



(51) International Patent Classification:

H01M 4/587 (2010.01)

(21) International Application Number:

PCT/CN2020/078773

(22) International Filing Date:

11 March 2020 (11.03.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

201910216007.X 21 March 2019 (21.03.2019) CN

(71) Applicant: NINGDE AMPEREX TECHNOLOGY

LIMITED [CN/CN]; No.1 Xingang Road, Zhangwan Town, Jiaocheng District, Ningde, Fujian 352100 (CN).

(72) Inventors: FENG, Pengyang; No.1 Xingang Road, Zhang-

wan Town, Jiaocheng District, Ningde, Fujian 352100 (CN). DONG, Jiali; No.1 Xingang Road, Zhangwan Town,

Jiaocheng District, Ningde, Fujian 352100 (CN). TANG, Jia; No.1 Xingang Road, Zhangwan Town, Jiaocheng District, Ningde, Fujian 352100 (CN). XIE, Yuansen; No.1 Xingang Road, Zhangwan Town, Jiaocheng District, Ningde, Fujian 352100 (CN).

(74) Agent: LEE AND LI - LEAVEN IPR AGENCY LTD.;

Unit 2202, Tower A, Beijing Marriott Center, No. 7, Jian Guo Men South Avenue, Dongcheng District, Beijing 100005 (CN).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,

(54) Title: ANODE MATERIAL, ANODE AND ELECTROCHEMICAL DEVICE COMPRISING ANODE MATERIAL

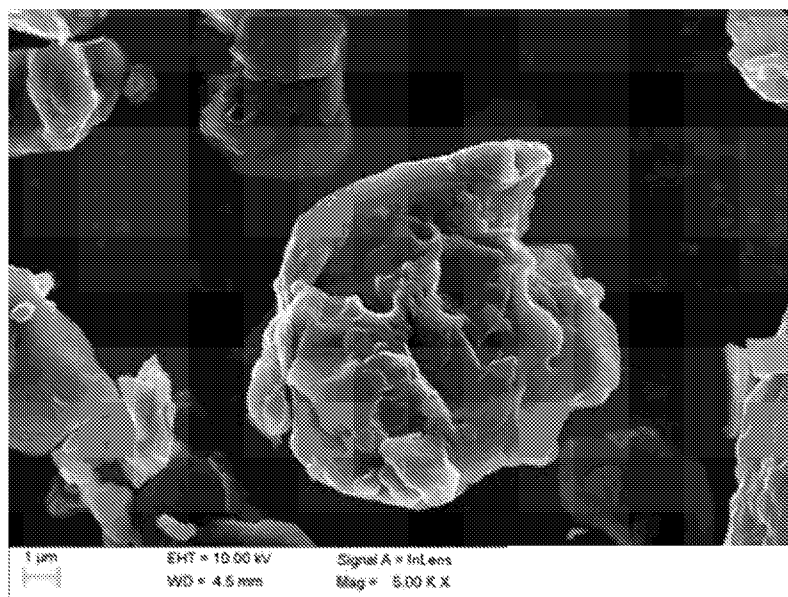


FIG. 1

(57) **Abstract:** Provided are an anode material, an anode and an electrochemical device comprising the anode material. The anode material meets the following relationship equations: $0.8 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 12$ (1); and $1.2 \leq 0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET \leq 5$ (2), wherein Dv50 represents a value in the volume-based particle size distribution of the anode material that is greater than the particle size of 50% of the particles, Dv99 represents a value in the volume-based particle size distribution of the anode material that is greater than the particle size of 99% of the particles, and BET is a specific surface area of the anode material, wherein Dv50 and Dv99 are expressed in μm and BET is expressed in m^2/g . The anode material is capable of significantly improving the rate performance of electrochemical devices.

[Continued on next page]



SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

ANODE MATERIAL, ANODE AND ELECTROCHEMICAL DEVICE COMPRISING ANODE MATERIAL

CROSS REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of priority from the China Patent Application No. 201910216007.X, filed on 21 March 2019, the disclosure of which is hereby incorporated by reference in its entirety.

Background of the Invention

Field of the Invention

The present application relates to the technical field of energy storage, and particularly to an anode material, an anode and an electrochemical device comprising the anode material.

Description of the Prior Art

With the development of power tools, the requirements for lithium-ion batteries suitable for power tools are also getting higher and higher. Particularly, the lithium-ion batteries are required to have a discharge performance of ultra-high power. This requires that the lithium ion batteries can achieve rapid intercalation and deintercalation of the lithium ions during the charge and discharge process.

Summary of the Invention

In order to meet the above-mentioned requirements for a super-large-rate lithium-ion battery, an embodiment of the present application provides an anode material. An embodiment of the present application also provides an anode, an electrochemical device, and an electronic device using the anode material.

According to a first aspect of the present application, the present application provides an anode material that meets the following relationship equations:

$$0.8 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 12 \quad (1), \text{ and}$$

$$1.2 \leq 0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET \leq 5 \quad (2)$$

wherein Dv50 represents a value in the volume-based particle size distribution of the anode material that covers the particle size of 50% of the particles, Dv99 represents a value in the volume-based particle size distribution of the anode material that covers the particle size of 99% of the particles, and BET is a specific surface area of the anode material, wherein Dv50 and Dv99 are expressed in μm and BET is expressed in m^2/g .

In some embodiments, the anode material includes a group consisting of natural graphite, artificial graphite, and a combination thereof.

In some embodiments, at least a part of the surface of the anode material comprises an amorphous carbon layer.

According to a second aspect of the present application, the present application provides an anode comprising an anode current collector and an anode active material layer, wherein the anode active material layer is disposed on at least one surface of the anode current collector, and the anode active material layer comprises any one of the foregoing anode materials.

In some embodiments, the anode active material layer of the anode has a C_{004}/C_{110} ratio of about 11.81 to about 17.08.

In some embodiments, the particle size D_{v99} of the anode material and the thickness THK of the anode active material layer meet the following relationship equation:

$$D_{v99} \leq 0.8 \text{THK} \leq 40 \quad (3), \text{ wherein THK is expressed in } \mu\text{m}.$$

In some embodiments, the coating weight of the anode material and the thickness THK of the anode active material layer meet the following relationship equation:

$$1.2 \leq \text{CW}/(\text{THK} \times 1540.25) \times 1000 \leq 1.9 \quad (4)$$

wherein CW represents the coating weight in mg of the anode active material layer in an area of 1540.25 mm^2 on one side of the anode.

In some embodiments, the anode active material layer further comprises a binder that includes one or more of polyvinylidene fluoride, a copolymer of vinylidene fluoride-hexafluoropropylene, a polyamide, polyacrylonitrile, a polyacrylate ester, polyacrylic acid, a polyacrylate salt, sodium carboxymethyl cellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene, polyhexafluoropropylene, styrene-butadiene rubber, an acrylate ester, and an epoxy resin.

In some embodiments, the anode further comprises a conductive coating between the anode active material layer and the current collector. The conductive coating comprises one or more of carbon fibers, Ketjen black, acetylene black, carbon nanotubes, and graphene.

In some embodiments, the anode active material layer has a CW of about 40 mg to about 100 mg.

In some embodiments, the anode material has a D_{v50} of about $4 \mu\text{m}$ to about $17 \mu\text{m}$, a D_{v99} of about $15 \mu\text{m}$ to about $35 \mu\text{m}$, and a specific surface area of about $1.0 \text{ m}^2/\text{g}$ to about $4.0 \text{ m}^2/\text{g}$.

In some embodiments, the anode has a porosity of about 31% to about 41%.

In some embodiments, the conductive coating has a thickness of about 0.5 μm to about 1.5 μm .

According to a third aspect of the present application, the present application provides an electrochemical device, which comprises a cathode, a separator, an electrolyte, and any one of the anodes described above.

In some embodiments, an anode active material layer on the anode has a C_{004}/C_{110} ratio of about 7.45 to about 9.57 after the electrochemical device is fully charged and disassembled.

The technical solution of the present application improves the rate performance of the lithium ion battery mainly by the following two aspects: screening the particle size and specific surface area of the raw material to meet a certain range so as to reduce the transmission path in the transmission of the lithium ions, thereby accelerating the rapid deintercalation of the lithium ions; and limiting the coating weight and thickness of the anode active material so as to improve the infiltration ability of the electrolyte, thereby ultimately accelerating the transmission rate of the lithium ions.

Additional aspects and advantages of the embodiments of the present application will be partly described or shown in the following description or interpreted by implementing the embodiments of the present application.

Brief description of the drawings

The drawings needed for describing the embodiments of the present application will be briefly described below to facilitate the description of the embodiments of the present application. Obviously, the drawings in the following description only show some embodiments of the present application. For those skilled in the art, the drawings of other embodiments can be obtained according to the structures illustrated in the drawings without creative effort.

Fig. 1 shows an SEM image of the anode material in Example 6.

Fig. 2 shows the relationship between the discharge time and the discharge cut-off voltage of the lithium ion batteries of Example 6 and Comparative Example 2 at a rate of 135C.

