

HIGH-STABILITY AND HIGH-CONDUCTIVITY COMPOSITE TITANIUM- PHOSPHORUS OXIDE AND PREPARATION METHOD THEREOF

TECHNICAL FIELD

[0001] The present invention relates to a kind of high-stability high-conductivity composite titanium-phosphorus oxide and preparation method thereof, also relate to aqueous ion battery.

BACKGROUND TECHNOLOGY

[0002] Intermittent renewable energy represented by solar energy and wind energy must be connected to the power grid through energy storage systems which store and release energy, so that large-scale energy storage technology is the basis for new energy promotion and energy innovation. This application places very strict requirements on battery technology: high safety performance, long cycle life, low LCOE (Levelized Cost of Energy) and wide temperature adaptability.

[0003] So far, the most widely used electrochemical energy storage technologies are lithium-ion battery (LIB) and lead-acid battery (LAB) technologies. But for energy storage systems, LIBs simply cannot maintain high cycle life in high temperature applications, and the risk of LIB thermal runaway requires complex battery management systems, high costs, and high operating expenses to ensure the safety of the system (1); LABs cannot achieve long cycle life at high depth of discharge (DOD), and the high temperature resistance of LAB is even worse than that of LIB (2). More importantly, energy storage applications with large-scale integration (above MWh level) have the characteristics of large investment and long operation and maintenance time. This requires high consistency in batteries and high safety in the integrated system. In recent years, a series of combustion accidents in energy storage systems and power stations shows that the intrinsic safety of battery still needs to be paid great attention, and it is also a problem that needs to be solved urgently for the scale promotion of the energy storage battery.

[0004] Aqueous ion battery, which adopts neutral salt solution as electrolyte, can avoid the flammable problem of organic electrolyte and overcome the high pollution and short life of traditional aqueous battery (such as lead-acid battery) and high cost (such as nickel-hydrogen battery). It has the characteristics of safety, low cost, long life, environmental friendliness and recyclability. It is a new type of battery system and an ideal system for large-scale energy storage technology requirements.

[0005] Aqueous sodium battery is one of the most promising energy storage batteries due to its low cost, long cycle life, high safety, environmental friendliness and other advantages. A core bottleneck restricting the development and large-scale application of aqueous sodium batteries is the stability and maturity of anode materials. Due to the advantages of high stability and low cost, NASICON structure titanium phosphorus oxide $\text{NaTi}_x\text{M}_y(\text{PO}_4)_3$ ($\text{M} = \text{Ti}, \text{V}, \text{Mn}, x + y = 2$) is considered to be

the most promising anode active material for aqueous sodium batteries. Its advantages include relatively high specific capacity, excellent thermal stability, low manufacturing cost, and suitable redox potential; at the same time, there are also some disadvantages: 1) The material itself has low electronic conductivity; 2) The material has relatively low ionic conductivity; 3) It is sensitive to pH environment, and the dissolution rate in alkaline solution ($\text{pH} > 12$) will increase sharply, resulting in attenuation. In order to achieve high energy density and long cycle of aqueous sodium batteries, the electrical conductivity and stability of anode materials for aqueous sodium batteries must be improved.

SUMMARY OF THE INVENTION

[0006] The main focus of the present invention is a high-stability, high electrical conductivity composite titanium phosphorus oxide and mass production method thereof. The composite titanium phosphorus oxide uses a second phase as the stable phase, which can greatly improve the ion transport conductivity and chemical stability; a coating phase formed by a water-soluble carbon-containing substance, which is added to a precursor mixing process and decomposed during a sintering process, can ensure high electronic conductivity. In the meantime, no additional carbon materials are required in the later electrode preparation process.

DESCRIPTION OF THE DRAWINGS

[0007] Fig. 1 shows the EIS curves of S1, S2 and S3;

[0008] Fig. 2 shows the cycling performance of S1, S2 and S3 under accelerated condition;

[0009] Fig. 3 shows the SEM images of S1, S2 and S3 after corrosion test.

