses high-toughness, high-density, high-conductivity, high-load, and self-supporting thick electrodes, wherein the thickness of the electrode is 0.1 mm - 5 mm, and the active material loading is 0.1 - 5 g /cm^2, and the porosity is 30% - 50%.

[0023] In one embodiment, the battery cell of this invention uses an anticorrosion current collector: it is composed of a metal current collector coated outside with an anti-corrosion conductive layer. The metal current collector can be aluminum foil, copper foil, nickel foil, etc.; the anti-corrosion conductive layer is a conductive organic film, such as polyethylene conductive film, polypropylene conductive film, ethylene-vinyl acetate conductive film, polyaniline conductive film, polypyrrole conductive film, poly phenyl sulfide conductive film, etc.

[0024] In one embodiment, both the positive and negative electrodes and the composite current collector of the invention can be individually wound , the position and shape of each component are automatically adjusted according to the winding curvature during a winding process , so as to avoid multiple bending areas and thickness variations along the length of the electrodes, especially the area near the middle of the core. Due to uneven winding curvature and shape changes, wrinkling and deformation of the separator and thick electrodes are possible, so that the positive and negative electrodes are not in full contact, resulting in a reaction dead zone.

[0025] In one embodiment, the flexible positive electrode or negative electrode of the invention uses positive electrode or negative electrode active material, carbon black as a conductive agent, and polytetrafluoroethylene emulsion (PTFE emulsion) as a main adhesive, wherein the PTFE in the mixture is caused to become fibrous by a high shear process and pressed into a self-supporting electrode sheet by a roller pressing process. The thickness of the electrode is uniform, and continuous preparation is possible.

[0026] In one embodiment, the electrode tab and current collector of the invention are integrated structure, and there is no need to weld the tab within the electrode, facilitating formation of a battery cell and effectively reducing battery impedance, and the current collector

is protected against corrosion, The battery cell only needs to be cut once at the positive and negative electrodes, and the entire cell structure only has two cut surfaces at the positive and negative current collectors, greatly reducing the risk of corrosion of the current collector.

[0027] In one embodiment, the negative and positive electrode groups of the invention comprise thick electrodes having a self-supporting structure, individually rolled and not combined with a composite current collector. The flexible thick electrode and the composite current collector are wound separately to avoid wrinkles and deformation of the separator and thick electrode due to a differences in internal and external curvature during the winding process.

[0028] In one embodiment, the positive and negative electrodes of this invention are the same in size, and they do not cover one another. The length of the electrode and the current collector can be adjusted freely, according to the design specifications of the battery cell, so that control is easy, and products of different specifications can be made.

[0029] The present invention may be better understood by reference to the following examples. Those skilled in the art can understand that the following examples are only for illustrating the present invention, not for limiting the scope of the present invention. The scope of the present invention is defined by the scope of the claims.

Examples

[0030] Example 1. A winding process for aqueous sodium salt battery comprises the following steps

1) The intended size of a battery cell determined where and how to cut the positive and negative aluminum foils so that the size and shape of the aluminum foil (tab) 7 would satisfy the required specifications, wherein the spacing between tabs was calculated based on the diameter of the battery cell.;

2) An aluminum foil (tab) 7 was attached to a conductive film 6 using a conductive glue. As shown in Figure 2, the conductive film completely wrapped the aluminum foil, and the tab end was exposed, resulting in a composite current collector 3;

3) A positive electrode active material, carbon black as a conductive agent, and polytetrafluoroethylene emulsion (PTFE emulsion) as a main adhesive were mixed evenly, and were pressed into a self-supporting flexible positive thick electrode 1 by a high shear and rolling process, the thickness was 2 mm, the active material loading was 0.37 g/cm^2, and the porosity was 38%. A negative electrode active material, carbon black as a conductive agent, and polytetrafluoroethylene emulsion (PTFE emulsion) as a main adhesive were mixed evenly, and were pressed into a self-supporting flexible negative thick electrode 2 by a high shear and rolling process, the thickness was 1.9 mm, the active material loading was 0.27 g/cm^2, and the porosity was 40%.