Detailed Description

The present application will be described below in detail. It should be understood that terms used in the specification and the appended claims shall not be explained as being

limited to meanings in a common sense and meanings found in dictionaries, but are explained based on meanings and concepts corresponding to the technical aspects of the present application on the basis of the principle that the inventor is allowed to properly define the terms to make an optimum explanation. Therefore, the implementations in the specification and the description in the drawings are merely specific examples used for the purpose of description rather than intentions to illustrate all technical aspects of the present application, and it should be understood that when the present application is filed, various alternative equivalents and variants may be made thereto.

As used in the present application, the terms "approximately", "substantially", "essentially", and "about" are used for describing and explaining a small variation. When used in connection with an event or circumstance, the term may refer to an example in which the event or circumstance occurs precisely, and an example in which the event or circumstance occurs approximately. For example, when used in connection with a value, the term may refer to a range of variation less than or equal to $\pm 10\%$ of the stated value, such as less than or equal to $\pm 5\%$, less than or equal to $\pm 4\%$, less than or equal to $\pm 3\%$, less than or equal to $\pm 2\%$, less than or equal to $\pm 1\%$, less than or equal to $\pm 0.5\%$, less than or equal to $\pm 0.1\%$, or less than or equal to $\pm 0.05\%$. For example, if a difference between two values is less than or equal to $\pm 10\%$ of an average value of the value (for example, less than or equal to $\pm 5\%$, less than or equal to $\pm 4\%$, less than or equal to $\pm 3\%$, less than or equal to $\pm 2\%$, less than or equal to $\pm 1\%$, less than or equal to $\pm 0.5\%$, less than or equal to $\pm 0.1\%$, or less than or equal to $\pm 0.05\%$), it could be considered that the two values are "substantially" the same.

In addition, amounts, ratios, and other values are sometimes presented in a range format in this application. It is to be understood that such a range format is provided for the sake of convenience and simplicity, and should be understood flexibly to include not only the numerical values that are explicitly defined in the range, but also all the individual values or sub-ranges that are included in the range, as if each value and sub-range are explicitly specified.

I. Anode material

The present application provides an anode material, which meets the following relationship equations:

$$0.8 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 12 \quad (1), \text{ and}$$

$$1.2 \leq 0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET \leq 5 \quad (2)$$

wherein Dv50, also referred to as "median particle size", represents a value in the volume-based particle size distribution of the anode material that covers the particle size of

50% of the particles, Dv99 represents a value in the volume-based particle size distribution of the anode material that covers the particle size of 99% of the particles, and BET is a specific surface area of the anode material, wherein Dv50 and Dv99 are expressed in μm and BET is expressed in m^2/g .

The research in the present application shows that the particle size and the specific surface area of the anode active materials such as graphite can affect the intercalation or deintercalation path of the lithium ions, the speed of intercalation or deintercalation of the lithium ions, and the reaction of the lithium ions with the electrolyte, thus affecting the high-rate charge and discharge performance of lithium ion batteries, affecting the thickness of the solid-electrolyte interface (SEI) film formed during the first lithium intercalation process, and affecting the first coulombic efficiency of the lithium-ion batteries. The use of small-size graphite with excellent isotropy and a porous structure on the surface can reduce the specific surface area of the basal plane and increase the specific surface area of the edge plane as much as possible while keeping the total specific surface area unchanged. The edge plane is a plane in the Lc direction, the basal plane is a plane in the La direction, wherein La is an average size of the graphite crystal along the a-axis direction, and Lc refers to the thickness of the graphite sheets stacked along the c-axis direction perpendicular thereto. The increase in the specific surface area of the edge plane and the formation of a graphite surface with a porous structure enable lithium ions to directly enter in between the graphite sheets from the defect sites at the edge plane to realize rapid lithium ion migration, thereby further realizing the high-rate discharge performance of the lithium ions. During cycling, the de-intercalation of the lithium ions is more likely to cause expansion along the direction Lc, and the small particle size of excellent isotropy will suppress the expansion between graphite sheets, thereby improving cycling performance.

It is found after extensive research in the present application that when Dv50 and Dv99 of the anode material meet the relationship equation of (1) $0.8 \leq 0.06 \times (\text{Dv50})^{2-2.5} \times \text{Dv50} + \text{Dv99} \leq 12$ and Dv50 and the specific surface area BET of the anode material meet the relationship equation of (2) $1.2 \leq 0.2 \times \text{Dv50} - 0.006 \times (\text{Dv50})^2 + \text{BET} \leq 5$, the characteristics of small particle size, high specific surface area at the edge plane, and low specific surface area at the basal plane of the anode material can be achieved. Fig. 1 is an SEM image showing the morphology of an anode material obtained in Example 6 of the present application. As shown in FIG. 1, the anode material meeting the relationship equations (1) and (2) has the characteristics of small particle size, excellent isotropy, and porous surface morphology.

In some embodiments, the anode material further meets the following relationship

equation:

$$1.0 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 11.6 \quad (1)'$$

In some embodiments, the anode material further meets the following relationship equation:

$$1.5 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 5.8 \quad (1)''.$$

In some embodiments, the anode material further meets the following relationship equation:

$$2.2 \leq 0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET \leq 3.6 \quad (2)'$$

In some embodiments, the anode material has a Dv50 meeting the relationship equation of $4 \leq Dv50 \leq 17$. In some embodiments, the anode material has a Dv50 meeting the relationship equation of $4 \leq Dv50 \leq 12$. In some embodiments, the anode material has a Dv50 meeting the relationship equation of $5 \leq Dv50 \leq 9$. In some embodiments, the anode material has a Dv99 meeting the relationship equation of $15 \leq Dv99 \leq 35$. In some embodiments, the anode material has a Dv99 meeting the relationship equation of $17 \leq Dv99 \leq 32$. In some embodiments, the anode material has a Dv99 meeting the relationship equation of $18 \leq Dv99 \leq 30$. The particle sizes Dv50 and Dv99 of the anode material can be measured by a Malvern particle size analyzer, by the following steps: dispersing the anode material in a dispersant (ethanol or acetone, or other surfactant); ultrasonically dispersing the obtained solution for 30 min; and testing the obtained sample after adding the obtained sample to the Malvern particle size analyzer. The specific surface area of the anode material can be measured by the Brunauer-Emmett-Teller (BET) test method. A Tri Star II specific surface analyzer is used. 3g to 6g of a sample is fed to a sample tube, positioned in a degassing station, heated, evacuated, and then cooled to room temperature after heating and evacuating. After removal, the weights of the sample and the sample tube are measured, and the sample is analyzed in an analysis station, followed by data processing and calculation.

In some embodiments, the anode material includes a group consisting of natural graphite, artificial graphite, and a combination thereof.

In some embodiments, the anode material further comprises a group consisting of crystalline silicon, silica, silicon alloy, and combinations thereof.

In some embodiments, the natural graphite or the artificial graphite includes one or more of mesophase graphite, microcrystalline graphite, and expanded graphite.

In some embodiments, at least a part of the surface of the graphite comprises amorphous carbon.

In some embodiments, the graphite surface is coated with amorphous carbon obtained by

carbonizing an asphalt coating or a resin coating.

In some embodiments, the precursor of the artificial graphite is one or more of coal-based raw coke, coal-based calcined coke, petroleum-based raw coke, and petroleum-based calcined coke, and the particle diameter D_{v50} of the coke is strictly controlled to about 4 μm to about 10.0 μm .

II. Anode

The present application provides an anode comprising an anode current collector and an anode active material layer disposed on at least one surface of the anode current collector, wherein the anode active material layer comprises any one of the anode materials according to the above embodiments. In some embodiments of the present application, the anode current collector may be, but is not limited to, copper foil or nickel foil.

In some embodiments, the anode active material layer has a d002 peak appearing at about 26.5379° to about 26.5448° and having a peak area of about 23190 (cts $\cdot$ $^\circ 2\text{Th.}$) to about 24916 (cts $\cdot$ $^\circ 2\text{Th.}$); a d004 peak appearing at about 54.632° to about 54.640° and having a peak area of about 891.79 (cts $\cdot$ $^\circ 2\text{Th.}$) to about 983.3 (cts $\cdot$ $^\circ 2\text{Th.}$); and a d110 peak appearing at about 77.50° to about 77.54° and having a peak area of about 57.58 (cts $\cdot$ $^\circ 2\text{Th.}$) to about 75.48 (cts $\cdot$ $^\circ 2\text{Th.}$).

For crystalline graphite materials, the Bruker X-ray diffractometer is used to test the XRD according to JIS K 0131-1996 General rules for X-ray diffractometric analysis and JB/T 4220-2011 Determination method of artificial graphite lattice parameters. The varying peak positions represent different sizes of graphite unit cells, which reflects the degree of graphitization of graphite materials. The peak area is obtained by integrating the peak intensity against the half-peak width. The ratio of the peak area of the 004 peak to the peak area of the 110 peak is C_{004}/C_{110} .

C_{004}/C_{110} affects the transmission path of the lithium ions. In some embodiments, the C_{004}/C_{110} ratio of the anode active material layer on the anode of the present application is from about 11.81 to about 17.08. In some embodiments, the C_{004}/C_{110} ratio of the anode active material layer on the anode of the present application is from about 12.00 to about 16.15. In some embodiments, the C_{004}/C_{110} ratio of the anode active material layer on the anode of the present application is from about 12.03 to about 15.45.