DETAILED DESCRIPTION

[0010] The main focus of the present invention is a high-stability, high electrical conductivity composite titanium phosphorus oxide and mass production method thereof, specifically including the following features:

1. The composite titanium phosphorus oxide is composed of a main phase, a stable phase and a coating phase;
2. The main phase is NASICON structure $\text{NaTi}_x\text{M}_y(\text{PO}_4)_3$, wherein $\text{M} = \text{Ti}, \text{V}, \text{Mn}$, $x + y = 2$;
3. Stable phase includes two types: one is $\text{M}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ($\text{M} = \text{Sr}, \text{Ca}, \text{Mn}, \text{Mg}, \text{Co}, \text{Cu}$), the other one is $\text{M}_1(\text{TiM}_2)(\text{PO}_4)_3$ ($\text{M}_1 = \text{Fe}, \text{Na}, \text{Mn}, \text{Sn}, \text{Ba}$; $\text{M}_2 = \text{Ge}, \text{Nb}, \text{Cr}, \text{Sn}$);
4. The coating phase is a hydrophilic amorphous carbon material formed by sintering a water-soluble carbon-containing precursor; the water-soluble carbon-containing precursor is selected

from polydopamine, resorcinol-formaldehyde resin, glucose, sucrose, fructose, polyvinylpyrrolidone (PVP), tannic acid, citric acid, polyvinyl alcohol, polypyrene, vitamin C and polyethylene glycol;

5. The content of stable phase is 0.01-1.0 wt.%;

6. The content of coating phase is 0-3 wt.%;

7. The thickness of coating phase is 2-50 nm.

[0011] Specific features of the preparation method in the present invention are as follows:

1. The sodium source is at least one of sodium phosphate, sodium carbonate, sodium dihydrogen phosphate, sodium hydroxide, and sodium acetate, and the primary particle size D50 is less than 3 μm ;

2. The titanium source is at least one of titanium dioxide, titanium hydroxide, metatitanic acid, and tetrabutyl titanate, and the primary particle size D50 is less than 1 μm ;

3. The phosphorus source is at least one of phosphoric acid, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonium phosphate, sodium dihydrogen phosphate, and disodium hydrogen phosphate, and the primary particle size D50 is less than 3 μm ;

4. According to the type of stable phase, the inorganic salt corresponding to the metal cation is selected as raw material, and the inorganic salt includes but is not limited to carbonate, phosphate, acetate, etc.;

5. If the raw material is insoluble in water and the particle size does not meet requirements, it should be pretreated with pulverization, which includes but is not limited to mechanical pulverization, jet pulverization, and ultrasonic pulverization; the form of pulverization includes direct pulverization of the material or pulverization of the material after dissolution in a solvent;

6. The solvent used in the preparation process is water;

7. No matter which preparation method is adopted, the titanium source needs to be added first in the preparation process, and after the dispersion is uniform, the sodium source and the phosphorus source are sequentially added;

8. The coating phase is added in the form of a liquid-phase carbonizable precursor, and the addition amount is calculated according to the high-temperature carbonization residual rate of different precursors; the molar ratio of coating phase to metal ion ranges from 1:1 to 5:1;

9. During the preparation process, the pH value of the slurry/mixture needs to be adjusted to 6-8 according to different material sources;

10. The pH value can be adjusted using hydroxide corresponding to the metal cation, or an inorganic acid corresponding to the anion;

11. After the slurry is dried, it is sintered under an inert atmosphere;

12. Drying techniques include but are not limited to spray drying, microwave drying, etc.;

13. Inert atmospheres include but are not limited to helium, nitrogen, argon, etc.; and

14. The sintering temperature is 600-1000°C, and the sintering time is 5-20 hours.

[0012] In one embodiment, the composite titanium phosphorus oxide of the present invention is composed of a main phase, a stable phase and a coating phase.

[0013] In one embodiment, the main phase of the present invention is $\text{NaTi}_2(\text{PO}_4)_3$.

