A High Stability, Low Cost and High Rate-capability Aqueous Sodium Ion Capacitor

TECHNICAL FIELD

[0001] The invention relates to a novel metal ion capacitor. The invention also relates to an aqueous sodium ion capacitor.

BACKGROUND OF THE INVENTION

[0002] Metal ion capacitors, including lithium ion capacitors and sodium ion capacitors, have two configurations. The first configuration includes a battery type anode and a capacitive cathode. Porous carbon materials with large specific surface area, such as activated carbon, are mainly used as the cathode materials. The ionic dissociation type materials are used as the anode materials. In the charging and discharge process, the combination of different energy storage mechanisms makes the energy density of metal ion capacitors higher than that of traditional electric double layer capacitors, and the power density higher than that of metal ion batteries. Due to the advantages of high energy density, high power density and long cycle stability, metal ion capacitors have a huge application prospect in electric vehicles, medical equipment and the national grid. However, in order to expand the voltage window of the new type of ion capacitor and reduce the consumption of electrolyte, the anode must be pre-embedded with associated ions. Generally, sodium reduced from sodium source additives is deposited on the anode to form pre-embedded ions, as exemplified in Chinese patent publication No. CN110335764A and CN113113235A. This makes the preparation process more complex, and its application is limited.

[0003] The second configuration is that the composite material of porous carbon material and metal oxide material is used as the cathode, and the carbon material is used as the anode. Due to the use of metal oxide materials for compounding, the safety performance will also be reduced. At the same time, the intrinsic properties of some metal oxide materials, such as the unstable characteristic of ternary nickel cobalt manganese and the manganese dissolution of

lithium manganate, will greatly affect the cycle performance. At present, metal ion capacitors are all organic systems, which have certain risks in the field of high safety applications.

SUMMARY OF THE INVENTION

[0004] In view of the shortcomings of the prior art, the purpose of the present invention is to provide a new type of metal ion capacitor. The cathode and anode electrodes are both hybrid electrodes. According to different rate capability and power performance requirements, the electrodes are composed of different proportions of battery type materials and capacitive materials. The electrolyte is water system or mixed electrolytes. The high ionic conductivity of water system electrolyte can greatly improve the power performance of metal ion capacitors, and has intrinsically safe characteristics. It can be applied to fields requiring high safety factors, such as aerospace, military equipment, etc.

DESCRIPTION OF THE DRAWINGS

[0005] FIG. 1 is a plot of charge and discharge curve of different samples.

[0006] FIG. 2 shows capacity retention after 30,000 cycles.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The invention provides a sodium ion capacitor, which is characterized in that the sodium ion capacitor comprises a cathode, an anode, a separator and an electrolyte. The cathode comprises a cathode active material, a conductive agent and a binder, and the cathode active material comprises a Prussian blue analog and a porous carbon material. The ratio of the Prussian blue analog to the porous carbon material is (5~70) : (95~30); The anode comprises an anode active material, a conductive agent and a binder, and the anode active material comprises a phosphate sodium storage material and a porous carbon material. The ratio of the sodium storage material to the porous carbon material is (10-80) : (90-20). Electrolytes include deionized water, electrolyte salts and additives.

[0008] The cathode material of the invention includes cathode active material, conductive material and adhesive, and the ratio of the three is (80-90) : (13-7) : (7-3).

[0009] The anode material of the invention includes anode active material, conductive material and adhesive, and the ratio of the three is (72-85) : (21-12) : (7-3).

[0010] The Prussian blue analog involved in the invention includes M1M2Fe (CN) $_6$ (M1 = Na, K, Zn, etc., M2 = Mn, Fe, Co, Ni, Cu, Zn, etc.).

[0011] The phosphate sodium storage material of the present invention comprises $NaTi_2(PO_4)_3$, $Na_3V_2(PO_4)_3$, $Na_4VFe(PO_4)_3$, $NaVPO_4F$, $FePO_4$, $NaFePO_4$, etc.

[0012] The porous carbon material according to the invention has a specific surface area of 1000-2200 m^2/g, a pore volume of 0.5-1.0 ml/g, an apparent density of 0.4-0.6 g/ml, and a particle size distribution of D90<10 μ m.

[0013] The electrolyte salt involved in this invention includes one or more of sodium perchlorate, sodium sulfate, sodium formate, sodium acetate, sodium nitrate, sodium chloride, sodium carbonate, sodium bromide, sodium acetate, sodium iodide and sodium oxalate, with a mass molar concentration of 1.0 - 2.0 mol/kg.

[0014] The electrolyte additive involved in the invention is polyethylene glycol, glycerin, trimethyl phosphate, sodium polyacrylate, sodium dodecylbenzene sulfonate, diethylene glycol dimethyl ether, methyl ethyl carbonate, propylene carbonate, methyl cellulose, carboxymethylcellulose, hydroxyethyl cellulose, dimethyl sulfone and sulfolane, with a weight ratio of 1.0-80%.