In order to achieve a high-rate discharge performance, a thin film coating process is used for the production of the anode in the present application. The thickness of the anode is reduced to enable rapid electrolyte infiltration, so that the lithium ions can be quickly

intercalated into and deintercalated from the surface of the anode material to complete the intercalation and deintercalation process of the lithium ions.

The thin film coating process can be achieved by controlling the particle size $Dv99$ of the anode material and the thickness THK of the anode active material layer, or by controlling the relationship between the thickness THK of the anode active material layer and the coating weight CW .

In some embodiments, the particle size $Dv99$ of the anode material and the thickness THK of the anode active material layer meet the following relationship equation:

$$Dv99 \leq 0.8THK \leq 40 \quad (3), \text{ wherein } Dv99 \text{ and } THK \text{ are expressed in } \mu\text{m}.$$

In some embodiments, the particle size $Dv99$ of the anode material and the thickness THK of the anode active material layer meet the following relationship equation:

$$Dv99 \leq 0.8THK \leq 25 \quad (3)', \text{ wherein } Dv99 \text{ and } THK \text{ are expressed in } \mu\text{m}.$$

In some embodiments, the coating weight of the anode material and the thickness THK of the anode active material layer meet the following relationship equation:

$$1.2 \leq CW / (THK \times 1540.25) \times 1000 \leq 1.9 \quad (4)$$

wherein THK is expressed in μm , and CW represents the coating weight in mg of the anode active material layer in an area of 1540.25 mm^2 on one side of the anode.

In some embodiments, the coating weight of the anode material and the thickness THK of the anode active material layer meet the following relationship equation:

$$1.3 \leq CW / (THK \times 1540.25) \times 1000 \leq 1.7 \quad (4)',$$

In some embodiments, the anode active material layer further comprises a binder that includes one or more of polyvinylidene fluoride, a copolymer of vinylidene fluoride-hexafluoropropylene, a polyamide, polyacrylonitrile, a polyacrylate ester, polyacrylic acid, a polyacrylate salt, sodium carboxymethyl cellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene, polyhexafluoropropylene, styrene-butadiene rubber, an acrylate ester, and an epoxy resin.

In some embodiments, the anode active material layer further comprises a conductive agent.

In some embodiments, the conductive agent comprises one or more of carbon fibers, Ketjen black, acetylene black, carbon nanotubes, and graphene.

In some embodiments, the anode further comprises a conductive coating between the anode active material layer and the current collector.

In some embodiments, the conductive coating comprises one or more of carbon fibers, Ketjen black, acetylene black, carbon nanotubes, and graphene.

In some embodiments, the conductive coating is disposed on at least a part of the surface of the current collector.

In some embodiments, the conductive coating further comprises a binder that includes one or more of polyvinylidene fluoride, a copolymer of vinylidene fluoride-hexafluoropropylene, a polyamide, polyacrylonitrile, a polyacrylate ester, polyacrylic acid, a polyacrylate salt, sodium carboxymethyl cellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene, polyhexafluoropropylene, styrene-butadiene rubber, an acrylate ester, and an epoxy resin.

In some embodiments, the conductive coating has a thickness of about 0.5 μm to about 1.5 μm .

An appropriate thickness of the conductive coating contributes to the conduction of electrons and increases the adhesion of the active material layer to the current collector to reduce the peeling of the active material layer during cycling, so that the lithium ion battery exhibits lowered charge transfer resistance and better dynamics.

In some embodiments, the anode active material layer has a CW of about 40 mg to about 100 mg.

In some embodiments, the anode active material layer has a density of about 0.032 mg/mm^2 to about 0.058 mg/mm^2 .

In some embodiments, the anode material has a Dv50 of about 4 μm to about 17 μm and a Dv99 of about 15 μm to about 35 μm , wherein $\text{Dv50} \leq \text{Dv99} \leq 4 \text{ Dv50}$; and a specific surface area BET of about 1.0 m^2/g to about 4.0 m^2/g . Moreover, the anode active material layer on the anode has a porosity of about 31% to about 41%.

In some embodiments, the adhesion strength between the anode active material layer and the current collector is about 1.0 N/m to about 15 N/m, and the cohesion strength between particles of the anode material is about 0.5 N/m to about 13 N/m.

In some embodiments, the adhesion strength between the anode active material layer and the current collector is about 2.8 N/m to about 4.2 N/m, and the cohesion strength between particles of the anode material is about 1.5 N/m to about 2.9 N/m.

In some embodiments, the slurry for producing the anode has a Dv50 of about 4.5 μm to about 9.1 μm , and a Dv90 of about 12.5 μm to about 27.6 μm .

III. Electrochemical device

An embodiment of the present application also provides an electrochemical device using the anode material of the present application.

In some embodiments, the anode active material layer on the anode has a $\text{C}_{004}/\text{C}_{110}$ ratio

of about 7.45 to about 9.57 after the electrochemical device is fully charged and disassembled. In some embodiments, the anode active material layer on the anode has a C_{004}/C_{110} ratio of about 7.95 to about 9.17 after the electrochemical device is fully charged and disassembled. In some embodiments, the anode active material layer on the anode has a C_{004}/C_{110} ratio of about 8.35 to about 8.97 after the electrochemical device is fully charged and disassembled. After a battery is fully charged and disassembled, the anode active material layer on the anode having a C_{004}/C_{110} ratio falling in such a range can improve the rate performance and dynamic performance of the battery. In some embodiments, after the electrochemical device is fully charged and disassembled, the anode active material layer on the anode has a 002 peak appearing at about 26.5379° to about 26.5423° and having a peak area of about 145955 (cts $\cdot$ $^\circ 2\text{Th.}$) to about 15145 (cts $\cdot$ $^\circ 2\text{Th.}$); a 004 peak appearing at about 54.629° to about 54.640° and having a peak area of about 517.345 (cts $\cdot$ $^\circ 2\text{Th.}$) to about 525.03 (cts $\cdot$ $^\circ 2\text{Th.}$); and a 110 peak appearing at about 77.49° to about 77.50° and having a peak area of about 60.365 (cts $\cdot$ $^\circ 2\text{Th.}$) to about 62.11 (cts $\cdot$ $^\circ 2\text{Th.}$).

In some embodiments, after the electrochemical device is fully charged and disassembled, the weight ratio of the element Li to the element S in the anode active material layer on the anode is about 25:1 to about 34:1.

In some embodiments, after the electrochemical device is fully charged and disassembled, the weight ratio of the element Li to the element P in the anode active material layer on the anode is about 11:1 to about 14:1.

In some embodiments, after the electrochemical device is fully charged and disassembled, the weight ratio of the element C to the element S in the anode active material layer on the anode is about 185:1 to about 439:1.

In some examples, the electrochemical device includes a cathode comprising a cathode material, an anode comprising an anode material of the present application, a separator, and an electrolyte. In some embodiments of the present application, the electrochemical device is a lithium ion battery. In the lithium ion battery, the cathode comprises a cathode material capable of absorbing and releasing lithium (Li) (hereinafter, sometimes referred to as "a cathode material capable of absorbing/releasing lithium (Li)") and a cathode current collector. In some embodiments of the present application, the cathode current collector may be, but is not limited to, aluminum foil or nickel foil. Examples of the cathode material capable of absorbing/releasing lithium (Li) may include one or more of lithium cobalt oxide, lithium nickel cobalt manganese oxide, lithium nickel cobalt aluminum oxide, lithium manganese oxide, lithium manganese iron phosphate, lithium vanadium phosphate, lithium vanadyl

phosphate, lithium iron phosphate, lithium titanium oxide or a lithium-containing manganese-based material.

In the cathode material, the chemical formula of lithium cobalt oxide may be $\text{Li}_x\text{Co}_a\text{M1}_b\text{O}_{2-c}$, wherein M1 is selected from the group consisting of nickel (Ni), manganese (Mn), magnesium (Mg), aluminum (Al), boron (B), titanium (Ti), vanadium (V), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), strontium (Sr), tungsten (W), yttrium (Y), lanthanum (La), zirconium (Zr), silicon (Si) and combinations thereof, and x, a, b and c are respectively in the following ranges: $0.8 \leq x \leq 1.2$, $0.8 \leq A \leq 1$, $0 \leq b \leq 0.2$, and $-0.1 \leq c \leq 0.2$.

In the cathode material, the chemical formula of lithium nickel cobalt manganese oxide or lithium nickel cobalt aluminum oxide may be $\text{Li}_y\text{Ni}_d\text{M2}_e\text{O}_{2-f}$, wherein M2 is selected from the group consisting of cobalt (Co), manganese (Mn), magnesium (Mg), aluminum (Al), boron (B), titanium (Ti), vanadium (V), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), strontium (Sr), tungsten (W), zirconium (Zr), silicon (Si), and combinations thereof, and y, d, e and f are respectively in the following ranges: $0.8 \leq y \leq 1.2$, $0.3 \leq d \leq 0.98$, $0.02 \leq e \leq 0.7$, and $-0.1 \leq f \leq 0.2$.

In the cathode material, the chemical formula of lithium manganese oxide is $\text{Li}_z\text{Mn}_{2-g}\text{M3}_g\text{O}_{4-h}$, wherein M3 is selected from the group consisting of cobalt (Co), nickel (Ni), magnesium (Mg), aluminum (Al), boron (B), titanium (Ti), vanadium (V), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), strontium (Sr), tungsten (W), and combinations thereof, and z, g and h are respectively in the following ranges: $0.8 \leq z \leq 1.2$, $0 \leq g < 1.0$, and $-0.2 \leq h \leq 0.2$.

