COATED SEPARATOR, PREPARATION METHOD FOR COATED SEPARATOR, AND BATTERY

TECHNICAL FIELD

[0001] The present application relates to the technical field of battery separators, and in particular to a coated separator, a preparation method for a coated separator and a battery.

BACKGROUND

[0002] A separator is one of the core components of lithium batteries. Its performance has a very important impact on the overall performance of lithium batteries and is one of the key technologies restricting the development of lithium batteries. As the application field of lithium batteries continues to expand and the impact of lithium battery products in people's lives continues to deepen, people's demands for the performance of lithium batteries are also getting higher and higher. In order to meet the development requirements of lithium batteries, a separator, as an important component of lithium batteries, should have good chemical stability and low manufacturing costs, besides, it is also an important trend to improve the safety performance of lithium batteries in the current development of lithium batteries.

[0003] In the existing related art, a coated separator may include a base film and a coating layer coated on at least one surface of the base film. The coating layer may include one-dimensional nanomaterials. However, the one-dimensional nanomaterials are stacked in a chaotic manner, which leads to too many voids and few contact points, thereby affecting the thermal stability of the separator.

SUMMARY

[0004] The present application provides a coated separator, a preparation method for coated separator and a battery, so as to improve the performance of the separator.

[0005] According to a first aspect of the present application, a coated separator is provided, including: a base film and a coating layer structure provided on at least one surface of the base film; where, the coating layer structure contains multiple material layers, and the coating layer structure contains one-dimensional nanomaterials and ceramic particles, and in a direction away from the base film, an average length of the one-dimensional nanomaterials in each material layer gradually decreases layer by layer.

[0006] In an embodiment, a proportion of a thickness of a coating layer distributed with ceramic particles in the coating layer structure to a total thickness of the coating layer structure reaches 80% or more. In an embodiment, a proportion of a thickness of a coating layer distributed with ceramic particles in the coating layer structure to a total thickness of the coating layer structure reaches 90% or more. In an embodiment, a proportion of a thickness of a coating layer distributed with ceramic particles in the coating layer structure to a total thickness of the coating layer structure reaches 100%.

[0007] In an embodiment, a mass ratio of the one-dimensional nanomaterials to the ceramic particles in the coating layer structure is 1:1-1:14.

[0008] In an embodiment, the ceramic particles include first ceramic particles and second ceramic particles; where, a particle diameter of the second ceramic particles is larger than a particle diameter of the first ceramic particles, and the particle diameter of the second ceramic particles is larger than a diameter of the one-dimensional nanomaterials.

[0009] In an embodiment, the particle diameter of the second ceramic particles is two or more times the diameter of the one-dimensional nanomaterials.

[0010] In an embodiment, the particle diameter of the second ceramic particles differs from at least one of the diameter of the one-dimensional nanomaterials and the particle diameter of the first ceramic particles by one order of magnitude or more.

[0011] In an embodiment, the diameter of the one-dimensional nanomaterials is 5-50 nm, an average particle diameter of the first ceramic particles is 10nm-60 nm, and an average particle diameter of the second ceramic particles is 100nm-600 nm.

[0012] In an embodiment, in the coating layer structure, a mass ratio of the first ceramic particles to the second ceramic particles is 5:1-1:5.

[0013] In an embodiment, at least one of the first ceramic particle and the second ceramic particle is an inorganic substance, which has a melting point above 200°C, is

electrically insulating, and is electrochemically stable within a use range of lithium battery.

[0014] In an embodiment, a surface of the first ceramic particles is grafted with a lithium-ion conductor functional group.

[0015] In an embodiment, the lithium-ion conductor functional group includes any one of hydroxyl (-OH), carbonyl (-C=O), fluorine (-F), and carboxyl (-COOH).

[0016] In an embodiment, an average length value of the one-dimensional nanomaterials in the coating layer structure is between 250nm and 400nm.

[0017] In an embodiment, the coated separator at least meets any of the following conditions:

a) anti-puncture force of coating layer ≥ 7N;

b) ion conductivity ≥ 0.8;

c) capacity retention rate ≥ 90%;

d) thermal contraction at 180°C/h ≤ 4%.

[0018] According to a second aspect of the present application, a preparation method for coated separator is provided for preparing the coated separator related to the first aspect and the alternatives thereof, including:

dispersion of ceramic particles: dispersing the ceramic particles in a first solvent to obtain a ceramic particle dispersion liquid;

dispersion of one-dimensional nanomaterials: dispersing the one-dimensional nanomaterials of different lengths in the same or different dispersants to obtain at least one one-dimensional nanomaterial dispersion liquid;

mixing and forming a slurry: preparing a mixed solution including the ceramic particle dispersion liquid and the one-dimensional nanomaterial dispersion liquid to form at least one corresponding slurry;

coating and forming a film: coating the at least one slurry on at least one surface of the base film and drying to obtain the coated separator.

[0019] In an embodiment, before the dispersion of ceramic particles, the method further includes:

ceramic particles screening: selecting first ceramic particles and second ceramic particles of different particle diameters, where an average particle diameter of the first ceramic particles is 10-60nm, and an average particle diameter of the second ceramic

particles is 100-600nm;

further, the method includes a pretreatment for ceramic particles: adding the first ceramic particles to a second solvent and placing them in a reaction kettle, adding a material to be grafted to perform a grafting reaction, so that a lithium-ion conductor functional group is grafted on a surface of the first ceramic particles.

[0020] In an embodiment, the material to be grafted includes any one of polycarbonate, polylactic acid, polyurethane, perfluoropropyl vinyl ether, and methyl isopropyl ketone.

[0021] According to a third aspect of the present application, a battery is provided, including the coated separator according to all the embodiments related to the first aspect or including the coated separator prepared by the preparation method for coated separator according to all the embodiments related to the second aspect;

further, the battery is a lithium battery.

[0022] In the coated separator, the preparation method for coated separator and the battery provided by the present application, since an average length of the one-dimensional nanomaterials in each material layer decreases gradually layer by layer and is distributed in an orderly manner, on the one hand, the formation of large gaps resulted from the chaotic and disorderly distribution of one-dimensional nanomaterials can be avoided; on the other hand, in order to avoid that too large stacking density of one-dimensional nanomaterials affects the transmission of lithium ions, the present application adds ceramic particles to the coating layer structure, so that the coating layer structure is a mixture of one-dimensional nanomaterials and ceramic particles. Addition of ceramic particles can avoid an excessive stacking density of one-dimensional nanomaterials, thereby forming a more effective lithium ion transmission channel, increasing the lithium ion transmission rate and effectively improving the performance of separator and battery.

BRIEF DESCRIPTION OF DRAWINGS

[0023] In order to more clearly illustrate the technical solutions in the embodiments of the present application or the prior art, the following will briefly introduce the drawings that need to be used in the description of the embodiments or the prior art. Obviously, the accompanying drawings in the following description are only some embodiments of the present application. For those skilled in the art, other drawings can also be obtained

according to these drawings without any creative effort.

[0024] FIG. 1 is a partial structural schematic diagram of a coated separator in an embodiment of the present application.

[0025] FIG. 2 is a schematic flow chart of a preparation method for coated separator in an embodiment of the present application.

[0026] FIG. 3 is a schematic diagram showing the change of a length value of l50 of a material layer with a coating layer position in a specific example of the present application.

[0027] Description of reference signs:

1-coated separator; 11-base film; 12-coating layer structure; 13-ceramic particles.

DESCRIPTION OF EMBODIMENTS

[0028] The technical solutions in the embodiments of the present application will be clearly and completely described below with reference to the accompanying drawings in the embodiments of the present application. Obviously, the described embodiments are only some of the embodiments of the present application, rather than all the embodiments. Based on the embodiments of the present application, all other embodiments obtained by those skilled in the art without making creative efforts belong to the protection scope of the present application.