[0015] The electrolyte solvent in this invention is deionized water.

[0016] The conductive materials in the cathode and anode involved in the present invention include any one or more of carbon black, conductive graphite, carbon nanotubes and graphene.

[0017] The adhesive involved in this invention is any one or more of polyvinylidene fluoride, polytetrafluoroethylene, sodium carboxymethylcellulose and polyacrylic acid.

[0018] The separator involved in the present invention includes any one or more of cellulose diaphragms, PET diaphragms, PP non-woven diaphragms and PE non-woven separator.

[0019] Literature or published articles are cited in this patent application. The cited

documents and published articles are used as the reference data of this application, so as to describe the latest level in the field related to the invention in more detail. At the same time, it should be noted that during the whole application process, the transitional terms "including", "including" or "characterized by" are synonymous, inclusive or open, and do not exclude additional and unlisted elements or method steps.

[0020] The invention can be better understood by referring to the following embodiments. Those skilled in the art can understand that the following examples are only to illustrate the invention, not to limit the scope of the invention. The scope of the invention is defined by the claims that follow.

EXAMPLES

[0021] **Example 1**. This example provides a new aqueous metal ion capacitor with high safety and high specific energy. The ion capacitor includes a cathode, anode, separator and electrolyte. Cathode active materials include Prussian blue and activated carbon mixed in a certain proportion, and anode active materials include phosphate compounds and activated carbon mixed in a certain proportion; The current collector is carbon coated stainless steel; PP non-woven fabric is selected as the separator.

[0022] In this embodiment, the cathode material is composed of cathode active material, conductive material and binder, and the proportion of Prussian blue and active carbon in the cathode active material is in accordance with the ratio in the table; The conductive material is graphene and conductive graphite (mass ratio of 2:5), and the binder is polytetrafluoroethylene lotion, in which the ratio of cathode active material, conductive agent and binder is 87:7:6.

[0023] In this embodiment, the anode material is composed of anode active material, conductive material and binder. The ratio of sodium titanium phosphate and active carbon in the anode active material is in accordance with the ratio in the table; The conductive material is activated carbon and acetylene black (mass ratio of 1:1), and the binder is polycarboxylic methyl cellulose sodium. The ratio of the anode active material, the conductive agent and the

binder is 80:14:6.

[0024] In this embodiment, the electrolyte salt is sodium acetate at 1 mol/Kg, and the ratio of deionized water to polyethylene glycol in the solution is 80:20.

[0025] The preparation method of the sodium ion capacitor in this embodiment includes the following steps:

(1) Preparation of anode: after the above anode active material and conductive agent are mixed evenly in proportion, the adhesive and proper amount of deionized water are added in proportion and stirred evenly to obtain an anode paste, and then the anode paste is coated on both surfaces of carbon coated stainless steel with a thickness of 15 μm to give an anode after drying, rolling and laminating;

(2) Preparation of cathode: after the above cathode active material and conductive agent are mixed evenly in proportion, the adhesive and proper amount of deionized water are added in proportion and stirred evenly to obtain a cathode slurry, which is then evenly coated on both surfaces of carbon coated stainless steel with a thickness of 15 μm to give a cathode after drying, rolling and punching; and

(3) Assembly of sodium ion capacitor: according to the order that the separator is located between the cathode and the anode, the cathode, the anode and the separator are superimposed, so that the separator is in a zigzag shape, and then a current collector is welded, sealed with aluminum plastic film, dried, injected with electrolyte, and left for 24 hours to take shape and form a sodium ion capacitor.

[0026] The voltage, rate capability performance and specific energy based on the mass of cathode and anode active materials of different proportion of cathode and anode active materials can be seen in Table 1.

Table 1

	Cathode active material		Anode active material		Specific energy （Wh/Kg） at different rate (C)			
	$NaMnFe(CN)_6$	porous carbon	$NaTi_2(PO_4)_3$	porous carbon	1C	5C	8C	10C

Example 1	5	95	10	90	40	38	35	33
Example 2	30	70	50	50	50	46	43	41
Example 3	95	5	90	10	45	42	41	39
Comparative 1	0	100	0	100	20	17	15	12
Comparative 2	100	0	100	0	30	10	3.1	0.5

[0027] Charging and discharging were performed according to the current density of 20mA/g. The charge-discharge curve of example 2, comparative 1 and comparative 2 are shown in Figure 1. The charge-discharge curve of the whole battery showed completely different electrochemical characteristics. Example 2 had a large linear slope in the range of 0.5-1.4V, which was mainly caused by the double-layer capacitance effect of the capacitive material, and a small slope in the range of 1.4-1.8V, which is caused by the ion insertion and removal reaction of the battery type material. Its maximum charging voltage is basically the same as the comparative 2 (battery type material). Due to the addition of capacitive materials, the capacity, energy and rate capability performance have been greatly improved; Compared with the comparative 1 (capacitive material), the full voltage of the battery in Example 2 increased from 1.4V to 1.8V due to the addition of the battery type material, and the energy density could be significantly improved.