The lithium ion battery further includes an electrolyte, which may be in one or more of a gel state, a solid state, and a liquid state. The liquid electrolyte comprises a lithium salt and a non-aqueous solvent.

The lithium salt is one or more selected from LiPF_6 , LiBF_4 , LiAsF_6 , LiClO_4 , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCH_3SO_3 , LiCF_3SO_3 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, LiBOB , and LiPO_2F_2 . For example, the lithium salt is LiPF_6 , because it can provide high ionic conductivity and improve cycling characteristics.

The non-aqueous solvent may be a carbonate compound, a carboxylate compound, an ether compound, a nitrile compound, other organic solvents or a combination thereof.

Examples of the carbonate compound include diethyl carbonate (DEC), dimethyl carbonate (DMC), dipropyl carbonate (DPC), methylpropyl carbonate (MPC), ethylpropyl carbonate (EPC), methyl ethyl carbonate (MEC), ethylene carbonate (EC), propylene

carbonate (PC), butylene carbonate (BC), vinyl ethylene carbonate (VEC), fluoroethylene carbonate (FEC), 1,2-difluoroethylene carbonate, 1,1-difluoroethylene carbonate, 1,1,2-trifluoroethylene carbonate, 1,1,2,2-tetrafluoroethylene carbonate, 1-fluoro-2-methylethylene carbonate, 1-fluoro-1-methylethylene carbonate, 1,2 -difluoro-1-methylethylene carbonate, 1,1,2-trifluoro-2-methylethylene carbonate, trifluoromethylethylene carbonate and combinations thereof.

In some embodiments, the content of the carbonate compound is about 1 wt% or more based on the total weight of the electrolyte. In some embodiments, the content of the carbonate compound is about 3 wt% or more. In some embodiments, the content of the carbonate compound is about 5 wt% or more. In some embodiments, the content of the carbonate compound is about 10 wt% or more. In some embodiments, the content of the carbonate compound is about 50 wt% or more. In some embodiments, the content of the carbonate compound is about 58 wt% or more. In some embodiments, the content of the carbonate compound is about 60 wt% or less. In some embodiments, the content of the carbonate compound is about 50 wt% or less. In some embodiments, the content of the cyclic carbonate compound is about 40 wt% or less. In some embodiments, the content of the carbonate compound is about 1 wt% to about 60 wt%. In some embodiments, the content of the carbonate compound is about 3 wt% to about 50 wt%.

Examples of the carboxylate compound include methyl acetate, ethyl acetate, n-propyl acetate, t-butyl acetate, methyl propionate, ethyl propionate, propyl propionate, γ -butyrolactone, decalactone, valerolactone, mevalonolactone, caprolactone, or a combination thereof.

In some embodiments, the content of the carboxylate compound is about 1 wt% or more based on the total weight of the electrolyte. In some embodiments, the content of the carboxylate compound is about 3 wt% or more. In some embodiments, the content of the carboxylate compound is about 5 wt% or more. In some embodiments, the content of the carboxylate compound is about 10 wt% or more. In some embodiments, the content of the carboxylate compound is about 60 wt% or less. In some embodiments, the content of the carboxylate compound is about 50 wt% or less. In some embodiments, the content of the carboxylate compound is about 40 wt% or less. In some embodiments, the content of the carboxylate compound is about 1 wt% to about 60 wt%. In some embodiments, the content of the carboxylate compound is about 3 wt% to about 50 wt%.

Examples of the ether compound include tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane, 2-methyl-1,3-dioxolane, 4-methyl-1,3-dioxolane, 1,3-dioxane, 1,4-dioxane,

dimethoxypropane, dimethoxymethane, 1,1-dimethoxyethane, 1,2-dimethoxyethane, diethoxymethane, 1,1-diethoxyethane, 1,2-diethoxyethane, ethoxymethoxymethane, 1,1-ethoxymethoxyethane, 1,2-ethoxymethoxyethane, $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$, $(\text{CF}_3)_2\text{CFCF}(\text{CF}_2\text{CF}_3)(\text{OCH}_3)$, $\text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}(\text{CH}_3)\text{OCF}_2\text{CHF}_2\text{CF}_3$, $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$, $\text{HCF}_2\text{CF}_2\text{OCH}_2\text{CF}_3$, $\text{HCF}_2\text{CF}_2\text{OCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$, $\text{HCF}_2\text{CF}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$, and combinations thereof.

In some embodiments, the content of the ether compound is about 0.01 wt% or more based on the total weight of the electrolyte. In some embodiments, the content of the ether compound is about 0.05 wt% or more. In some embodiments, the content of the ether compound is about 1 wt% or more. In some embodiments, the content of the ether compound is about 2 wt% or more. In some embodiments, the content of the ether compound is about 10 wt% or less. In some embodiments, the content of the ether compound is about 6 wt% or less. In some embodiments, the content of the ether compound is about 5 wt% or less. In some embodiments, the content of the ether compound is about 0.01 wt% to about 10 wt%. In some embodiments, the content of the ether compound is about 1 wt% to about 6 wt%.

Examples of the nitrile compound include butanedinitrile, glutaronitrile, adipodinitrile, 1,5-dicyanopentane, 1,6-dicyanohexane, 1,7-dicyanoheptane, 1,8-dicyanooctane, 1,9-dicyanononane, 1,10-dicyanodecane, 1,12-dicyanododecane, tetramethylbutanedinitrile, 2-methylglutaronitrile, 2,4-dimethylglutaronitrile, 2,2,4,4-tetramethylglutaronitrile, 1,4-dicyanopentane, 1,4-dicyanopentane, 2,5-dimethyl-2,5-hexanedinitrile, 2,6-dicyanoheptane, 2,7-dicyanooctane, 2,8-dicyanononane, 1,6-dicyanodecane, 1,2-dicyanobenzene, 1,3-dicyanobenzene, 1,4-dicyanobenzene, 3,5-dioxo-pimelonitrile, 1,4-bis(cyanoethoxy)butane, ethylene glycol bis(2-cyanoethyl)ether, diethylene glycolbis(2-cyanoethyl)ether, triethylene glycolbis(2-cyanoethyl)ether, tetraethylene glycolbis(2-cyanoethyl)ether, 3,6,9,12,15,18-hexaoxaicosanoic dinitrile, 1,3-bis(2-cyanoethoxy)propane, 1,4-bis(2-cyanoethoxy)butane, 1,5-bis(2-cyanoethoxy)pentane, ethylene glycol bis(4-cyanobutyl)ether, 1,3,5-pentanetricarbonitrile, 1,2,3-propanetricarbonitrile, 1,3,6-hexanetricarbonitrile, 1,2,6-hexanetricarbonitrile, 1,2,3-tris(2-cyanoethoxy)propane or 1,2,4-tris(2-cyanoethoxy)butane, and combinations thereof.

In some embodiments, the content of the nitrile compound is about 0.01 wt% or more based on the total weight of the electrolyte. In some embodiments, the content of the nitrile compound is about 0.05 wt% or more. In some embodiments, the content of the nitrile compound is about 1 wt% or more. In some embodiments, the content of the nitrile compound is about 2 wt% or more. In some embodiments, the content of the nitrile compound is about

10 wt% or less. In some embodiments, the content of the nitrile compound is about 6 wt% or less. In some embodiments, the content of the nitrile compound is about 5 wt% or less. In some embodiments, the content of the nitrile compound is about 0.01 wt% to about 10 wt%. In some embodiments, the content of the nitrile compound is about 1 wt% to about 6 wt%.

Examples of other organic solvents include dimethyl sulfoxide, 1,3-propane sultone, sulfolane, methyl sulfolane, 1,3-dimethyl-2-imidazolidinone, N-methyl-2-pyrrolidone, formamide, dimethylformamide, trimethyl phosphate, triethyl phosphate, trioctyl phosphate, propyl phosphate, and combinations thereof.

In some embodiments, the electrochemical device of the present application is provided with a separator between the cathode and the anode to prevent a short circuit. The material and shape of the separator used in the electrochemical device of the present application are not particularly limited, and may be any of the techniques disclosed in prior art. In some embodiments, the separator includes a polymer or an inorganic substance or the like formed of a material which is stable in the electrolytic solution of the present application.

For example, the separator may include a substrate layer and a surface treatment layer. The substrate layer is a non-woven fabric, film, or composite film having a porous structure, and the material of the substrate layer is at least one selected from the group consisting of polyethylene, polypropylene, polyethylene terephthalate, and polyimide. Particularly, a porous polypropylene film, a porous polyethylene film, a polypropylene nonwoven fabric, a polyethylene nonwoven fabric, and a porous polypropylene-polyethylene-polypropylene composite film may be used.

At least one surface of the substrate layer is provided with a surface treatment layer, which may be a polymer layer or an inorganic layer, or a layer formed by mixing a polymer and an inorganic material.