[0029] In the description of the present application, it should be understood that the orientation or positional relationship indicated by the terms “upper portion”, “lower portion”, “upper end”, “lower end”, “lower surface”, “upper surface” and the like, which is based on the accompanying drawings, is only used to facilitate the description of the present application and simplify the description, instead of indicating or implying that the device or element referred to must have a specific orientation or be constructed and operated in a specific orientation, and therefore cannot be understood as limiting the scope of the present application.

[0030] In the description of the present application, the terms “first” and “second” are only used for descriptive purposes and cannot be understood as indicating or implying relative importance or implicitly indicating the number of indicated technical features. Therefore, a feature defined by “first” or “second” may explicitly or implicitly include one

or more such features.

[0031] In the description of the present application, “a plurality of” means more, such as two, three, four, etc., unless otherwise clearly and specifically limited.

[0032] In the description of the present application, unless otherwise clearly stated and limited, the terms “connection” and the like should be understood in a broad sense. For example, it may be a fixed connection, a detachable connection, or an integrated connection; it may be a mechanical connection, an electrical connection or in communication with each other; it may be a direct connection, or an indirect connection through an intermediate medium; it may be an internal connection of two components or an interaction relationship between two components. For those of ordinary skill in the art, the specific meanings of the above terms in the present application can be understood according to specific circumstances.

[0033] The technical solution of the present application will be described in detail below with specific embodiments. The following specific embodiments can be combined with each other, and the same or similar concepts or processes may not be repeated again in some embodiments.

[0034] Before proposing this application, the applicant conducted a series of research and experiments on existing separators.

[0035] Where, in order to solve the problem that the accumulation of one-dimensional nanomaterials in the coating layer is chaotic and disorderly, which is prone to too many voids and few contact points, the applicant proposed a corresponding solution, by making a length of the one-dimensional nanomaterials decrease gradually layer by layer (reflected by a decrease of a length description value of one-dimensional nanomaterials in each material layer). Since a void accumulated by long nanomaterials is large, the closer to a bottom layer, the larger the void, and the shorter nanomaterials on an upper layer can fill these voids to a certain extent, after a layer-by-layer deposition, there are no too many voids inside the coating layer, and there are more contact points. When heated, the compact structure of the coating layer can inhibit a thermal deformation of the separator, thereby improving heat resistance of the coated separator. For this solution, the applicant also proposed a patent application (application number: PCT/CN2022/077087, application date: February 21, 2022), and the present application introduces the entire content of

PCT/CN2022/077087, namely all content of PCT/CN2022/077087 can be used as support for the present application.

[0036] However, the applicant found in further research that although the above solution can improve the heat resistance of the separator compared to the disordered arrangement of one-dimensional nanomaterials, the overall performance of the separator is still not ideal. The applicant found through research and experiments that the reason is that the stacking method of length of one-dimensional nanofiber decreasing layer by layer makes the coating layer have the greatest packing density and also makes the nanofiber have the most contacts with each other. However, an excessively high packing density of one-dimensional nanofiber hinders the transmission channel of lithium ions, affects the transmission rate of lithium ions, and then limits the performance of the separator.

[0037] Based on this discovery, and through a series of research, tests and verifications, the applicant obtained the technical solution of the present application. Since an orderly arrangement of one-dimensional nanofiber is a major initiative of the applicant, the problems for further research and solutions obtained based on the orderly arrangement are also a major initiative, and the entire research process should be regarded as an inseparable part of this solution, and considered as a whole when evaluating the creativity of the present application.

[0038] Please refer to FIG. 1. An embodiment of the present application provides a coated separator 1, including: a base film 11 and a coating layer structure 12 provided on at least one surface of the base film 11. The coating layer structure 12 contains multiple material layers, One-dimensional nanomaterials and ceramic particles 13 are distributed in the coating layer structure 12. Along a direction away from the base film, an average length of the one-dimensional nanomaterials in each material layer decreases layer by layer. Correspondingly, an average size of gap between the one-dimensional nanomaterials in each material layer also gradually decreases.

[0039] In the embodiment of the present application, considering that the problem of a low ion conduction rate resulted from excessively small gaps due to an excessively dense coating layer of one-dimensional nanomaterials, introduction of ceramic particles can effectively improve the ion conduction rate. However, if the one-dimensional nanomaterials are distributed disorderly, in a case of additionally introducing extra ceramic

particles, it is prone to disordered mixing, which results in a phenomenon that in some local areas, the lithium ion transmission channels are small, while in other local areas, the lithium ion transmission channels are large, making the transmission speed of lithium ions in different areas very different, thus easily causing problems in the growth and development of lithium dendrites (which can easily lead to self-discharge), further causing battery capacity attenuation and safety issues. In the present application, on the basis of reducing the average length of the one-dimensional nanomaterials in each material layer layer by layer, ceramic particles are incorporated into the one-dimensional nanomaterials; and the use of the ceramic particles can avoid an excessive stacking density of the one-dimensional nanomaterials, thereby forming more effective lithium ion transmission channels, and increasing a lithium ion transmission rate, which can effectively improve the performance of separators and batteries.

[0040] In an embodiment, a mass ratio of the one-dimensional nanomaterials to the ceramic particles in the coating layer structure 12 is 1:1-1:14. As a specific embodiment, for example, the mass ratio of the one-dimensional nanomaterials to the ceramic particles in the coating layer structure 12 can be any one of 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, 1:10, 1:11, 1:12, 1:13, and 1:14, or a range between any two of them. Of course, the mass ratio of the one-dimensional nanomaterials to the ceramic particles in the coating layer structure 12 can also take other values. The specific values are not limited in the present application, as long as the ratio is between 1:1 and 1:14, they are all within the protection scope of the present application.

[0041] In an embodiment, the ceramic particles in the coating layer structure 12 include first ceramic particles and second ceramic particles; where a particle diameter of the first ceramic particles is comparable to a diameter of the one-dimensional nanomaterials; and the particle diameter of the second ceramic particles is much larger than the diameter of the one-dimensional nanomaterials.

[0042] Specifically, the diameter of the one-dimensional nanomaterials is 5-50 nm, an average particle diameter of the first ceramic particles is 10-60 nm, and an average particle diameter of the second ceramic particles is 100-600 nm.

[0043] In the embodiment of the present application, the one-dimensional nanomaterials of different lengths distributed in multiple material layers are mixed with

multi-scale ceramic particles. The one-dimensional nanomaterials at the bottom are long and the one-dimensional nanomaterials at the top are short. The one-dimensional nanomaterials in the same material layer are evenly distributed and have small length difference in different regions. The introduced multi-scale ceramic particles can fully accelerate the transmission of lithium ions. Where, the multi-material layer distribution refers to multiple material layers formed by obvious changes in the size of the nanofiber in a thickness direction, which can be multiple layers that are essentially separable, or can also be an artificial layering based on obvious size changes (e.g., 10% of a total thickness of a coating layer is defined as one layer, or 20%, 30%, 40%, etc. of the total thickness of the coating layer is defined as one layer; the multi-material layer distribution can also be defined based on an interface where the size changes significantly in the structure, which is not specifically limited here).