[0014] In one embodiment, the stable phase of the present invention includes two types: one is $\text{M}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ ($\text{M} = \text{Sr}, \text{Ca}, \text{Mn}, \text{Mg}, \text{Co}, \text{Cu}$); the other one is $\text{M}_1(\text{TiM}_2)(\text{PO}_4)_3$ ($\text{M}_1 = \text{Fe}, \text{Na}, \text{Mn}, \text{Sn}, \text{Na}$; $\text{M}_2 = \text{Ge}, \text{Nb}, \text{Cr}, \text{Sn}$).

[0015] In one embodiment, the content of the stable phase is 0.01-1.0%.

[0016] In another embodiment, the coating phase of the present invention is added in the form of a liquid-phase carbonizable precursor, and exists in the form of amorphous carbon after sintering. The content of coating phase is 0-3%, and the thickness is 2-100 nm.

[0017] In another embodiment, in the preparation method of the present invention, the particle size of the original material, the order of adding the material (first adding the titanium source, then adding the phosphorus source and the sodium source), and the adjustment of the pH value of the mixed slurry are the key technical points to achieve stable phase and coating phase generation.

[0018] Compared with prior art, advantages of the present invention are as follows:

1. By adding dopant metal ions, a second phase is formed as a stable phase during sintering. The stable phase and the main phase have the same crystal structure and will not produce lattice distortion; at the same time, the stable phase, which is evenly distributed in the main phase, has stronger ionic bond force. So, the stable phase can support the crystal structure of the main phase and enhance its chemical stability. Compared with the existing common doping technology(3), the stable phase and the main phase form a uniform distribution, and the stability of the crystal lattice is higher.

2. Suitable content of stable phase can improve the ionic conductivity of titanium phosphorus oxide without destroying the crystal structure stability of sodium titanium phosphate.

3. The coating phase is a hydrophilic amorphous carbon material, which is formed by carbonization of a liquid-phase carbonizable precursor under an inert atmosphere. On the one hand, it can improve the electrical conductivity of the material, and on the other hand, it can provide a stable chemical and electrochemical reaction interface.

4. The liquid-phase carbonizable precursor is a water-soluble substance, which can form an ionic mixture with the main phase, and evenly covers the surface of the sintered particles after carbonization. Meanwhile, the amount of the liquid-phase carbonizable precursor should not be too high, so as not to hinder the synthesis and growth of grains during the sintering process.

[0019] The present invention tests ion resistance and electronic resistance by the following method: selecting PFTE as binder, the resulting powder was mixed with the binder in a ratio = 90:10, and then

the slurry was coated on a Ti foil current collector by the method of tape casting. The electrode obtained after drying and rolling had an active material loading of 0.3g/cm^2 . 1M sodium sulfate was used as electrolyte, and the impedance Nyquist spectrum was obtained using a symmetrical battery (Z' and Z'' in the spectrum are the real and imaginary parts of the impedance at different frequencies), and the ohmic resistance and the ionic resistance were thus determined.

[0020] The present invention tests coating phase content by the following method: using differential heat-thermogravimetry to determine coating phase content.

[0021] The present invention tests specific capacity by the following method: 10 mg of electrode powder was pressed with a pressure of 30 MPa on a stainless-steel mesh as the working electrode, with a Pt electrode as the counter electrode, and Ag/AgCl as the reference electrode. A CV curve of the electrode was obtained, the scan rate was 0.1 mv/s, and the specific capacity was calculated according to the peak area.

[0022] The present invention tests cycling performance by the following method: Using the prepared three samples as the negative electrode, manganese oxide as the positive electrode, and stainless steel as the current collector, the full battery was assembled, and 1M sodium sulfate was used as electrolyte. In order to get results quickly, accelerated test was used. The conditions were: pH of electrolyte was adjusted to 10, testing temperature was 60°C , the test voltage range was 1.0-1.9V.

[0023] The present invention tests alkali corrosion by the following method: The powder obtained by sintering was dissolved in 1M sodium hydroxide solution, and magnetically stirred at 80°C for 10 days to test XRD and SEM.