[0028] The capacity retention at 3C of Example 3 is greater than 93% after long cycle time of 30,000 cycles(see Figure 2).

What is claimed is:

1. A sodium ion capacitor, comprising a cathode, an anode, a separator and an electrolyte, wherein the cathode comprises a cathode active material, a conductive agent and a binder, and the cathode active material comprises a Prussian blue analog and a porous carbon material, wherein the ratio of the Prussian blue analog to the porous carbon material is (5~70): (95~30),

   wherein the anode comprises an anode active material, a conductive agent and a binder, and the anode active material comprises a phosphate sodium storage material and a porous carbon material, wherein the ratio of the sodium storage material to the porous carbon material is (10-80): (90-20),

   wherein the electrolyte comprises deionized water, electrolyte salts and additives.
2. The sodium ion capacitor according to claim 1, wherein the cathode comprises a cathode active material, a conductive material and a binder, wherein the ratio of the three is (80-90): (13-7): (7-3).
3. The sodium ion capacitor according to claim 1, wherein the anode comprises an anode active material, a conductive material and a binder, wherein the ratio of the three is (72-85): (21-12): (7-3).
4. The sodium ion capacitor according to claim 1, wherein the Prussian blue analog is selected from M1M2Fe (CN) $_6$, wherein M1 = Na, K or Zn, M2 = Mn, Fe, Co, Ni, Cu or Zn.
5. The sodium ion capacitor according to claim 1, wherein the phosphate sodium storage material is selected from $NaTi_2(PO_4)_3$, $Na_3V_2(PO_4)_3$, $Na_4VFe(PO_4)_3$,$NaVPO_4F$, $FePO_4$ and $NaFePO_4$.
6. The sodium ion capacitor according to claim 1, wherein the specific surface area of the porous carbon material is 1,000-2,200 m^2/g, the pore volume is 0.5-1.0 ml/g, the apparent density is 0.4-0.6 g/ml, and the particle size distribution is D90 < 10 μm.

7. The sodium ion capacitor according to claim 1, wherein the electrolyte salt is one or more of sodium perchlorate, sodium sulfate, sodium formate, sodium acetate, sodium nitrate, sodium chloride, sodium carbonate, sodium bromide, sodium acetate, sodium iodide and sodium oxalate, and the mass molar concentration is 1.0 - 2.0 mol/kg.
8. The sodium ion capacitor according to claim 1, wherein solvent of the electrolyte is deionized water.
9. The sodium ion capacitor according to claim 1, wherein the additive is selected from polyethylene glycol, glycerin, trimethyl phosphate, sodium polyacrylate, sodium dodecyl benzene sulfonate, diethylene glycol dimethyl ether, methyl ethyl carbonate, propylene carbonate, methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, dimethyl sulfone, and sulfolane, wherein the weight ratio is 1.0-80%.
10. The sodium ion capacitor according to claim 1, wherein the anode and cathode comprise a conductive material selected from carbon black, conductive graphite, carbon nanotubes and graphene.
11. The sodium ion capacitor according to claim 2, wherein the cathode binder is selected from polyvinylidene fluoride, polytetrafluoroethylene, sodium carboxymethyl cellulose and polyacrylic acid.
12. The sodium ion capacitor according to claim 3, wherein the anode binder is selected from polyvinylidene fluoride, polytetrafluoroethylene, sodium carboxymethyl cellulose and polyacrylic acid.
13. The sodium ion capacitor according to claim 1, wherein the separator is selected from cellulose membrane, PET membrane, PP non-woven membrane and PE non-woven membrane.
14. A method for preparing the sodium ion capacitor of claim 1, comprising:

    (1) preparation of anode, wherein after the anode active material and conductive agent are mixed evenly in proportion, the binder and a proper amount of

deionized water are added and stirred evenly to obtain an anode paste, and then the anode paste is coated on both surfaces of carbon coated stainless steel with a thickness of 15 um to give an anode i after drying, rolling and stamping;

(2) preparation of cathode, wherein, after the cathode active material and conductive agent are mixed evenly in proportion, the binder and a proper amount of deionized water are added and stirred evenly to obtain a cathode slurry, and then the slurry is uniformly coated on both surfaces of carbon coated stainless steel with a thickness of 15 um to give a cathode after drying, rolling and punching; and

(3) assembly of sodium ion capacitor, wherein, according to the order that the separator is located between the cathode and the anode, the cathode, the anode and the separator are superimposed, wherein the separator is Z-shaped, and a current collector is welded, sealed with aluminum plastic film, dried, injected with electrolyte, and let stand for 24 hours to take shape and form a sodium ion capacitor.