[0044] In an embodiment, a proportion of a thickness of a coating layer distributed with ceramic particles 13 in the coating layer structure 12 to a total thickness of the entire coating layer structure reaches 80% or more. In an embodiment, a proportion of a thickness of a coating layer distributed with ceramic particles 13 in the coating layer structure 12 to a total thickness of the entire coating layer structure reaches 90% or more. In an embodiment, a proportion of a thickness of a coating layer distributed with ceramic particles 13 in the coating layer structure 12 to a total thickness of the entire coating layer structure reaches 100%. In this way, the ceramic particles are relatively evenly dispersed in the coating layer structure to more effectively avoid an excessive stacking density of one-dimensional nanomaterials, thereby forming more effective lithium ion transmission channels, increasing the lithium ion transmission rate, and effectively improving the performance of separators and batteries. Besides, as a feasible embodiment, when the coating layer structure has an obvious layering, each layer contains ceramic particles, which can further increase the transmission rate of lithium ions and improve the performance of separators and batteries.

[0045] Besides, by setting an average particle diameter (D50) of the first ceramic particles to be comparable to a diameter of the one-dimensional nanomaterials, the gaps between the one-dimensional nanomaterials can be expanded and then improve the lithium ion conductivity; by setting an average particle diameter (D50) of the second ceramic

particles to be much larger than the average particle diameter of the first ceramic particles and the diameter of the one-dimensional nanomaterials, the anti-puncture property of the coating layer against the outside can be improved. Where, the meaning of "much larger than" herein represents 2 times or more. The applicant has confirmed through research that if the average particle diameter of the first ceramic particles is too small, it is prone to serious agglomeration, which will lead to a low lithium ion conductivity of the coating layer; and if the average particle diameter of the first ceramic particles is too large, it will not fully fill into the gaps between the one-dimensional nanomaterials. If the average particle diameter of the second ceramic particles is too small, the anti-puncture property will be reduced, and if the average particle diameter of the second ceramic particles is too large, the heat resistance of the coating layer will be sacrificed. Therefore, the average particle diameter of the first ceramic particles proposed in the present application is 10-60 nm, and the average particle diameter of the second ceramic particles is 100-600 nm, which are the feasible values after verification.

[0046] In an embodiment, the average particle diameter of the first ceramic particles may be, for example, any one of 10 nm, 15 nm, 20 nm, 25 nm, 30 nm, 35 nm, 40 nm, 45 nm, 50 nm, 55 nm, and 60 nm, or a range between any two of them. The average particle diameter of the second ceramic particles may be, for example, any one of 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 375 nm, 400 nm, 450 nm, 500 nm, 550 nm, and 600 nm, or a range between any two of them. Of course, the average particle diameter of the first ceramic particles and the average particle diameter of the second ceramic particles can also take other values. The specific values are not limited in the present application. As long as the average particle diameter of the first ceramic particles is 10-60 nm and the average particle diameter of the second ceramic particles is 100-600 nm, they all fall within the protection scope of the present application. And those skilled in the art should know that when the diameter of the one-dimensional nanomaterials changes, the average particle diameter of the first ceramic particles and the average particle diameter of the second ceramic particles will also change accordingly. As long as the particle diameter of the first ceramic particles is comparable to the diameter of the one-dimensional nanomaterials, and the particle diameter of the second ceramic particles is much larger than the diameter of the one-dimensional nanomaterials, they will not deviate from the scope of protection of

the present application.

[0047] In an embodiment, in the coating layer structure, a mass ratio of the first ceramic particles to the second ceramic particles is 5:1-1:5; thereby further improving the lithium ion conductivity of the coating layer, and at the same time, guaranteeing the anti-puncture property of the coating layer (the anti-puncture force of the coating layer ≥ 7N) and the thermal contraction performance (180℃/1h ≤ 4%) more effectively. The applicant found that when there are too many first ceramic particles, it is prone to a poor anti-puncture property, and if there are too few first ceramic particles, the expanding caused will be limited, thereby reducing the conductivity of lithium ions; and too many second ceramic particles will lead to a decrease in heat resistance, and too few second ceramic particles will lead to a decrease in anti-puncture property. Therefore, the mass ratio of the first ceramic particles to the second ceramic particles in the coating layer structure proposed in the present application is 5:1-1:5, which is a feasible value after verification.

[0048] Specifically, the mass ratio of the first ceramic particle to the second ceramic particle in the coating layer structure can be, for example, any one of 5:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, and 1:5, or a range between any two of them. Of course, the mass ratio of the first ceramic particles to the second ceramic particles in the coating layer structure can also take other values, and the specific values are not limited in the present application. As long as the mass ratio is within 5:1-1:5, it falls into the protection scope of the present application.

[0049] In an embodiment, a surface of the first ceramic particles is grafted with a lithium-ion conductor functional group. Specifically, the lithium-ion conductor functional group is introduced on the surface of the first ceramic particles through a grafting reaction. The lithium-ion conductor functional groups abundant on the surface of the first ceramic particles can greatly improve the lithium ion transmission capability. The grafted functional groups only work on the surface of the ceramic particles, and the particle diameter of the second ceramic particles is larger than that of the first ceramic particles, so the gap formed by the second ceramic particle is larger, and it is difficult for the lithium-ion conductor functional group to work; while the particle diameter of the first ceramic particles is small, and the gap formed by the first ceramic particles is small, which

can better promote the effect of the lithium-ion conductor and improve the lithium ion conductivity.

[0050] Regarding the manner in which the length of the one-dimensional nanomaterials decreases layer by layer along the coating layer in the embodiments of the present application, further details are as follows.

[0051] Where, the coating layer has three material layers as shown in FIG. 1 (here, the multi-material layer distribution is defined based on the interface where the size change is obvious in the coating layer structure). Where, the average length of the one-dimensional nanomaterials in the bottom layer is longer than the average length of the one-dimensional nanomaterials in the middle layer, which is in turn longer than the average length of the one-dimensional nanomaterials in the top layer. A difference in average length among respective layers of one-dimensional nanomaterials can be configured arbitrarily. The lengths of the one-dimensional nanomaterials in the same layer may be the same or different. In one embodiment, the one-dimensional nanomaterials may be at least one of the following: nanocellulose, aramid nanofiber, and polyimide nanofiber. The material selection of the one-dimensional nanomaterials in the embodiments of the present application is not limited to the above examples.

[0052] In one embodiment, the one-dimensional nanomaterials in different material layers form different length description values for the same second target proportion.

[0053] The length description value of the one-dimensional nanomaterials in the material layer indicates:

when the quantity of the one-dimensional nanomaterials in a material layer is gradually accumulated in an order from short to long, a ratio of the accumulated quantity to a total quantity of the one-dimensional nanomaterials in the material layer reaches the corresponding length of the one-dimensional nanomaterials when the second target proportion is reached; correspondingly, among the one-dimensional nanomaterials in the corresponding material layer, the proportion of the one-dimensional nanomaterials having a length smaller than the corresponding length description value can reach the target proportion; the above description shows the statistical significance of the length description value of the one-dimensional nanomaterials. When the length description value is actually determined, an actual calculation method can be processed according to

common sense in the field.

[0054] In an example, the second target proportion is in a range of 5%-40%, or in a range of 60%-99%. For example, it can be any one of 5%, 10%, 20%, 40%, 60%, 70%, 80%, 90%, and 99%, or a range between any two of them.

[0055] Where, in one embodiment, along the direction away from the base film, for the same second target proportion, the length description value of the one-dimensional nanomaterials of each material layer gradually decreases. Furthermore, a layer-by-layer length reduction trend of one-dimensional nanomaterials can be formed.

[0056] In addition, for the length description value of the corresponding material layer, although the meaning of the length description value is defined above by accumulating the quantity and determining the length description value based on the accumulation result, it does not necessarily mean that this statistic process is included in the actual preparation and acceptance process. In the actual solution, for any product, as long as the one-dimensional nanomaterials in the material layer are analyzed using values with the same statistically significance, the rule of obtained length description value meets the above description, that is, it does not deviate from the scope of protection of the present embodiment. In some solutions, the above length rule can be ensured by selecting the length of one-dimensional nanomaterials or specifically preparing the length of one-dimensional nanomaterials in advance.