[0024] The test results are as follows:

1. Compared with the controlled sample, the ionic resistance and electronic resistance of the composite titanium phosphorus oxide decreased by about 30%, and the specific capacity increased by about 10% (see Table 1 below and Figure 1).
2. The cycle stability has been greatly improved. In the case of accelerated testing, the 100-cycle capacity retention rate has increased from 70% to 80% and 90% (see Figure 2).
3. At the same time, the corrosion resistance test shows that the composite titanium phosphorus oxide still maintains a complete crystalline form after being soaked in a strong alkaline solution, while the controlled sample has been corroded (see Figure 3).

Table 1: composition and test data of experimental samples (S1 and S2) and control (S3)

S1	Main phase	$\text{NaTi}_2(\text{PO}_4)_3$
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	Raw materials	Sodium carbonate, ammonium dihydrogen phosphate, titanium dioxide
	Stable phase	$\text{Mn}(\text{TiCr})(\text{PO}_4)_3$
	Raw materials	Manganese Carbonate, Chromium Carbonate, Ammonium Dihydrogen Phosphate
	Content of stable phase	0.5%
	Content of coating phase	2.1%
	Ionic resistance $\Omega\cdot\text{cm}$	0.17
	Electronic resistance $\Omega\cdot\text{cm}$	0.38
	Specific capacity mAh/g	78.7
S2	Main phase	$\text{NaTi}_2(\text{PO}_4)_3$
	Raw materials	Sodium Dihydrogen Phosphate, Diammonium Hydrogen Phosphate, Titanium Hydroxide
	Stable phase	$\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$
	Raw materials	Magnesium Hydroxide, Titanium Hydroxide, Diammonium Hydroxide Phosphate
	Content of stable phase	0.1%
	Content of coating phase	0.9%
	Ionic resistance $\Omega\cdot\text{cm}$	0.13
	Electronic resistance $\Omega\cdot\text{cm}$	0.45
	Specific capacity mAh/g	75.9
S3	Main phase	$\text{NaTi}_2(\text{PO}_4)_3$
	Raw materials	Sodium carbonate, diammonium hydrogen phosphate, titanium oxide
	Stable phase	none
	Raw materials	none
	Content of stable phase	none
	Content of coating phase	none
	Ionic resistance $\Omega\cdot\text{cm}$	0.25
	Electronic resistance $\Omega\cdot\text{cm}$	0.51
	Specific capacity mAh/g	70.8

[0025] The present invention may be better understood by reference to the following examples. 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.

Experimental and control samples

[0026] Experimental sample S1: The raw materials of main phase were sodium carbonate, ammonium dihydrogen phosphate, and titanium dioxide powder; the raw materials of stable phase were manganese carbonate, chromium carbonate, and ammonium dihydrogen phosphate. The amounts of raw materials corresponded to a ratio of main phase to stable phase of 99.5: 0.5. The titanium source was dispersed evenly by stirring in deionized water, and then the sodium source and phosphorus source and the raw materials of the stable phase were added. Sucrose was added as the coating phase, and the ratio of sucrose to total metallic ion was 8:1, the pH value of the slurry was adjusted to 6.5, and the obtained slurry was dried by microwave to obtain a powder precursor. The composite titanium-phosphorus oxide ceramic powder was obtained after sintering the precursor at 700 °C for 10 h under a nitrogen atmosphere.

[0027] Experimental sample S2: Main phase raw materials were sodium dihydrogen phosphate, diammonium hydrogen phosphate, and titanium hydroxide powder; stable phase raw materials were magnesium hydroxide, magnesium hydroxide, titanium hydroxide, and diammonium hydrogen phosphate, wherein the amounts of raw materials corresponded to a ratio of main phase to stable phase of 99.9: 0.1. The titanium source was uniformly dispersed by stirring in deionized water, and the sodium source and phosphorus source and the raw materials of the stable phase were added. Citric acid was added as a coating phase so that the ratio of citric acid to metal ions was 5:1, the pH value of the slurry was adjusted to 7, and the obtained slurry was spray-dried to obtain a powder precursor. A composite titanium phosphorus oxide ceramic powder was obtained after sintering the precursor at 750°C for 6 h under a nitrogen atmosphere.