The inorganic layer comprises inorganic particles and a binder. The inorganic particles are at least one selected from the group consisting of alumina, silica, magnesia, titania, hafnium dioxide, tin oxide, cerium dioxide, nickel oxide, zinc oxide, calcium oxide, zirconia, yttria, silicon carbide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide and barium sulfate, or a combination of more than one thereof. The binder is one selected from the group consisting of polyvinylidene fluoride, a copolymer of vinylidene fluoride-hexafluoropropylene, a polyamide, polyacrylonitrile, a polyacrylate ester, polyacrylic acid, a polyacrylate salt, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene, and polyhexafluoropropylene, or a combination of more than one thereof. The polymer layer contains a polymer, and the material of the polymer includes at

least one of a polyamide, polyacrylonitrile, a polyacrylate ester, polyacrylic acid, a polyacrylate salt, polyvinylpyrrolidone, polyvinyl ether, polyvinylidene fluoride or poly(vinylidene fluoride-hexafluoropropylene).

The separator needs to be mechanically robust to withstand the stretching and puncture of the electrode material, and the separator usually has a pore size of less than 1 micron. Various separators including microporous polymer films, non-woven fabric mats and inorganic films have been used in lithium-ion batteries, of which polymer films based on microporous polyolefin materials are the separators most commonly used in combination with the electrolytes. Microporous polymer films can be made very thin (usually about 5 μm to 25 μm) and highly porous (usually about 20% to 50%) to reduce the electrical resistance and improve the ion conductivity. At the same time, the polymer film still has mechanical robustness. Those skilled in the art should understand that various separators widely used in lithium ion batteries are suitable for use in the present application.

Although a lithium ion battery is exemplified above, other suitable electrochemical devices that the cathode material of the present application can be used therewith may occur to those skilled in the art after reading this application. Such electrochemical devices include any device in which an electrochemical reaction takes place, and specific examples include all kinds of primary batteries, secondary batteries, fuel cells, solar cells, or capacitors. In particular, the electrochemical device is a lithium secondary battery including a lithium metal secondary battery, a lithium ion secondary battery, a lithium polymer secondary battery or a lithium ion polymer secondary battery.

IV. Electronic device

An embodiment of the present application provides an electronic device, which may be any device using an electrochemical device according to an embodiment of the present application.

According to some embodiments of the present application, the electronic device comprises, but is not limited to, notebook computers, pen-input computers, mobile computers, e-book players, portable phones, portable fax machines, portable copiers, portable printers, head-mounted stereo headphones, video recorders, LCD TVs, portable cleaners, portable CD players, mini disc players, transceivers, electronic notebooks, calculators, memory cards, portable recorders, radios, backup power sources, motors, vehicles, motorcycles, scooters, bicycles, lighting apparatus, toys, game consoles, clocks, electric tools, flashing light, cameras, large batteries for household use, and lithium ion capacitors.

Hereinafter, the benefits and advantages brought by the present application are explained

by taking a lithium ion battery as an example in connection with a specific embodiment for preparing an anode material of the present application and a test method for an electrochemical device. However, those skilled in the art will understand that the preparation methods described in the present application are merely exemplary, and any other suitable preparation methods also fall within the protection scope of the present application.

V. Examples

Performance test

(1) SEM test

A scanning electron microscope (SEM) was used for obtaining a morphological structure of a sample through interaction of an electron beam and the sample and by using secondary electron signals for imaging. The SEM used in the present application was a JEOL Company JSM-6360LV Model SEM and an X-ray energy spectrometer fitted thereto, which were used for analyzing the morphological structure and element distribution of the sample.

(2) DC resistance test (DCR)

The lithium-ion battery was charged to 4.2 V at a constant current of 1.5C, and then charged to 0.05C at a constant voltage; allowed to stand for 30 min; and discharged at 0.1C for 10 s (sampled once every 0.1 s to record the corresponding voltage U1), and then discharged at 1C for 360 s (sampled once every 0.1 s to record the corresponding voltage U2). The charging and discharging procedure was repeated 5 times. "1C" is the current value when the battery capacity is completely discharged within 1 hour.

DCR is calculated according to the following formula: $R=(U2-U1)/(1C-0.1C)$. The DCR mentioned in the present application is a value at 50% SOC (state of charge).

(3) High-rate discharge test (at 135C for 3 s)

The lithium-ion battery was discharged to 3.0 V at a constant current of 1C under normal temperature, and allowed to stand for 10 min. Then the battery was charged to 4.2 V at a constant current of 1.5C, and then charged to 0.02C at a constant voltage of 4.2 V. After standing for 5 min, the lithium-ion battery was discharged at a constant current of 135C for 3 seconds, and the voltage at the end of 3 seconds was taken as a criterion for evaluating the high-rate discharge performance of the lithium-ion battery at 135C.

(4) Cycle test at 45°C

The test battery was allowed to stand for 5 min at a test temperature of 45°C. The lithium-ion battery was charged to 4.2 V at a constant current of 1.5C, and then charged to 0.05C at a constant voltage of 4.2 V; allowed to stand for 5 min; and discharged to 3.0 V at a constant current of 1.5C and allowed to stand for 5 min. The charge and discharge process

was repeated 500 times, and the discharge capacity after each cycle was recorded. The capacity retention rate after a cycle of the lithium-ion battery was calculated by the following formula:

Capacity retention rate after a cycle = (Discharge capacity after a cycle / Discharge capacity of the first cycle) x 100%

1. Examples 1-22 and Comparative Examples 1-3

In order to discuss the effects of Dv50 and Dv99 on the performance of the anode material, in Examples 1-22 and Comparative Examples 1-3 of the present application, the effects of the variables Dv50 and the correlation coefficient between Dv50 and Dv99 ($0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99$), and the variables Dv50 and the correlation coefficient between Dv50 and BET ($0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET$) on the cold-pressing effect of the anode, the adhesion strength between the anode active material layer and the anode current collector, and the DCR of a lithium ion battery producing with a corresponding anode material were studied, wherein Dv50 and Dv99 were expressed in μm .

In the present application, a Malvern particle size analyzer was used to measure the particle size of the anode material. The anode material was dispersed in a dispersant (ethanol), and ultrasonicated for 30 min. Then, the sample was added to the Malvern particle size analyzer and tested. From the small particle-size side of the volume-based particle size distribution of the anode material, the particle size that reaches a 50% cumulative volume distribution is Dv50, that is, the average particle size of the anode material; and from the small particle-size side of the volume-based particle size distribution of the anode material, the particle size that reaches 99% cumulative volume distribution is Dv99 of the anode material.

The preparation process in Examples 1-22 and Comparative Examples 1-3 were as follows.

Preparation of anode: Artificial graphite meeting the relationship equations $0.8 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 12$ (1) and $1.2 \leq 0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET \leq 5$ (2), styrene-butadiene rubber (SBR), and sodium carboxymethylcellulose (CMC) were dispersed in deionized water solvent at a weight ratio of 97.4: 1.2: 1.4, mixed uniformly by fully stirring, coated on a Cu foil anode current collector pre-coated with a 1 μm -thick acetylene black conductive coating, dried, and cold pressed to obtain an anode. The artificial graphite in Examples 1-21 and Comparative Examples 1-3 contained amorphous carbon on the surface, and the artificial graphite in Example 22 did not contain amorphous carbon on the surface.

Preparation of cathode: The cathode active material lithium cobalt oxide (LiCoO_2), the

conductive agent acetylene black, and the binder polyvinylidene fluoride (PVDF) were mixed uniformly at a weight ratio of 96:2:2 by fully stirring in a suitable amount of N-methylpyrrolidone (NMP) solvent, coated onto an Al foil cathode current collector, dried, and cold pressed to obtain a cathode.

Separator: A 12 μm porous PE polymer film was used as a separator.

Electrolyte: Under a dry argon atmosphere, EC, PC, and DEC (at a weight ratio of about 1:1:1) were mixed, and then LiPF_6 was added and mixed until uniform, wherein the concentration of LiPF_6 was 1.15 mol/L. Based on the total weight of the electrolyte, 3% of fluoroethylene carbonate was added to the electrolyte.

Preparation of the lithium-ion batteries: The cathode, the separator, and the anode were laminated in order such that the separator was located between the cathode and the anode for isolation. It was wound, placed in an outer package, injected with an electrolyte, encapsulated, formed, degassed, and trimmed to obtain a lithium-ion battery.

Table 1 lists the adopted Dv50, the correlation coefficient between Dv50 and Dv99, and the correlation coefficient between Dv50 and BET of the graphite, the appearance of the anode, the DC resistance (DCR), and the discharge voltage at 135C for 3 s of the lithium ion battery in Examples 1-22 and Comparative Examples 1-3.