[0057] Where, for the length description value for the one-dimensional nanomaterials of the material layer, for example, it may be as follows.

[0058] A value l10 of the one-dimensional nanomaterials in a material layer refers to: a length of corresponding one-dimensional nanomaterials when the quantity of the one-dimensional nanomaterials of respective lengths in the corresponding material layer is gradually accumulated in order from short to long, and a ratio of the accumulated quantity to the total quantity of the one-dimensional nanomaterials in the corresponding material layer reaches 10%;

a value l50 of the one-dimensional nanomaterials in the material layer refers to: a length of corresponding one-dimensional nanomaterials when the quantity of the one-dimensional nanomaterials of respective lengths in the corresponding material layer is gradually accumulated in order from short to long, and a ratio of the accumulated quantity

to the total quantity of the one-dimensional nanomaterials in the corresponding material layer reaches 50%. The l50 can also be understood as characterizing the average length of the corresponding material layer to a certain extent;

a value l90 of the one-dimensional nanomaterials in the material layer refers to: a length of corresponding one-dimensional nanomaterials when the quantity of the one-dimensional nanomaterials of respective lengths in the corresponding material layer is gradually accumulated in order from short to long, and a ratio of the accumulated quantity to the total quantity of the one-dimensional nanomaterials in the corresponding material layer reaches 90%.

[0059] In the case of realizing the decrement of l50 (i.e., the average length), the decrement of one or more other length description values (for example, l90, l10) can also be realized.

[0060] In one embodiment,

a length value of L10 of the one-dimensional nanomaterials in the coating layer structure is between 100nm and 300nm;

a length value of L50 of the one-dimensional nanomaterials in the coating layer structure is between 250nm and 400nm;

a length value of L90 of the one-dimensional nanomaterials in the coating layer structure is between 350nm and 900nm;

where,

the L10 of the one-dimensional nanomaterials in the coating layer structure represents: a length description value of the one-dimensional nanomaterials in the coating layer structure when 10% is used as the first target proportion;

the L50 of the one-dimensional nanomaterials in the coating layer structure represents: a length description value of the one-dimensional nanomaterials in the coating layer structure when 50% is used as the first target proportion, which can also be referred to as the average length of the one-dimensional nanomaterials in the coating layer structure;

the L90 of the one-dimensional nanomaterials in the coating layer structure represents: a length description value of the one-dimensional nanomaterials in the coating layer structure when 90% is used as the first target proportion.

[0061] The length description value of the one-dimensional nanomaterials in the coating layer structure shows:

a length of corresponding one-dimensional nanomaterials when the quantity of the one-dimensional nanomaterials in the coating layer structure is gradually accumulated in order from short to long, and a ratio of the accumulated quantity to the total quantity of one-dimensional nanomaterials in the coating layer structure reaches the first target proportion;

and for the one-dimensional nanomaterials in the coating layer structure, it satisfies: L50/L10>1.3, and L90/L50>1.3;

the L10 of the one-dimensional nanomaterials in the coating layer structure represents: a length description value of the one-dimensional nanomaterials in the coating layer structure when 10% is used as the first target proportion;

the L50 of the one-dimensional nanomaterials in the coating layer structure represents: a length description value of the one-dimensional nanomaterials in the coating layer structure when 50% is used as the first target proportion, which can also be referred to as the average length of the one-dimensional nanomaterials in the coating layer structure;

the L90 of the one-dimensional nanomaterials in the coating layer structure represents: a length description value of the one-dimensional nanomaterials in the coating layer structure when 90% is used as the first target proportion.

[0062] The above description shows the statistical significance of the length description value of the coating layer structure. When the length description value is actually determined, an actual calculation method can be processed according to common sense in the field.

[0063] In addition, for the length description value of the coating layer structure, although the meaning of the length description value is defined above by accumulating the quantity and determining the length description value based on the accumulation result, it does not necessarily mean that this statistic process is included in the actual preparation and acceptance process. In the actual solution, for any product, as long as the one-dimensional nanomaterials in the material layer are analyzed using values with the same statistically significance, the rule of obtained length description value meets the

above description, that is, it does not deviate from the scope of protection of the present embodiment. In some solutions, the above length rule can be ensured by selecting the length of one-dimensional nanomaterials or specifically preparing the length of one-dimensional nanomaterials in advance.

[0064] In one example, for the one-dimensional nanomaterials in the coating layer structure, L10=110nm, L50=310nm, and L90=850nm.

[0065] In a direction away from the base film, a fitting result of a relationship between the length value of l50 of the one-dimensional nanomaterials in respective material layers and a coating layer position where a material layer is located (a position in the thickness direction of the coating layer) can be understood with reference to the curves 1, 2a and 2b in FIG. 3. Furthermore, it can be reflected in the curves that as the thickness increases (that is, as a distance between the coating layer position where the material layer is located and the base film increases), the length value of L50 gradually decreases.

[0066] In FIG. 3, the coating layer position on the abscissa is to characterize: along the thickness direction, the location of the coating layer position in the coating layer structure, the material layer being located at the coating layer position; if it is characterized by a percentage, it can be characterized as: a percentage of a distance between the coating layer position and the base film relative to an overall thickness of the coating layer structure, the material layer being located at the coating layer position. For example, 10% means that the distance between the coating layer position and the base film accounts for 10% of the overall thickness of the coating layer structure.

[0067] For the curve 1, as the distance between the coating layer position where the material layer is located and the base film increases, the length value of l50 of the one-dimensional nanomaterials in the material layer can be fitted as a linear change. At this time, the relationship between a length value x of the l50 and the coating layer position Y can be, for example, expressed as: $Y= kx+b$ ($k<0$, $b>0$).

[0068] For the curve 2a, as the distance between the coating layer position where the material layer is located and the base film increases, the length values of l50 of the one-dimensional nanomaterials in the material layer can show a first fast and then slow change trend.

[0069] For the curve 2b, as the distance between the coating layer position where the

material layer is located and the base film increases, the length values of l50 of the one-dimensional nanomaterials in the material layer can show a first slow and then fast change trend.

[0070] In order to realize the above change trend of linear change, first fast and then slow, and first slow and then fast, it can be realized through the length configuration of the one-dimensional nanomaterials in the coating layer structure. Furthermore, the length configuration of the one-dimensional nanomaterials in the coating layer structure can be selected according to the desired change trend.

[0071] For example, if a linear change is required (for example, as shown in the curve 1), the length configuration of the one-dimensional nanomaterials in the coating layer structure needs to satisfy: $2 \geq L90/L50 > 1.5$;

if it is necessary to achieve a change trend that is first slow and then fast (for example, as shown in the curve 2b), the length configuration of the one-dimensional nanomaterials in the coating layer structure needs to satisfy: $L50/L10 > 2$, $1.5 \geq L90/L50 \geq 1.3$;

if it is necessary to achieve a change trend that is first fast and then slow (for example, as shown in the curve 2a), the length configuration of the one-dimensional nanomaterials in the coating layer structure needs to satisfy: $L90/L50 > 2$.

[0072] Since the prior art is not dedicated to forming a layered structure, it is impossible for the prior art to disclose or reveal the length configurations for different change trends in the above solutions.

[0073] At the same time, embodiments of the present application also provide a battery, including the coated separator related to any one of the above solutions.

[0074] In addition, please refer to FIG. 2, an embodiment of the present application also provides a preparation method for a coated separator for preparing the coated separator related to the first aspect and the alternatives thereof. The preparation method includes:

S1: dispersion of ceramic particles: dispersing the ceramic particles in a first solvent to obtain a ceramic particle dispersion liquid.