4) A battery cell was formed by alternately stacking the positive electrode group, the negative electrode group and two layers of separator 4 as shown in Figure 1, and then winding around the core 5 with an outer diameter of 50 mm. The positive electrode group included a flexible thick positive electrode sheet 1 and a composite current collector 3, the negative electrode group included a flexible thick negative electrode sheet 2 and a composite current collector 3. During the winding process, the inner side of a tab overlapped with the outer side of another tab, and the positive and negative tabs were staggered. The cell diameter was 16 cm and the height was 30 cm.。

5) Using sodium chloride aqueous solution as an electrolyte, an aqueous sodium salt battery was prepared with a capacity of 90 Ah.

[0031] Example 2. A winding process of a high-capacity aqueous sodium salt battery comprises the following steps:

1) An aluminum foil (tab) 7 was attached to a conductive film 6 using a conductive glue. As shown in Figure 3, the conductive film completely wrapped the aluminum foil, and the whole aluminum foil was directly exposed as the tab end, resulting in a composite current collector 3.

2) A positive electrode active material, carbon black as a conductive agent, and polytetrafluoroethylene emulsion (PTFE emulsion) as a main adhesive were mixed evenly, and

were pressed into a self-supporting flexible positive thick electrode 1 by a high shear and rolling process, the thickness was 1.2 mm, the active material loading was 0.23 g/cm^2, and the porosity was 40.6%. A negative electrode active material, carbon black as a conductive agent, and polytetrafluoroethylene emulsion (PTFE emulsion) as a main adhesive were mixed evenly, and were pressed into a self-supporting flexible negative thick electrode 2 by a high shear and rolling process, the thickness was 1.2 mm, the active material loading was 0.16 g/cm^2, and the porosity was 39.8%.

3) A battery cell was formed by alternately stacking the positive electrode group, the negative electrode group and two layers of separator 4 as shown in Figure 1, and then winding them around core 5. The positive electrode group included a flexible thick positive electrode sheet 1 and a composite current collector 3, while the negative electrode group included a flexible thick negative electrode sheet 2 and a composite current collector 3. As shown in Figure 4, during the winding process, the positive and negative electrode tabs were staggered in opposite directions. The cell diameter was 11 cm and the height was 25 cm.

4) Using sodium sulfate aqueous solution as an electrolyte, an aqueous sodium salt battery was prepared with a capacity of 70Ah. Standard charge and discharge and different rate discharge tests were carried out on the battery according to a rated capacity of 0.2C (14Ah). Standard charge was that the battery was charged at a constant current of 0.2C (14A) to a cut-off voltage of 1.85 V at 25^{o}C and left for 10 minutes. Standard discharge was that the battery was discharged at a constant current of 0.2C (14A) to a cut-off voltage of 1.1V at 25 ^{o}C, and left for 10 minutes. The test data are shown in Figure 5A and Figure 5B.

[0032] Due to the use of an all-tab structure, there was no need for tab welding, the AC impedance of the battery was 0.12 mΩ, and the battery was charged and discharged with a current of 0.2C (14Ah) for 3915 cycles, the capacity retention rate was 88.24%, and the rate discharge performance was good. The data are shown in Table 1 below.

Table 1: Rate discharge performance

Discharge current	0.1C （7A）	0.2C （14A）	0.5C （35A）	1C （70A）	2C （140A）	3C （210A）	4C （280A）
Capacity ratio	104.20%	100.00%	98.30%	97.70%	95.40%	94.60%	91.80%

Note: Under the standard charging condition of 25 °C， the battery was charged at a constant current of 0.2C (14A) to the cut-off voltage of 1.85 V; then the battery was discharged under different conditions to a cut-off voltage of 1.1 V. The capacity ratio is shown in Table 1 above. At 25 °C, the discharge capacity under the condition of discharge current 0.2C (14A) was 100% capacity.

[0033] The documents or published articles cited in this patent application are collectively incorporated by reference into this application for a more detailed description of the current state of the art related to the present invention. Also the transitional terms "comprises", "includes" or "is characterized by" are synonymous, inclusive or open ended, and do not exclude additional, unrecited elements or method steps.