[0028] Control sample S3: The main phase raw materials were sodium carbonate, diammonium hydrogen phosphate and titanium oxide powder. The titanium source was uniformly dispersed by stirring in deionized water, and the sodium source, phosphorus source and the raw materials of the stable phase were added; the pH value of the slurry was adjusted to 7.4, and the obtained slurry was vacuum dried to obtain a powder precursor. Pure titanium phosphorus oxide ceramic powder was obtained after sintering the precursor at 650°C for 20 h under a nitrogen atmosphere.

[0029] Literature or published articles cited in this patent application are incorporated by reference into this application in order to fully describe the state of the art. It is also important to note that 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.

References

1. Thermal runaway caused fire and explosion of lithium-ion battery, Journal of Power Sources 208(2012) 210-224.
2. Lifetime prediction and sizing of lead-acid batteries for microgeneration storage applications,

10.1049/iet-rpg:20080021.

3. Outstanding electrochemical performance of sodium vanadium phosphate cathode co-modified by carbon-coating and titanium-doping for Na-ion batteries, *Ceramics International*, 45(2019)12570-12574.

What is claimed is:

1. A titanium-phosphorus oxide, comprising a main phase, stable phase and coating phase, wherein the main phase is $\text{NaTi}_x\text{M}_y(\text{PO}_4)_3$, wherein $\text{M} = \text{Ti}, \text{V}$ or Mn , and $x + y = 2$; wherein the stable phase is $\text{M}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ or $\text{M}_1(\text{TiM}_2)(\text{PO}_4)_3$, wherein $\text{M} = \text{Sr}, \text{Ca}, \text{Mn}, \text{Mg}, \text{C}$ or Cu ; $\text{M}_1 = \text{Fe}, \text{Na}, \text{Mn}, \text{Sn}$ or Na , $\text{M}_2 = \text{Ge}, \text{Nb}, \text{Cr}$ or Sn .
2. The titanium-phosphorus oxide of claim 1, wherein the proportion of the stable phase is 0.01-1.0%;
3. The titanium-phosphorus oxide of claim 1, wherein the coating phase is formed by sintering a water-soluble carbon-containing precursor, is not more than 3% in proportion, and is 2-100 nm.thick, wherein said precursor is selected from polydopamine, resorcinol-formaldehyde resin, glucose, sucrose, fructose, polyvinylpyrrolidone (PVP), tannic acid, citric acid, polyvinyl alcohol, polypyrene, vitamin C and polyethylene glycol.
4. The titanium-phosphorus oxide of claim 1, wherein the main phase is $\text{NaTi}_2(\text{PO}_4)_3$, and the stable phase is $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ or $\text{Mn}(\text{TiCr})(\text{PO}_4)_3$.
5. A method of preparing the titanium-phosphorus oxide of claim 1, comprising the following steps: (a) dispersing a titanium source in water uniformly, then adding a sodium source and a phosphorus source in sequence; (b) adding stable phase raw materials; (c) adding coating phase raw materials and adjusting the pH of the resulting slurry to 6-8; (d) drying the slurry to obtain a precursor powder; (e) sintering the precursor powder to obtain a ceramic powder of the titanium-phosphorus oxide.
6. The method of claim 5, wherein the sodium source is selected from sodium phosphate, sodium carbonate, sodium dihydrogen phosphate, sodium hydroxide and sodium acetate, and its particle diameter of D50 is less than 3 μm
7. The method of claim 5, wherein the titanium source is selected from titanium dioxide, titanium hydroxide, metatitanic acid and tetrabutyl titanate, and its particle size of D50 is less than 1 μm ;
8. The method of claim 5, wherein the phosphorus source is selected from phosphoric acid, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonium phosphate, sodium dihydrogen phosphate and disodium hydrogen phosphate, and its particle size of D50 is less than 3 μm .
9. The method of claim 5, wherein the raw material of the stable phase is selected from manganese carbonate, chromium carbonate, diammonium phosphate, magnesium hydroxide, titanium hydroxide and dihydrogen phosphate.
10. The method of claim 5, wherein the molar ratio of coating phase to main phase ranges from 1:1 to 5:1.

11. The method of claim 5, wherein the precursor is sintered at 600-1000°C for 5-20 hours under an inert atmosphere.