[0075] Specifically, ceramic particles are dispersed in a first solvent to obtain a dispersion liquid. The first solvent is selected from any one of water, N-methylpyrrolidone,

ethanol, acetone, etc. The ceramic particles are uniformly dispersed in the solvent through high-speed stirring, high-pressure homogenization, sand grinding and dispersion and other means. A mass concentration of the ceramic particles in the dispersion liquid is 2%-40%.

S2: dispersion of one-dimensional nanomaterials: dispersing the one-dimensional nanomaterials of different lengths in the same or different dispersants to obtain at least one one-dimensional nanomaterial dispersion liquid.

[0076] Specifically, one-dimensional nanomaterials of different lengths are dispersed in a dispersant to obtain a dispersion liquid. The dispersant is selected from any one of water, N-methylpyrrolidone, ethanol, acetone, etc. The one-dimensional nanomaterials are uniformly dispersed in the dispersant through high-speed stirring, high-pressure homogenization, sand grinding and dispersion and other means. A mass concentration of the one-dimensional nanomaterials in the dispersant is 2%-30%.

[0077] Where, at least part of one-dimensional nanomaterials of different lengths are realized based on the selection of raw material for the one-dimensional nanomaterials. For example, when the one-dimensional nanomaterials made of different raw materials are selected, the one-dimensional nanomaterials of different lengths can be formed.

[0078] In other examples, the one-dimensional nanomaterials of different lengths can also be formed through corresponding technical means.

[0079] A raw material of a one-dimensional nanomaterial or a cut-off one-dimensional nanomaterial can be cut for once or more times, so as to form a one-dimensional nanomaterial of a different length.

[0080] Where, a shorter one-dimensional nanomaterial can be formed based on a raw material of a one-dimensional nanomaterial with a length by cutting the one-dimensional nanomaterial, for example, by cutting the one-dimensional nanomaterial into half of the raw material, and in other examples, by not cutting into half.

[0081] Any existing means or improved means that can realize the cutting of one-dimensional nanomaterials can be used as a specific example of the embodiment of the present application. In a specific example, it can be realized by etching the one-dimensional nanomaterials, for example, by etching the one-dimensional nanomaterials into half the length of the raw material.

[0082] Based on the required layering, the raw material can be cut once or multiple

times. For example, one-dimensional nanomaterials can be etched to half of a length of the raw materials, then a part of one-dimensional nanomaterials of half of the length can be retained, and the other part of one-dimensional nanomaterials of half of the length can be cut so as to obtain one-dimensional nanomaterials of quarter of the length. At this point, a three-layered structure may be formed. In other examples, a part of one-dimensional nanomaterials of quarter of the length can be further cut; and the number of cutting can be configured arbitrarily based on demand.

[0083] Of course, at least one of the following joining processes can also be implemented, and at least part of one-dimensional nanomaterials of different lengths can be formed through one or more times of joining:

joining one raw material of a one-dimensional nanomaterial to an end of another raw material of a one-dimensional nanomaterial;

joining one joined one-dimensional nanomaterial to an end of one raw material of a one-dimensional nanomaterial;

joining one joined one-dimensional nanomaterial to an end of another joined one-dimensional nanomaterial.

[0084] It can be seen that an object to be joined can be one end of one raw material of a one-dimensional nanomaterial and one end of another raw material of a one-dimensional nanomaterial; or, one end of one raw material of a one-dimensional nanomaterial and one end of one joined one-dimensional nanomaterial; or, one end of one joined one-dimensional nanomaterial and one end of another joined one-dimensional nanomaterial.

[0085] Where, through the joining of one-dimensional nanomaterials, a longer one-dimensional nanomaterial can be formed based on a raw material of a one-dimensional nanomaterial of a length. For example, two raw materials of one-dimensional nanomaterial may be joined to form a one-dimensional nanomaterial with twice the length. In other examples, raw materials of one-dimensional nanomaterial (or joined one-dimensional nanomaterials) of different lengths can also be used.

[0086] Any existing means or improved means that can realize the joining of one-dimensional nanomaterials can be used as a specific example of the embodiment of the present application.

[0087] For example, the joining of one-dimensional nanomaterials can be achieved based on materials rich in a hydroxyl functional group (such as polyethylene glycol, PEG). Thus, the above-mentioned joining may include:

mixing one-dimensional nanomaterials to be joined with a material rich in hydroxyl functional group (e.g., PEG) in a solution;

adding molecular sieve particles as a catalyst to the solution;

heating the solution, then cooling down, and filtering to remove the molecular sieve particles, so as to obtain joined one-dimensional nanomaterials.

[0088] As a specific example, nanocellulose fiber is taken as an example. A hydroxyl content of an end portion of nanocellulose fiber is significantly higher than that of a middle region of nanocellulose. In order to increase a length of nanocellulose fiber, the activity of hydroxyl groups can be fully utilized as follows:

(1) mixing nanocellulose fibers and polyethylene glycol (PEG), where a molecular weight of PEG is 50000-1000000g/mol and PEG accounts for 1% of a mass of nanocellulose fibers, and stirring the two components thoroughly to form a corresponding solution;

(2) adding 13A molecular sieve particles to the above solution, where a size of the molecular sieve particle is 1mm-10mm, and the molecular sieve serves as a catalyst;

(3) heating in water bath to 80 °C for 1-2 hours;

(4) cooling to a normal temperature, filtering to remove the 13A molecular sieve particles, so as to obtain the joined nanocellulose fibers.

[0089] In the above solutions, by adding the materials rich in hydroxyl functional group (such as PEG), it is possible to form a bridged connection between the nanocellulose fibers; and using the molecular sieve (such as 13A molecular sieve) as a catalyst, the polymerization reaction between PEG and nanocellulose fibers can be accelerated, so as to finally form a structure of nanocellulose fiber-PEG-nanocellulose fiber. Based on the required layering, it is possible to realize the joining of the raw material for one or more times. For example, the raw material of one-dimensional nanomaterial may be joined each other to obtain one-dimensional nanomaterials with twice the length of the raw materials first, then a part of the one-dimensional nanomaterials with twice the length can be retained, and then another part of one-dimensional nanomaterials with twice the length can

be joined to the raw material or the one-dimensional nanomaterial with twice the length to obtain a one-dimensional nanomaterial with three times the length or four times the length. At this point, a three-layered structure may be formed. In other examples, further joining can be carried out, and the number of joining can be arbitrarily configured according to requirements.

[0090] In a solution of step S2, one-dimensional nanomaterials of various lengths can be dispersed in the same dispersant; and then based on the slurry corresponding to the same dispersant, delamination is achieved after coating. In another solution of step S2, different dispersants can also be formed based on one-dimensional nanomaterials of different lengths (the lengths of one-dimensional nanomaterials in different dispersants are different), and then different dispersion liquids and slurries can be formed. When coating, various slurries can also be coated in layers based on the length of the one-dimensional nanomaterials.

[0091] In one example, in step S2, one-dimensional nanomaterials of various lengths can be fully dispersed in a dispersant to obtain a dispersion liquid, and the dispersant, for example, can be selected from any one of water, ethanol, methanol, etc. The dispersion method, for example, can be ultrasonic treatment, high-speed stirring, high-pressure homogenization, sand grinding and other methods, through which one-dimensional nanomaterials can be uniformly dispersed in the dispersant. The concentration of the one-dimensional nanomaterials in the dispersion liquid may range from 0.01 wt% to 50 wt%.

[0092] S3: mixing and slurry-forming: preparing a mixed solution including the ceramic particle dispersion liquid and the one-dimensional nanomaterial dispersion liquid to form at least one corresponding slurry.