Table 1

	Value of $(0.06 \times (\text{Dv50})^2 - 2.5 \times \text{Dv50} + \text{Dv99})$	Value of $(0.2 \times \text{Dv50} - 0.006 \times (\text{Dv50})^2 + \text{BET})$	Dv50 (μm)	Cold-pressed appearance	DCR (m Ω)	Discharge voltage(V) at 135C for 3 s
Example 1	1	2.2	7	Excellent	11.02	2.52
Example 2	1	2.7	7	Excellent	10.82	2.54
Example 3	1	3.6	7	Excellent	10.7	2.55
Example 4	1	5.0	7	Excellent	10.58	2.57
Example 5	5	2.2	7	Excellent	11.26	2.5
Example 6	5	2.7	7	Excellent	11.05	2.51
Example 7	5	3.6	7	Excellent	10.89	2.53
Example 8	5	5.0	7	Excellent	10.72	2.55
Example 9	8	2.2	7	Slight protrusion of particles	11.38	2.43
Example 10	8	2.7	7	Slight protrusion of particles	11.21	2.46
Example 11	8	3.6	7	Slight protrusion of particles	11.1	2.49

Example 12	8	5	7	Slight protrusion of particles	10.83	2.53
Example 13	12	2.2	7	Scratches and protrusions of particles	11.88	2.4
Example 14	12	2.7	7	Scratches and protrusions of particles	11.62	2.41
Example 15	12	3.6	7	Scratches and protrusions of particles	11.38	2.43
Example 16	12	5	7	Scratches and protrusions of particles	11.22	2.45
Example 17	5	2.7	5	Excellent	10.01	2.57
Example 18	5	2.7	6	Excellent	10.89	2.55
Example 19	5	2.7	7.5	Excellent	11.16	2.5
Example 20	5	2.7	8	Excellent	11.27	2.46
Example 21	5	2.7	9	Excellent	12.29	2.36
Example 22	5	2.7	7	Excellent	13.89	2.12
Comparative Example 1	15	2.7	7	Scratches and protrusions of particles	12.01	2.4
Comparative Example 2	0.5	2.7	7	Excellent	11.86	2.32
Comparative Example 3	5	5.5	7	Excellent	16.87	2.29

The analysis of Example 6 and Comparative Examples 1-2 shows that, when Dv50 and the value of relationship equation (2) remain unchanged, by adjusting the value of relationship equation (1), the anode material in Example 6 that meets relationship equation (1) $0.8 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 12$ has a lower DCR and a higher discharge voltage at 135C for 3 s, compared with the anode materials in Comparative Example 1 and Comparative Example 2 that do not meet relationship equation (1). The anode material meeting relationship equations (1) and (2) has a lower DCR and a higher discharge voltage at 135C for 3 s. This is mainly because that the anode material meeting relationship equations (1) and (2) has the following functions: effectively shortening the deintercalation path of the lithium ions to realize the rapid intercalation or deintercalation of the lithium ions, thereby improving the high-rate charge and discharge performance of the lithium ion battery; reducing the specific surface area of the basal plane and increasing the specific surface area of the edge plane as much as possible while maintaining the total specific surface area unchanged, which allows the lithium

ions to directly enter in between the graphite sheets from the defect sites at the edge plane to realize rapid lithium ion migration, thereby further realizing a high-rate discharge performance of the lithium ions; and suppressing the expansion between the graphite sheets, thus improving cycling performance.

It can be seen from the respective analysis of Examples 1-4, Examples 5-8, Examples 9-12, and Examples 13-16 that when relationship equation (1) $0.8 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 12$ and relationship equation (2) $1.2 \leq 0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET \leq 5$ are met, and the value of relationship equation (1) and $Dv50$ remain constant: as the value of relationship equation (2) increases, DCR tends to decrease and the discharge voltage at 135C for 3 s tends to increase. This may be because when the value of relationship equation (1) and $Dv50$ remain constant, as the value of relationship equation (2) increases, the BET value increases accordingly. In the situation where the particle size distribution of the anode material remains basically the same within the range, as the contact area between the material and the electrolyte increases, the solvated lithium transported by the electrolyte will reach the surface of the anode material more easily, the SEI film formed by the electrolyte is in a proper range, the side reactions are suppressed during the charge and discharge process, thereby accelerating the intercalation or deintercalation of the lithium ions, and resulting in reduced resistance in the transmission of the lithium ions and optimized discharge performance. Within this range, the contact between particles becomes good, contact impedance is reduced, and the possibility of overlapped distribution of two large particles in the anode is reduced, and the risk of scratches and protrusions of the particles is lowered. It has been found through research that when the specific surface area BET of the anode material is about $1.0 \text{ m}^2/\text{g}$ to about $4.0 \text{ m}^2/\text{g}$, the lithium ion battery prepared therefrom has better electrochemical performance.

Analysis of Example 22 and Example 6 shows that compared to Example 22 where a graphite anode without an amorphous carbon coating is used, the use of an amorphous carbon-coated graphite anode in Example 6 shows a lower DCR and higher discharge voltage at 135C for 3 s. This may be because the amorphous carbon structure coated on the graphite surface enables the lithium ions to quickly enter the surface of the amorphous carbon during the initial stage of lithium intercalation and deintercalation, and direct lithium intercalation and deintercalation occur on the surface of the amorphous carbon. Thus, high-rate charge and discharge of the lithium battery are achieved.

Moreover, Fig. 2 shows the result of a high-rate discharge test (at 135C for 3 s) of the lithium ion batteries in Example 6 and Comparative Example 2. It can be seen from the

discharge voltage-time curve at a rate of 135C in Fig. 2 that after continuous discharge at 135C for 3 s, the cut-off voltage in Example 6 can still be maintained at a high level. This indicates that during the discharge process of the lithium ion battery in Example 6, electrochemical polarization is alleviated, and kinetic performance is improved.

2. Examples 23-30

The thin film coating process can further optimize the high-rate charge and discharge performance of lithium ion batteries on the basis of the modification of the graphite anode material. The thin film coating process depends largely on the thickness of the anode active material layer after cold pressing. The coating weight is closely related to the battery power and cycle performance.

Therefore, on the basis of the foregoing examples, the influence of the relationship between the Dv99 of the anode material and the thickness THK of the anode active material layer, and the relationship between the thickness THK of the anode active material layer and the coating weight CW of the anode active material layer on the performance were studied in Examples 23-30.

The preparation process of the anodes in Examples 23-30 were as follows.

Preparation of anode: Artificial graphite meeting the relationship equations $0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 = 5$ and $0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET = 2.7$, styrene-butadiene rubber (SBR), and sodium carboxymethylcellulose (CMC) were dispersed in a deionized water solvent at a weight ratio of 97.4: 1.2: 1.4, mixed uniformly by fully stirring, coated on a Cu foil anode current collector pre-coated with a 1 μ m-thick acetylene black conductive coating, dried, and cold pressed to obtain an anode, wherein the artificial graphite had amorphous carbon on its surface. The Dv99 of the anode material and the single-side cold pressed thickness THK of the anode active material layer were controlled to meet the following relationship equation: $Dv99 \leq 0.8THK \leq 40$; and the thickness THK of the anode active material layer and the coating weight CW of the anode material were controlled to meet the following relationship equation: $1.2 \leq CW / (THK \times 1540.25) \times 1000 \leq 1.9$.

CW represents the coating weight in mg of the anode active material layer (graphite+binder+dispersant) in an area of 1540.25 mm² on one side of the anode after cold pressing.

By adjusting the gap between the coating roller and the back roller during the coating process, anodes with coatings having varying THKs and CWs were obtained, thereby further obtaining anodes that meet the above-mentioned relationship equations.

The preparation processes of the cathode, the separator, the electrolyte and the lithium

ion battery were the same as the preparation processes of the cathode, the separator, the electrolyte and the lithium ion battery in Examples 1-22 and Comparative Examples 1-3.

Table 2 shows the adopted Dv99, 0.8THK, and the correlation coefficient between CW and THK (compacted density) of the graphite, the appearance of the anode, the DC resistance (DCR), the discharge voltage at 135C for 3 s, and the capacity retention rate after 500 cycles at 1.5C at 45°C of the lithium ion battery in Examples 23-30.

Table 2

	$1.2 \leq CW/(THK \times 1540.25) \times 1000 \leq 1.9$	Dv99 (μm)	0.8THK(μm)	Cold-pressed appearance	Discharge voltage at 135C for 3 s	Capacity retention rate
Example 23	1.60	20	20	Protrusions of particles	2.51	87.90%
Example 24	1.50	20	21	Slight protrusion of particles	2.52	87.80%
Example 25	1.3	20	24	Excellent	2.54	87.30%
Example 26	1.45	20	22	Excellent	2.53	87.70%
Example 27	1.45	15	22	Excellent	2.56	86.90%
Example 28	1.45	18	22	Excellent	2.55	87.20%
Example 29	1.45	22	22	Slight protrusion of particles	2.50	87.80%
Example 30	1.45	30	22	Protrusions of particles, and scratches	2.49	87.90%

The analysis of Examples 23-30 shows that when other factors remain unchanged, the appearance of Examples 23-29 meeting relationship equation (3) $Dv99 \leq 0.8THK \leq 40$ is better than that of Example 30 with an anode material not meeting relationship equation (3). This is mainly because that with a Dv99 within this range, the occurrence of large particles blocking the tip of the coater blade is reduced during the coating process, and the appearance of scratches after cold pressing is reduced. After the cold pressing, there will be fewer large protrusions.

By adjusting the relationship between the thickness THK of the anode active material layer and the coating weight CW of the anode material, it is found with the anode material meeting relationship equation (3) $Dv99 \leq 0.8THK \leq 40$ and relationship equation (4) $1.2 \leq CW/(THK \times 1540.25) \times 1000 \leq 1.9$, both the discharge voltage at 135C for 3 s and the cold-pressed appearance are improved to some extent. This may be because within this range, the transmission path of the lithium ions becomes shorter, electrode polarization is slight, side

reactions are reduced, and the consumption of the lithium ions is lowered, showing a high discharge voltage at 135C for 3 s, and good dynamic performance. Moreover, the appearance of the surface of the anode is good.

