UNITED STATES DISTRICT COURT
DISTRICT OF NEW JERSEY

AMPEREX TECHNOLOGY LIMITED, Plaintiff, v. **MAXELL, LTD. and MAXELL HOLDINGS, LTD.,** Defendants.	**Civil Action No.:2:21-cv-08461** **Judge: Honorable Kevin McNulty** **JURY TRIAL DEMANDED**

AMENDED COMPLAINT FOR DECLARATORY JUDGMENT

Plaintiff Amperex Technology Limited ("ATL"), for its complaint against Defendants Maxell, Ltd. and Maxell Holdings, Ltd. (collectively "Maxell") alleges as follows:

NATURE OF ACTION

1. ATL brings this action seeking a declaratory judgment that the ATL lithium ion battery products including, without limitation ATL's Cell Nos. 465867, 575577N, 785075 and "all ATL products substantially similar in form, function, manufacture, or design" ("Accused ATL Products") do not infringe any of the following patents (collectively referred to as the "Maxell LIB Patents"):

   a. U.S. Patent No. 8,691,446 ("the '446 Patent," attached as Ex. 1),

   b. U.S. Patent No. 9,350,019 ("the '019 Patent," attached as Ex. 2),

   c. U.S. Patent No. 9,077,035 ("the '035 Patent," attached as Ex. 3), and

   d. U.S. Patent No. 9,166,251 ("the '251 Patent," attached as Ex. 4).

2. ATL further seeks declaratory judgment that it has not infringed, induced others to infringe, or contributed to the infringement by others under 35 U.S.C. § 271 (or any subsection thereof) of the Maxell LIB Patents.

3. ATL further seeks declaratory judgment that ATL's customers have not infringed and do not infringe under 35 U.S.C. § 271 (or any sub-section thereof) any claim of the Maxell LIB Patents based on their purported making, sale, offer for sale, importation, and/or use of ATL's products based on their purported making, using, importing, offering to sell, or selling products and/or services that include ATL's products.

4. ATL also seeks to enjoin Defendants and their officers, employees, and agents from (1) alleging that ATL or its customers infringe the Maxell LIB Patents; (2) taking any action to suggest that ATL or its customers require a license from any of the Defendants for use of the Maxell LIB Patents; or (3) pursuing infringement actions against ATL's customers on the basis of those customers' making, sale, offer for sale, importation, and/or use of ATL's products, or on the basis of their making, using, importing, offering to sell, or selling products and/or services that include ATL's products.

5. ATL seeks this necessary relief because Maxell, which has asserted that it has the right to license the Maxell LIB Patents, has threatened or implied litigation against ATL and its customers. Maxell has alleged that ATL's customers infringe the Maxell LIB Patents by their use of the Accused ATL Products, and has demanded that ATL take a license to Maxell LIB Patents and pay an exorbitant, unreasonable, and unjustified royalty. Maxell has threatened litigation against ATL and has implied litigation against ATL's customers if ATL does not pay for a license to the Maxell LIB Patents.

6. In making its infringement allegations against ATL and its customers, Maxell has referenced various components of the Accused ATL Products, ATL documentation, and alleged reverse engineering reports and thereby has established a substantial controversy and risk that Maxell could file a lawsuit against ATL for infringement of the Maxell LIB Patents.

7. In fact, on March 26, 2021, Maxell's attorneys sent ATL a letter in which Maxell threatened that if ATL does not "enter into a licensing agreement by Friday, April 9, 2021, Maxell will be left with no choice but to pursue litigation."

8. Maxell's allegations have cast inappropriate uncertainty over ATL and its lithium ion battery products and have created a concrete and immediate justiciable controversy between ATL and the Defendants.

9. Maxell's allegations lack merit. ATL does not infringe any claim of the Maxell LIB Patents. The Accused ATL Products do not infringe any claim of the Maxell LIB Patents. Nor do ATL's customers infringe any claim of the Maxell LIB Patents. Accordingly, ATL brings this case to clear its name and that of its lithium ion products, and to protect its customers against meritless claims of infringement.

10. An actual and justiciable controversy therefore exists under 28 U.S.C. §§ 2201-2202 between ATL and Maxell as to whether ATL is infringing or has infringed the Maxell LIB Patents.