[0093] Specifically, the ceramic particle dispersion liquid obtained in step S1 is mixed with the one-dimensional nanomaterial dispersion liquid obtained in step S2, and the mixing method may adopt high-speed stirring, high-pressure homogenization, sand grinding and dispersion, etc. An adhesive is then added into the mixed solution. The adhesive is at least one of polyvinyl alcohol, polyacrylonitrile, polyacrylic acid, styrene-butadiene rubber, carboxymethylcellulose, polyvinylidene fluoride, polyvinylpyrrolidone and polyimide. The adhesive accounts for 1%-10% of a solid mass in

the mixed solution of the one-dimensional nanomaterial dispersion liquid and the ceramic particle dispersion liquid.

[0094] S4: coating and film-forming: coating the at least one slurry to the base film, and drying the base film and the slurry to obtain the coated separator.

[0095] Specifically, through coating, the slurry prepared above is coated on the base film and dried, obtaining the coated separator. The coating method is any one of spray coating, dip coating, micro-gravure roller coating, printing coating, extrusion coating, and wire rod coating. The base film is, for example, a polyolefin base film with a thickness of 3μm -30 μm, a drying temperature of 40°C -130 °C, and a coating speed of 10 m/min -200 m/min.

[0096] Where, as a feasible way, before the dispersion of ceramic particles, the following is further included:

S11: ceramic particles screening: selecting first ceramic particles and second ceramic particles of different particle diameters, wherein an average particle diameter of the first ceramic particles is 10-60nm, and an average particle diameter of the second ceramic particles is 100-600nm;

S12: ceramic particles pretreatment: adding the first ceramic particles to a second solvent and putting them in a reaction kettle, adding a material to be grafted to perform a grafting reaction, so that lithium-ion conductor functional groups are grafted on a surface of the first ceramic particles. Specifically, the first ceramic particles are added to the second solvent, and then put them into the reaction kettle together, and then the material to be grafted is added. Through a certain reaction temperature, reaction pressure, and reaction time, the lithium-ion conductor functional groups can be grafted on the first ceramic particles.

[0097] The first ceramic particle is not particularly limited, but it can be a material that has a melting point of 200°C or above, high electrical insulation property, and is electrochemically stable within a use range of a lithium ion battery. Examples include oxide-based ceramics such as alumina, silica, titanium oxide, zirconium dioxide, magnesium oxide, cerium oxide, yttria, and zinc oxide; and nitride-based ceramics such as silicon nitride, titanium nitride, and boron nitride; and ceramics such as silicon carbide, calcium carbonate, magnesium sulfate, aluminum sulfate, aluminum hydroxide oxide,

potassium titanate, talc, kaolinite, clay, pearl clay, halloysite, pyrophyllite, montmorillonite, sericite, mica, amesite, bentonite, asbestos, zeolite, calcium silicate, magnesium silicate, diatomaceous earth, and silica sand, which can be used alone or in combination.

[0098] The second ceramic particle is not particularly limited, but it can be a substance that has a melting point of 200°C or above, high electrical insulation, and is electrochemically stable within a use range of a lithium ion battery. The same or different inorganic materials as the first ceramic particles can be selected. The second solvent is any one of water, ethanol, acetone, NMP, etc., and the material to be grafted is polycarbonate, polylactic acid, polyurethane, perfluoropropyl vinyl ether, methyl isopropyl ketone, etc. The reaction temperature is 100°C -200°C, the reaction pressure is 0.1 Mpa -0.5Mpa, and the reaction time is 10 min -50min. After the reaction is completed, the liquid solvent is removed to leave a solid, and the first ceramic particles grafted with the lithium-ion conductor can be obtained.

[0099] On this basis, the dispersion of the ceramics in S1 is specifically implemented as follows:

the first ceramic particles pretreated in S12 are mixed with the second ceramic particles and then dispersed in the first solvent to obtain a ceramic particle dispersion liquid.

[0100] The product performance of some embodiments of the present application will be analyzed through experiments below.

[0101] Example 1

[0102] In the present embodiment, the coated separator is prepared through the following steps:

S1: ceramic particles screening: selecting first ceramic particles and second ceramic particles of different particle diameters; where, an average particle diameter of the first ceramic particles is 40 nm, an average particle diameter of the second ceramic particles is 300 nm, and both the first ceramic particles and the second ceramic particles are aluminum oxide;

S2: dispersion of ceramic particles: mixing the second ceramic particles and the first ceramic particles in a ratio of 1:1, and uniformly dispersing them in N-methylpyrrolidone through high-speed stirring to obtain a ceramic particle dispersion

liquid; where, a mass concentration of ceramic particles in the dispersion liquid is 20%;

S3: dispersion of one-dimensional nanomaterials: dispersing the one-dimensional nanomaterials of different lengths in a dispersant to obtain a dispersion liquid, where, the dispersant is N-methylpyrrolidone, the dispersion method is high-speed stirring, and a mass concentration of one-dimensional nanomaterials in the dispersant is 15%;

S4: mixing and forming a slurry: mixing the ceramic particle dispersion liquid obtained in S2 with the one-dimensional nanomaterial dispersion liquid obtained in S3 to obtain a mixed solution, where the mixing method adopted is high-speed stirring; then adding an adhesive to the mixed solution, the adhesive being polyvinyl alcohol; where, the adhesive accounts for 8% of a solid mass in the mixed solution of the one-dimensional nanomaterial dispersion liquid and the ceramic particle dispersion liquid;

S5: coating and forming film: coating the at least one slurry on the base film through coating, and drying the base film and the slurry to obtain the coated separator; where, the base film is a polyethylene film with a thickness of 9 μm, a drying temperature of 100 °C, and a coating speed of 100m/min, and the resulting coating thickness is 2 μm.

[0103] Where, the one-dimensional nanomaterials are deposited on a surface of the base film to form a layered structure (i.e., layered one-dimensional nanomaterials of different lengths). During a deposition process on the base film, due to the surface energy, the longest one-dimensional nanomaterials (which have the largest surface energy, is the most unstable, and are most likely to adhere once it comes into contact with an interface with a small surface energy) are deposited first, while the second longest ones are deposited later, and the shortest one-dimensional nanomaterials are finally deposited, forming a layered structure that gradually accumulates from long to short.

[0104] Examples 2-29 and Comparative examples 1-5 are also obtained, utilizing the same method. Where, referring to Table 1, performance of the corresponding separators in Examples 1-29 and Comparative examples 1-5 are illustrated. Except for the difference in preparation parameters listed in Table 1, all Examples and Comparative examples are consistent with Example 1 in other aspects, which will not be repeated again.

[0105] Where, Example 30 shown in Table 1 only differs from Example 1 in that a ceramic particles pretreatment step is performed before the step S1 dispersion of ceramic

particles, which includes: adding the first ceramic particles to a second solvent, putting them together into a reaction kettle, then adding a material to be grafted, maintaining a certain reaction temperature, reaction pressure, and reaction time, and grafting a lithium-ion conductor functional group on the first ceramic particles. Where, the second solvent is acetone, and the material to be grafted is polycarbonate. The reaction temperature is 150°C, the reaction pressure is 0.3Mpa, and the reaction time is 20 minutes. After the reaction is completed, the liquid solvent is removed to leave a solid, and the first ceramic particles grafted with the lithium-ion conductor functional group can be obtained.