3. Examples 31-36

To discuss the influence of the conductive coating on the anode current collector on the performance of lithium-ion batteries, the influence of the presence, type and thickness of the conductive coating on the anode current collector on the electrochemical performance of lithium ion batteries were further discussed in Examples 31-36 on the basis of the foregoing research.

The preparation method of Examples 31-34 was basically the same as that of Example 26 described above, except that the thickness of the conductive coating on the current collector of Examples 31-34 varied.

The preparation method of Example 35 was basically the same as that of Example 26 described above, except that the conductive coating on the current collector of Example 35 was a graphene coating.

The preparation method of Example 36 was basically the same as that of Example 26 described above, except that no conductive coating was present on the current collector of Example 35.

Table 3 shows the thickness of the conductive coating on the current collector, the type of the conductive coating, the DCR, the discharge voltage at 135C for 3 s, and the capacity retention rate after 500 cycles at 1.5C at 45°C of the lithium-ion battery in Examples 31-36.

Table 3

	Thickness of conductive coating (μm)	Type of conductive coating	DCR ($\text{m}\Omega$)	Discharge voltage at 135C for 3 s
Example 26	1	Acetylene black	11.10	2.53
Example 31	0.5	Acetylene black	12.09	2.39
Example 32	0.8	Acetylene black	11.77	2.51
Example 33	1.1	Acetylene black	11.06	2.53
Example 34	1.5	Acetylene black	10.59	2.57
Example 35	1	Graphene	11.03	2.55
Example 36	0	No	13.28	2.26

The analysis of Examples 26 and 31-36 shows that when the conductive coating on the current collector is from about 0.5 μm to about 1.5 μm , the DCR of the anode is low. This is

because the conductive coating on the current collector contributes to the conduction of electrons and increases the adhesion of the active material layer to the current collector to reduce the peeling of the active material layer during cycling, so that lowered charge transfer resistance and better dynamics are exhibited.

4. Examples 37-41

On the basis of foregoing research, the influence of porosity of the anode active material and C₀₀₄/C₁₁₀ of the anode material before and after charging on the electrochemical performance of the lithium ion batteries was further discussed in Examples 37-41.

The preparation method of Examples 37-41 was basically the same as that of Example 32 described above, except that the porosity of the active material layer in Examples 37-41 varied.

Table 4 shows the porosity of the active material layer, DCR, C₀₀₄/C₁₁₀ before and after charging, the discharge voltage at 135C for 3 s and the capacity retention rate after 500 cycles at 1.5C at 45°C in Examples 37-41.

Table 4

	Porosity of active material layer (%)	DCR (mΩ)	C ₀₀₄ /C ₁₁₀ ratio before charge	C ₀₀₄ /C ₁₁₀ ratio after charge	Discharge voltage at 135C for 3 s	Capacity retention rate
Example 32	35	11.77	14.80	8.51	2.51	88.0%
Example 37	31	12.0	16.01	9.05	2.47	88.70%
Example 38	33	11.89	15.36	8.89	2.50	88.50%
Example 39	38	11.27	13.41	8.38	2.55	88.1%
Example 40	41	11.07	12.61	8.02	2.58	87.50%
Example 41	55	11.09	11.17	7.28	2.57	85.70%

From Examples 32 and 37-40, it can be seen that when the porosity is 31% to 41%, the DCR and the discharge performance at 135C for 3 s have been improved to some extent. This may be because the porosity in such a range allows the electrolyte to penetrate the surface of the graphite layer more easily, such that the lithium ions can directly reach the surface of graphite to complete lithium intercalation, which greatly shortens the transmission path of the lithium ions, enables the SEI film to be in a proper range, and reduces excessive lithium ion loss. With a too large porosity, although the dynamic performance has been improved to some extent, the cycle life is greatly reduced since more SEI films are formed and more lithium ions are consumed, as shown in Example 41.

When the C₀₀₄/C₁₁₀ ratio is within a certain range, the solvated lithium ions are ensured

to well infiltrate with the electrolyte to reach the graphite surface better and undergo intercalation and deintercalation quickly, and the excessive formation of an SEI film is reduced to maintain a good cycle life.

Described above are embodiments listed in the present application. However, since the applicant cannot exhaust all the embodiments, all other equivalent embodiments which are obtained based on the teaching of the present application fall within the protection scope of the present application. In summary, the present application provides a simple method suitable for use in industrial production to prepare an anode material with high rate performance.

References throughout the specification to "some embodiments", "partial embodiments", "one embodiment", "another example", "example", "specific example" or "partial examples" mean that at least one embodiment or example of the application includes specific features, structures, materials or characteristics described in the embodiments or examples. Thus, the descriptions appear throughout the specification, such as "in some embodiments", "in an embodiment", "in one embodiment", "in another example", "in an example", "in a particular example" or "for example", are not necessarily the same embodiment or example in the application. Furthermore, the particular features, structures, materials or characteristics herein may be combined in any suitable manner in one or more embodiments or examples.

The above description summarizes the features of several embodiments, which will enable those of ordinary skill in the art to better understand various aspects of the present application. Those of ordinary skill in the art can readily use the present application as a basis for designing or modifying other compositions to achieve the same objectives and/or the same advantages as the embodiments herein. It is also to be understood by those of ordinary skill in the art that these equivalent examples do not depart from the spirit and scope of the present application, and it is possible to make various changes, substitutions and modifications to the present application without departing from the spirit and scope of the present application. Although the methods disclosed herein have been described with reference to the specific operations that are performed in a specific order, it should be understood that these operations can be combined, subdivided, or reordered to form an equivalent method without departing from the teachings of the present application. Therefore, the order and grouping of operations are not a limitation to the present application unless specifically indicated herein.

We Claim:

1. An anode material, which meets the following relationship equations:

$$0.8 \leq 0.06 \times (Dv50)^2 - 2.5 \times Dv50 + Dv99 \leq 12 \quad (1), \text{ and}$$

$$1.2 \leq 0.2 \times Dv50 - 0.006 \times (Dv50)^2 + BET \leq 5 \quad (2)$$

wherein Dv50 represents a value in the volume-based particle size distribution of the anode material that is greater than the particle size of 50% of the particles, Dv99 represents a value in the volume-based particle size distribution of the anode material that is greater than the particle size of 99% of the particles, and BET is a specific surface area of the anode material, wherein Dv50 and Dv99 are expressed in μm and BET is expressed in m^2/g .

2. The anode material according to claim 1, comprising a group consisting of natural graphite, artificial graphite, and a combination thereof, wherein at least a part of the surface of the anode material comprises amorphous carbon.

3. An anode, comprising an anode current collector and an anode active material layer disposed on at least one surface of the anode current collector, wherein the anode active material layer comprises an anode material according to any one of claims 1-2.

4. The anode according to claim 3, wherein the anode active material layer of the anode has a C_{004}/C_{110} ratio of 11.81 to 17.08.

5. The anode according to any one of claims 3-4, wherein the particle size Dv99 of the anode material and the thickness THK of the anode active material layer meet the following relationship equation:

$$Dv99 \leq 0.8THK \leq 40 \quad (3)$$

wherein THK is expressed in μm .

6. The anode according to any one of claims 3-5, wherein the coating weight of the anode material and the thickness THK of the anode active material layer meet the following relationship equation:

$$1.2 \leq CW / (THK \times 1540.25) \times 1000 \leq 1.9 \quad (4)$$

wherein CW represents the coating weight in mg of the anode active material layer in an area of 1540.25 mm^2 on one side of the anode.

7. The anode according to any one of claims 3-6, wherein the anode active material layer further comprises a binder that includes one or more of polyvinylidene fluoride, a copolymer of vinylidene fluoride-hexafluoropropylene, a polyamide, polyacrylonitrile, a polyacrylate ester, polyacrylic acid, a polyacrylate salt, sodium carboxymethyl cellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene, polyhexafluoropropylene, styrene-butadiene rubber, an acrylate ester, and an epoxy resin.

8. The anode according to any one of claims 3-7, further comprising a conductive coating between the anode active material layer and the current collector, the conductive coating comprises one or more of carbon fibers, Ketjen black, acetylene black, carbon nanotubes, and graphene.
9. The anode according to any one of claims 3-8, wherein the anode active material layer has a CW of 40 mg to 100 mg.
10. The anode according to any one of claims 3-9, wherein the anode material has a Dv50 of 4 μm to 17 μm , a Dv99 of 15 μm to 35 μm , and a specific surface area of 1.0 m^2/g to 4.0 m^2/g .
11. The anode according to any one of claims 3-10, wherein the anode active material layer has a porosity of 31% to 41%.
12. The anode according to any one of claims 8-11, wherein the conductive coating has a thickness of 0.5 μm to 1.5 μm .
13. An electrochemical device, comprising a cathode, a separator, an electrolyte, and an anode according to any one of claims 3 to 12.
14. The electrochemical device according to claim 13, wherein the anode active material layer of the anode has a $\text{C}_{004}/\text{C}_{110}$ ratio of 7.45 to 9.57 after the electrochemical device is fully charged and disassembled.