PARTIES

11. Plaintiff Amperex Technology Limited ("ATL") is a Chinese corporation having a principal place of business at 3503 Wharf Cable TV Tower, 9 Hoi Shing Road, Tsuen Wan N.T., Hong Kong.

12. Upon information and belief, Defendant Maxell, Ltd. is a Japanese corporation with a registered place of business at 1 Koizumi, Oyamazaki, Oyamazaki-cho, Otokuni-gun, Kyoto, Japan.

13. Upon information and belief, Defendant Maxell Holdings, Ltd. is a Japanese corporation with a registered place of business at 1 Koizumi, Oyamazaki, Oyamazaki-cho, Otokuni-gun, Kyoto, Japan.

JURISDICTION AND VENUE

14. This action arises under the Declaratory Judgment Act, 28 U.S.C. §§ 2201 *et seq.*, under the patent laws of the United States, 35 U.S.C. §§ 1 *et seq*. This Court has subject matter jurisdiction pursuant to 28 U.S.C. §§ 1331 and 1338(a).

15. Because this action presents an actual controversy with respect to the noninfringement of the Maxell LIB Patents, the Court may grant the declaratory relief sought pursuant to 28 U.S.C. §§ 2201 and 2202.

16. This Court has personal jurisdiction over Maxell by virtue of its sufficient minimum contacts with this forum based on business it conducts within the State of New Jersey, including in this judicial district.

17. Defendants are subject to this Court's specific and general personal jurisdiction under due process and/or the New Jersey Long Arm Statute due at least to Defendants' substantial business in this forum, including: (i) U.S. operations headquartered in this District; (ii) regularly doing or soliciting business, engaging in other persistent courses of conduct, and/or deriving substantial revenue from licensing its patents and from goods and services provided to individuals in New Jersey and in this District; and (iii) by virtue of its significant and active litigation it has initiated in the United States, including in this District. For example, Maxell has purposely availed itself of this Court by recently filing and continuing to litigate a patent infringement complaint in an unrelated case in this District. Thus, it would be reasonable and fair for this Court to exercise jurisdiction consistent with the principles underlying the U.S. Constitution, and would not offend traditional notions of fair play and substantial justice.

18. Upon further information and belief, Defendants have also established minimum contacts with this District and regularly transact and do business within this District, including advertising, promoting and selling products over the internet, through intermediaries,

representatives and/or agents located within this District and litigating patent infringement actions in this District.

19. Upon further information and belief, Defendants have purposefully directed activities at citizens of this State and located within this District.

20. Venue in the District of New Jersey is proper pursuant to 28 U.S.C. § 1391(c)(3) because Defendants are not residents in the United States and thus may be sued in any judicial district.

21. Venue in this district is also proper per 28 U.S.C. §§ 1391(b)(2) and 1400(b) because a substantial part of the events giving rise to the claims in this action occurred in this District and Defendants' agent resides or may be found in this District. Specifically, Maxell's wholly-owned U.S. subsidiary, Maxell Corporation of America ("Maxell America"), is located at 3 Garret Mountain Plaza, Suite 300, Woodland Park, New Jersey, 07424-3352.

22. Upon information and belief, Maxell America functions as Maxell's U.S. operations and corporate headquarters for North America, and Maxell has and continues to conduct substantial business with and through Maxell America.

BACKGROUND

23. Founded in 1999, ATL is the world's leading producer and innovator of lithium-ion batteries. ATL is a global company known worldwide for its high-tech, high-volume prowess in developing, producing and packaging high quality rechargeable lithium-ion battery cells and packs.

24. ATL is now the world's largest lithium ion battery manufacturer for smartphones and one of the largest and most successful lithium ion battery manufacturer for all consumer electronics. ATL's market share continues to grow, and it has manufactured well over 1 billion lithium ion batteries per year for the past three years. In contrast, upon information and belief,

Maxell does not maintain a significant market share in the industry, and its production is a fraction of ATL's production.

25. In March 2020, Maxell contacted ATL and alleged that ATL's products infringed the Maxell LIB Patents, and demanded that ATL license the Maxell LIB Patents.

26. From May 2020 until February 2021, ATL and Maxell engaged in several rounds of discussions regarding the Maxell LIB Patents.