[0106] Table 1

Serial number		Distribution of one-dimensional nanomaterials	Diameter of one-dimensional nanomaterials	Length of one-dimensional nanomaterials L50	Primary particle diameter of first ceramic particles	Primary particle diameter of second ceramic particles	A mass ratio of one-dimensional nanomaterials to ceramic particles	A mass ratio of first ceramic particles to second ceramic particles	Lithium ion conductivity (mS/cm)	Battery capacity retention rate after storage at 60ºC for 30 days (%)	Anti-puncture force of coating layer (N)	Thermal contraction (180ºC/h)
Comparison of the proportions of one-dimensional materials to ceramic particles	Example 1	Layered distribution	20	300	40	300	1:1	1:1	1	93	7	1.5
	Example 2	Layered distribution	20	300	40	300	1:5	1:1	1.2	91	10	2
	Example 3	Layered distribution	20	300	40	300	1:8	1:1	1.25	91	11	2.2
	Example 4	Layered distribution	20	300	40	300	1:10	1:1	1.33	91	13	2.5
	Exampl	Layered distribution	20	300	40	300	1:12	1:1	1.4	90	15	2.8

	e 5											
	Example 6	Layered distribution	20	300	40	300	1:14	1:1	1.43	90	15	3.1
	Example 7	Layered distribution	20	300	40	300	1:15	1:1	1.4	86	17	17
	Example 8	Layered distribution	20	300	40	300	2:1	1:1	0.6	94	6	1.6
No ceramic particle	Comparative example 1	Layered distribution	20	300	/	/	/	/	0.4	94	4	1.5
No one-dimensional nanomaterial	Comparative example 2	Layered distribution	/	/	40	300	0	1:1	1.1	84	18	15
Comparison between first ceramic particles and second ceramic particles	Example 9	Layered distribution	20	300	40	300	1:1	7:1	0.8	92	5	1.5
	Example 10	Layered distribution	20	300	40	300	1:1	3:1	0.85	92.5	6	1.6
	Exa	Layered	20	300	40	300	1:1	5:1	0.9	93	7	1.6

	mple 11	distribution										
	Example 12	Layered distribution	20	300	40	300	1:1	1:5	1	92	8	1.6
	Example 13	Layered distribution	20	300	40	300	1:1	1:3	1.1	91	8	1.6
	Example 14	Layered distribution	20	300	40	300	1:1	1:7	0.8	90	10	5.4
	Example 15	Layered distribution	20	300	10	300	1:1	1:1	0.9	93	7	1.5
	Example 16	Layered distribution	20	300	25	400	1:1	1:1	1	92	7	1.5
	Example 17	Layered distribution	20	300	10	600	1:1	1:1	0.8	90	8	1.5
	Example 18	Layered distribution	20	300	50	100	1:1	1:1	0.8	91	7	1.5
	Example 19	Layered distribution	20	300	60	300	1:1	1:1	1	91	7	1.5
	Example 20	Layered distribution	20	300	30	600	1:1	1:1	1	92	7	1.5
	Exampl	Layered distribution	20	300	40	600	1:1	1:1	1.2	90	10	1.6

	e 21											
	Example 22	Layered distribution	20	300	15	375	1:1	1:1	0.9	91	8	1.5
	Example 23	Layered distribution	20	300	10	400	1:1	1:1	0.85	91	8	1.5
	Example 24	Layered distribution	20	300	5	300	1:1	1:1	0.7	93	7	1.5
	Example 25	Layered distribution	20	300	100	300	1:1	1:1	1.1	88	7	2.1
	Example 26	Layered distribution	20	300	40	50	1:1	1:1	0.7	94	5	1.5
	Example 27	Layered distribution	20	300	40	800	1:1	1:1	1.3	86	13	5.6
	Example 28	Layered distribution	20	300	40	/	1:1	/	0.7	93	4	1.5
	Example 29	Layered distribution	20	300	/	300	1:1	0	1.0	86	9	4.5
Grafting treatment	Example 30	Layered distribution	20	300	40	300	1:1	1:1	1.7	95	7	1.5
Layering comparison	Comparati	Non-layering	20	300	40	300	1:1	1:1	0.9	86	7	1.5

	ve exa mpl e 3											
	Co mpa rati ve exa mpl e 4	Non-layering	20	300	40	300	1:5	1:1	0.95	86	10	2
	Co mpa rati ve exa mpl e 5	Non-layering	20	300	40	300	1:12	1:1	1	85	15	2.8

[0107] From Table 1, according to the comparison of Examples 1-8, it can be seen that when an excessive amount of one-dimensional nanomaterial (Example 8) is added, the lithium ion conductivity of the coated separator is much lower, as compared to adding other proportions of one-dimensional nanomaterials. When there is an excessive amount of ceramic particles (Example 7), the battery capacity retention rate of the coated separator decreases, and the thermal contraction decreases; when a ratio of one-dimensional nanomaterials to ceramic particles is (1:1-1:14), as a proportion of ceramic particles increases, the battery capacity retention rate at high-temperature gradually decreases, the lithium ion conductivity gradually increases, the anti-puncture property gradually improves, and the heat resistance gradually decreases. The main reason for this phenomenon is that an increase in the proportion of ceramic particles can further expand the gaps between coating layers, thereby increasing the lithium ion conductivity. However, if the gaps are large, self-discharge will be enhanced, leading to attenuation of the storage

capacity under high-temperature; the expansion of the gaps will also lead to a reduced number of contact points between materials in the coating layer, resulting in poor heat resistance in a hot environment; and the anti-puncture property of the ceramic particles is better than that of the one-dimensional nanomaterials, so the anti-puncture property is improved.

[0108] It can be seen from the comparison of Examples 9-14 that, among ceramic particles, as a proportion of second ceramic particles (sub-micron ceramic particles) increases (Examples 9-13), the lithium ion conductivity of the coated separator gradually increases, the battery capacity retention rate gradually decreases, the anti-puncture property gradually increases, and the heat resistance remains unchanged. However, when a content of the first ceramic particles (nanoceramic particles) is too high (Example 9), the lithium ion conductivity of the coated separator is low and the anti-puncture property is poor; and when a content of the first ceramic particles is too low (Example 14), the heat resistance of the coated separator is larger. The main reason for this phenomenon is that the second ceramic particles are beneficial to increasing the large gaps in the coating layer, which in turn can improve the conductivity of lithium batteries, and large-size second ceramic particles have excellent anti-puncture property. However, if the gaps are too large, self-discharge is enhanced, resulting in an attenuation of the high-temperature storage capacity; the expansion of the gaps also leads to a decrease in the number of contact points between materials in the coating layer, resulting in poor heat resistance in a hot environment.

[0109] From the comparison of Examples 15-27, it can be seen that when the particle diameter of the first ceramic particles is too small (Example 24), the lithium ion conductivity of the coated separator is low; when the particle diameter of the first ceramic particles is too large (Example 25), the battery capacity retention rate of the coated separator is low; when the particle diameter of the second ceramic particles is too small (Example 26), the lithium ion conductivity of the coated separator is low, and the anti-puncture property is reduced; when the particle diameter of the second ceramic particles is too large (Example 27), the battery capacity retention rate of the coated separator is low, and the heat resistance is reduced. The main reason for this phenomenon is that when the particle diameter of the first ceramic particles is small, the agglomeration

problem of the first ceramic particles becomes more serious, which in turn leads to a narrowed lithium ion transmission channel and a low lithium ion conductivity; when the particle diameter of the first ceramic particles is too large, the gaps in the coating layer increase, which in turn increases self-discharge and decreases the battery capacity retention rate; when the particle diameter of the second ceramic particles is small, the gaps in the coating layer become narrower, the lithium ion conductivity decreases, and the reduction in size weakens the ability to resist external puncture; when the diameter of the second ceramic particles is too large, the gaps in the coating layer will increase sharply, resulting in a decrease in battery capacity retention rate. In addition, excessively large gaps will cause the coated separator to be prone to gap narrowing when the separator is heated, which is macroscopically manifested as a decrease in heat resistance.