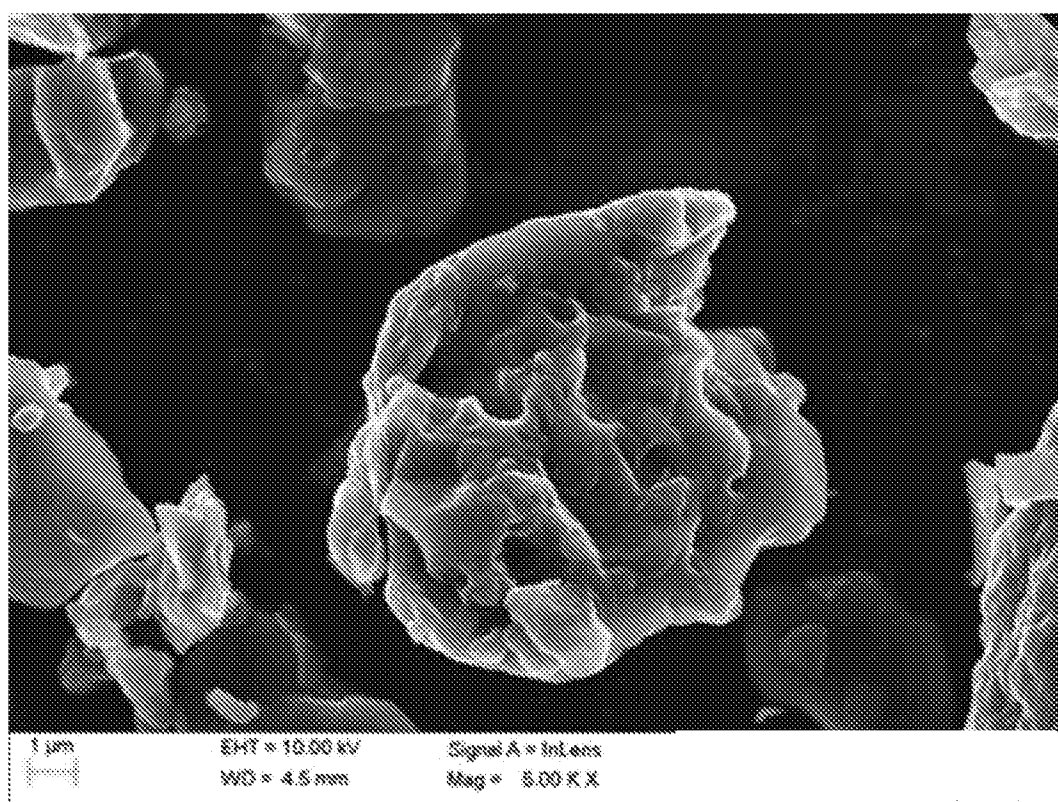


FIG. 1

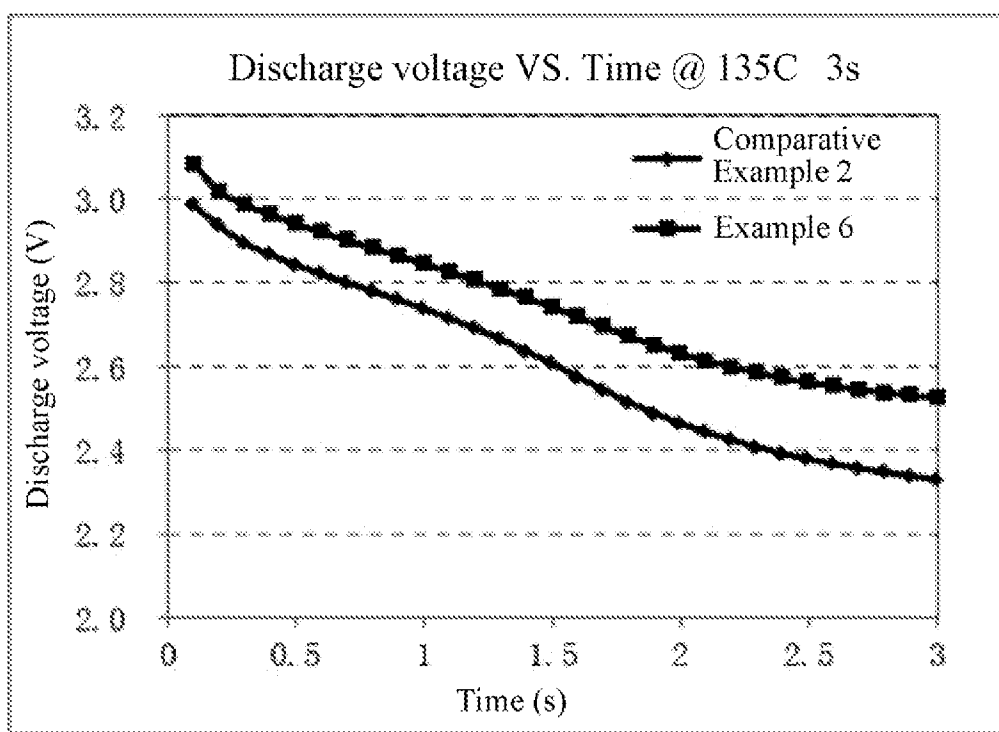


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2020/078773

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/587(2010.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI; EPODOC; CNPAT; CNKI; IEEE: anode?, electrode?, graphite, carbon, diameter, size, D50, Dv50, D90, Dv90, D99, Dv99, BET, surface w area?, batter???, thin, thickness

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 109841831 A (NINGDE AMPEREX TECHNOLOGY LTD.) 04 June 2019 (2019-06-04) claims 1-14	1-14
X	GUO, Yongxing. "Study on preparation and safety of lithium ion power batteries" <i>Chinese Doctoral Dissertations Full-text Database Engineering Science and Technology II</i> , No. 11, 15 November 2010 (2010-11-15), see pages 40-55	1-3, 5-13
Y	GUO, Yongxing. "Study on preparation and safety of lithium ion power batteries" <i>Chinese Doctoral Dissertations Full-text Database Engineering Science and Technology II</i> , No. 11, 15 November 2010 (2010-11-15), see pages 40-55	4, 14
Y	CN 108808068 A (NINGDE AMPEREX TECHNOLOGY LTD.) 13 November 2018 (2018-11-13) see paragraphs 15, 31, 59	4, 14
Y	CN 108807847 A (NINGDE AMPEREX TECHNOLOGY LTD.) 13 November 2018 (2018-11-13) see paragraphs 15, 31, 62	4, 14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 May 2020

Date of mailing of the international search report

04 June 2020

Name and mailing address of the ISA/CN

National Intellectual Property Administration, PRC
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088
China

Authorized officer

ZHOU, Wenjuan

Facsimile No. (86-10)62019451

Telephone No. 86-10-53961467

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2020/078773

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 103367710 A (TDK CORP.) 23 October 2013 (2013-10-23) the whole document	1-14
A	CN 106170880 A (IMERYS GRAPHITE & CARBON SWITZERLAND LTD.) 30 November 2016 (2016-11-30) the whole document	1-14
A	JP 6278135 B1 (TDK CORP.) 14 February 2018 (2018-02-14) the whole document	1-14
A	CN 105190948 A (ENERG2 TECHNOLOGIES INC.) 23 December 2015 (2015-12-23) the whole document	1-14

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2020/078773

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	109841831	A	04 June 2019	None			
CN	108808068	A	13 November 2018	EP	3567659	A1	13 November 2019
				CN	108808068	B	27 September 2019
				US	2019348678	A1	14 November 2019
CN	108807847	A	13 November 2018	CN	110010851	A	12 July 2019
				EP	3561913	A1	30 October 2019
				US	2019334172	A1	31 October 2019
				CN	109994706	A	09 July 2019
				CN	108807847	B	07 May 2019
CN	103367710	A	23 October 2013	JP	2013229301	A	07 November 2013
				US	9236604	B2	12 January 2016
				US	2013260243	A1	03 October 2013
				CN	103367710	B	28 October 2015
				JP	5601388	B2	08 October 2014
CN	106170880	A	30 November 2016	HK	1231457	A1	22 December 2017
				HU	E037398	T2	28 August 2018
				EP	3131848	B1	28 March 2018
				US	2017033360	A1	02 February 2017
				EP	3375754	A1	19 September 2018
				JP	2017513793	A	01 June 2017
				NO	3131848	T3	25 August 2018
				DK	3131848	T3	22 May 2018
				MX	2016012115	A	19 January 2017
				ES	2667211	T3	10 May 2018
				EP	3131848	A2	22 February 2017
				KR	20160145565	A	20 December 2016
				PL	3131848	T3	28 September 2018
				WO	2015158741	A2	22 October 2015
				WO	2015158741	A3	23 December 2015
				CA	2942243	A1	22 October 2015
				BR	112016021042	A2	15 August 2017
JP	6278135	B1	14 February 2018	JP	2018139171	A	06 September 2018
CN	105190948	A	23 December 2015	US	10454103	B2	22 October 2019
				CN	105190948	B	26 April 2019
				CN	110112377	A	09 August 2019
				US	2019267622	A1	29 August 2019
				US	2014272592	A1	18 September 2014
				US	2017346084	A1	30 November 2017
				WO	2014143213	A1	18 September 2014