What is claimed is

1. A rolled battery cell, comprising a positive electrode group, a negative electrode group, a separator and a core, wherein the positive electrode group is composed of a layer of composite current collector sandwiched between two layers of thick flexible positive electrode sheets, and the negative electrode group is composed of a layer of composite current collector sandwiched between two layers of thick flexible negative electrode sheets, wherein the positive electrode group, the negative electrode group and two separators are wound around the core, wherein one separator is wound between the positive electrode group and the negative electrode group, wherein the positive electrode group is wound outside the negative electrode group. The composite current collector of the positive electrode group is the same material as that of the negative electrode group. The composite current collectors of the positive and negative electrode groups can use the entire aluminum foil as a full tab, or the aluminum foil tab can be cut into multiple tabs, wherein the spacing between tabs is calculated according to the diameter of the core so that the inner and outer sides of the tabs overlap when winding the composite current collector.
2. The rolled battery cell of claim 1, wherein the thick flexible positive electrode comprises positive electrode active material selected from MnO_2, $NaMnO_2$, $KMnO_2$, compounds containing a tetrahedral or octahedral anionic structure, Prussian blue analogs, and NaMFe (CN) $_6$ (M = Ni, Co, Fe, Cu), carbon black as conductive agent, polytetrafluoroethylene emulsion (PTFE emulsion) as a main adhesive, wherein said PTFE in the mixture is caused to become fibrous using a high shear process and pressed into a self-supporting electrode sheet by a roller pressing process.
3. The rolled battery cell of claim 1, wherein the thick flexible negative electrode comprises negative electrode active material selected from phosphate compounds, $NaTi_2$ (PO_4) $_3$, Na_3V_2 (PO_4) $_3$, metal oxides, MoO_3, $Na_2V_6O_{16}$, activated carbon, and Prussian blue analogs, carbon black as a conductive agent, polytetrafluoride emulsion

(PTFE emulsion) as a main adhesive, wherein said PTFE in the mixture is caused to become fibrous using a high shear process and pressed into a self-supporting electrode sheet by a roller pressing process.

4. The rolled battery cell of claim 1, wherein the thickness of the thick flexible electrode is 0.1 mm - 5 mm, the active material loading is 0.1 - 5 g/cm^2, and the porosity is 30% - 50%.
5. The rolled battery cell of claim 1, wherein the core is a plastic round tube made from polyethylene, polypropylene, or polyvinyl chloride, and the outer diameter of the round tube is 10 mm - 60 mm.
6. The rolled battery cell of claim 1, wherein both the thick flexible positive and negative electrode sheets and the composite current collector can be individually wound into a roll shape, wherein the position and shape of each roll can be automatically adjusted according to the winding curvature, so as to avoid multiple bending areas and thickness variations along the length of a whole electrode.
7. The rolled battery cell of claim 1, wherein the current collector is protected against corrosion, wherein the composite current collector is composed of a metal current collector covered on the outside by an anticorrosion conductive layer, wherein said metal can be aluminum, copper, or nickel; wherein the anticorrosive conductive layer can be a polyethylene conductive film, polypropylene conductive film, ethylene-vinyl acetate lipid-conductive film, polyaniline conductive film, polypyrene conductive film, or polystyrene sulfide conductive film.
8. A method for preparing the rolled battery cell of claim 1, comprising steps of stacking a negative electrode group, a separator, a positive electrode group, and a separator in such order, and then rolling them into the shape of a cylinder or elliptical cylinder, which is then placed into a plastic cylindrical or square shell, wherein injecting an aqueous electrolyte into the shell produces an aqueous sodium salt battery.
9. The method of claim 7, wherein an electrode tab is integrated with a current collector

so that there is no need to weld a tab within an electrode, effectively reducing battery impedance.

10. The method of claim 7, wherein a current collector is protected against corrosion, wherein the positive and negative electrodes need to be cut only once so that the entire battery cell has only two cut surfaces on the positive and negative current collectors, greatly reducing the risk of corrosion of the current collector.

11. The method of claim 8, wherein the negative and positive electrode groups comprise thick self-supporting electrodes, individually rolled and not integrated with a current collector.。

12. The method of claim 8, wherein the flexible thick electrode and the composite current collector are rolled separately to avoid wrinkles in the separator and thick electrode due to differences in internal and external curvatures during a winding process.

13. The method of claim 8, wherein the positive and negative electrodes have the same size, and do not cover one another, wherein the length of each electrode and the current collector can be adjusted freely according to the design specifications of the battery cell, resulting in ease of control, and products of different specifications.