[0110] It can be seen from Comparative examples 1 and 2 that when there is only one-dimensional nanomaterial in the coating layer, the coated separator has excellent heat resistance, but the lithium ion conductivity and anti-puncture property are poor; when there are only the first ceramic particles in the coating layer, the heat resistance of the coated separator decreases and the anti-puncture property decreases, but it has very excellent lithium ion conductivity; when there are only the second ceramic particles in the coating layer, the heat resistance of the coated separator decreases significantly, and the lithium ion transmission capacity is small, but it has high anti-puncture property. It can be seen from the comparison of Examples 1-8 that when the mass ratio of one-dimensional nanomaterials to ceramic particles exceeds 1:1 (Example8), the lithium ion transmission capacity and anti-puncture property of the coated separator are not improved. When the mass ratio of one-dimensional nanomaterials to ceramic particles is lower than 1:14 (Example 7), the lithium ion transmission capacity and anti-puncture property of the coated separator are significantly improved, but the heat resistance decreases significantly. When the mass ratio of the first ceramic particles to the second ceramic particles exceeds 6:1 (Example 9), the heat resistance and lithium ion transmission capacity of the coated separator are relatively high, but the anti-puncture property decreases. When the mass ratio of the first ceramic particles to the second ceramic particles is lower than 1:6 (Example 13), the heat resistance and anti-puncture property of the coated separator are improved, but the lithium ion transmission capacity is reduced. Only when the mass ratio of the first ceramic

particles, the second ceramic particles, and the one-dimensional nanomaterials is within a certain range, the various indicators of the coated separator can have the best comprehensive performance (Example 5).

[0111] From the comparison of Examples 1, 2, 5 and Comparative examples 3-5, it can be seen that when the one-dimensional nanomaterial is not delaminated, the lithium ion conductivity of the coated separator is low, and the battery capacity retention rate decreases. The main reason for this phenomenon is that if the one-dimensional nanomaterial is not delaminated, the agglomeration phenomenon between the materials will be very serious. The agglomerates will block the pores of the base film, resulting in low lithium ion conductivity; in addition, the sizes of the voids in coating layer structure are different, and the self-discharge problem is serious, which will lead to the decline of capacity retention rate.

[0112] In the description of this specification, the description of referring to "an implementation mode", "an embodiment", "specific implementation process", "an example", etc. means that the specific features, structures, materials, or characteristics described in conjunction with the embodiment or example, are included in at least one embodiment or example of the application. In this specification, schematic representations of the above terms do not necessarily refer to the same embodiment or example. Furthermore, the specific features, structures, materials or characteristics described can be combined in any suitable manner in any one or more embodiments or examples.

[0113] Finally, it should be noted that, the above embodiments are only used to illustrate the technical solutions of the present application, but not to limit them. Although the present application has been described in detail with reference to the foregoing embodiments, those skilled in the art should understand that: the technical solutions described in the foregoing embodiments can still be modified, or some or all of the technical features thereof can be equivalently replaced; and these modifications or replacements do not make the essence of the corresponding technical solutions deviate from the scope of technical solutions of the embodiments of the present application.

CLAIMS

1. A coated separator (1), comprising: a base film (11) and a coating layer structure (12) provided on at least one surface of the base film (11); wherein the coating layer structure (12) contains multiple material layers, and the coating layer structure (12) contains one-dimensional nanomaterials and ceramic particles (13), and in a direction away from the base film (11), an average length of the one-dimensional nanomaterials in each material layer gradually decreases layer by layer.

2. The coated separator (1) according to claim 1, wherein a proportion of a thickness of a coating layer distributed with ceramic particles to a total thickness of the coating layer structure (12) reaches than 80% or more; preferably reaches 90% or more; and more preferably, reaches 100%.

3. The coated separator (1) according to claim 1 or 2, wherein a mass ratio of the one-dimensional nanomaterials to the ceramic particles (13) in the coating layer structure (12) is 1:1-1:14.

4. The coated separator (1) according to claim 3, wherein the ceramic particle (13) comprises first ceramic particles and second ceramic particles; a particle diameter of the second ceramic particles is larger than a particle diameter of the first ceramic particles, and the particle diameter of the second ceramic particles is two or more times a diameter of the one-dimensional nanomaterials.

5. The coated separator (1) according to claim 4, wherein

the particle diameter of the second ceramic particles differs from at least one of the diameter of the one-dimensional nanomaterials and the particle diameter of the first ceramic particles by one order of magnitude or more.

6. The coated separator (1) according to claim 5, wherein

the diameter of the one-dimensional nanomaterials is 5-50 nm, an average particle diameter of the first ceramic particles is 10-60 nm, and an average particle diameter of the second ceramic particles is 100-600 nm.

7. The coated separator (1) according to claim 4, wherein in the coating layer structure (12), a mass ratio of the first ceramic particles to the second ceramic particles is 5:1-1:5.

8. The coated separator (1) according to claim 4, wherein at least one of the first

ceramic particle and the second ceramic particle is an inorganic substance, the inorganic substance having a melting point 200°C or more, being electrically insulating, and being electrochemically stable within a use range of lithium battery.

9. The coated separator (1) according to any one of claims 1 to 8, wherein a surface of the first ceramic particle is grafted with a lithium-ion conductor functional group;

wherein, the lithium-ion conductor functional group comprises any one of hydroxyl (-OH), carbonyl (-C=O), fluorine (-F), and carboxyl (-COOH).

10. The coated separator (1) according to claim 1, wherein the coated separator at least meets any of the following conditions:

a) anti-puncture force of coating layer ≥ 7N;

b) ion conductivity ≥ 0.8;

c) capacity retention rate ≥90%;

d) thermal contraction at 180°C/h ≤ 4%.

11. The coated separator according to any one of claims 1 to 10, wherein

an average length value of the one-dimensional nanomaterials in the coating layer structure is between 250nm and 400nm.

12. A preparation method for coated separator, for preparing the coated separator according to any one of claims 1 to 11, comprising:

dispersion of ceramic particles (S1): dispersing the ceramic particles in a first solvent to obtain a ceramic particle dispersion liquid;

dispersion of one-dimensional nanomaterial (S2): dispersing the one-dimensional nanomaterial of different lengths in the same or different dispersants to obtain at least one one-dimensional nanomaterial dispersion liquid;

mixing and forming a slurry (S3): preparing a mixed solution including the ceramic particle dispersion liquid and the one-dimensional nanomaterial dispersion liquid to form at least one corresponding slurry;

coating and forming a film (S4): coating the at least one slurry on at least one surface of the base film and drying to obtain the coated separator.

13. The preparation method for coated separator according to claim 12, wherein, before the dispersion of ceramic particles, the method further comprises:

ceramic particles screening: selecting first ceramic particles and second ceramic

particles of different particle diameters, wherein an average particle diameter of the first ceramic particles is 10-60nm, and an average particle diameter of the second ceramic particles is 100-600nm;

14. The preparation method for coated separator according to claim 13, wherein, before the dispersion of ceramic particles,

the method further comprises a pretreatment for ceramic particles: adding the first ceramic particles to a second solvent and placing them in a reaction kettle, adding a material to be grafted to perform a grafting reaction, so that a lithium-ion conductor functional group is grafted on a surface of the first ceramic particles.

15. The preparation method for coated separator according to claim 14, wherein the material to be grafted comprises any one of polycarbonate, polylactic acid, polyurethane, perfluoropropyl vinyl ether, and methyl isopropyl ketone.

16. The preparation method for coated separator according to claim 14, wherein the dispersion of ceramic particles specifically comprises:

mixing pretreated first ceramic particles and the second ceramic particles and dispersing them in the first solvent to obtain a ceramic particle dispersion liquid.

17. A battery, comprising the coated separator according to any one of claims 1 to 11 or comprising a coated separator prepared by the preparation method for coated separator according to any one of claims 12 to 16;

wherein, the battery is a lithium battery.