27. On March 26, 2021, Maxell sent ATL correspondence that threatened it would "pursue litigation" and "seek injunctive relief and recover monetary damages" over the Maxell LIB Patents absence the entry of "a licensing agreement by Friday, April 9, 2021."

28. Consequently, ATL has a reasonable apprehension, and there exists a substantial controversy and risk, that Defendants could imminently file an action against ATL and allege that ATL infringes directly and/or indirectly the Maxell LIB Patents. Maxell's claims and allegations have cast uncertainty over ATL and its products and have created a concrete and immediate justiciable controversy between ATL and the Defendants. ATL thus brings this case to clear its name and that of its lithium ion products, and to protect its customers against claims of infringement that lack merit.

29. In the March 26, 2021 correspondence, Maxell's counsel claimed that it represented "Maxell, Ltd." and "Maxell Holdings, Inc." and that these entities owned and controlled licensing of the Maxell LIB Patents.

30. Subsequent to ATL's filing of the Original Complaint in this matter, Maxell informed ATL that Maxell Holdings, Inc. did not exist, but declined to explain why they previously claimed to represent it or whether it had any ownership interest in the Maxell LIB Patents. Upon information and belief, the entity referred to as Maxell Holdings, Inc. in the Original Complaint is

Maxell Holdings, Ltd.

COUNT I - DECLARATORY JUDGMENT OF NONINFRINGEMENT OF U.S. PATENT NO. 8,691,446

31. ATL realleges and incorporates paragraphs 1 to 28 as if fully set forth herein.

32. Maxell Holdings, Ltd. is the owner of the ’446 Patent, entitled “Nonaqueous secondary battery and method of using the same.” The ’446 Patent issued on April 8, 2014. A true and correct copy of the ’446 Patent is attached as Exhibit 1.

33. Maxell provided ATL with a claim chart purporting to demonstrate how each and every element of claim 1 of the ’446 Patent is met by ATL’s Accused Products and accusing ATL’s customers of infringement. By way of example, and without limitation, ATL products do not infringe the ’446 Patent (under any sub-section of 35 U.S.C. § 271) because they do not meet the (1) “wherein the positive electrode contains, as an active material, at least two lithium-containing transition metal oxides having different average particle sizes, wherein said at least two lithium-containing transition metal oxides having different average particle sizes have different compositions of elements between them,” and (2) “said lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (1): LixM1 yM2 zM3 vO2 (1) … x, y, z and v are numbers satisfying the equations respectively: 0.97≦x<1.02, 0.8≦y<1.02, 0.002≦z≦0.05, and 0≦v≦0.05” limitations, as required by the claims of the ’446 Patent. The allegations in this paragraph are exemplary and do not preclude ATL from contending that the claims are not infringed for additional reasons.

34. ATL has never had any intent to cause its customers or anyone else to infringe the ’446 Patent.

35. An actual and justiciable controversy therefore exists between ATL and Maxell regarding whether any of the Accused ATL Products have infringed any of the asserted claims of

the ’446 Patent. A judicial declaration is necessary to determine the parties’ respective rights regarding the ’446 Patent.

36. ATL seeks a judgment declaring that the Accused ATL Products do not directly or indirectly infringe any asserted claims of the ’446 Patent, either literally or under the doctrine of equivalents under 35 U.S.C. § 271 (or any sub-section thereof).

37. ATL further seeks and is entitled to a declaratory judgment that its customers do not and have not infringed under 35 U.S.C. § 271 (or any sub-section thereof) any claim of the ’446 Patent by using the Accused ATL Products (or any other ATL Products).

COUNT II - DECLARATORY JUDGMENT OF NONINFRINGEMENT OF U.S. PATENT NO. 9,350,019

38. ATL realleges and incorporates paragraphs 1 to 35 as if fully set forth herein.

39. Maxell Holdings, Ltd. is the owner of the ’019 Patent, entitled “Nonaqueous secondary battery and method of using the same.” The ’019 Patent issued on May 24, 2016. A true and correct copy of the ’019 Patent is attached as Exhibit 2.

40. Maxell provided ATL with a claim chart purporting to demonstrate how each and every element of claim 1 of the ’019 Patent is met by the Accused ATL Products and accusing ATL’s customers of infringement. By way of example, ATL products do not infringe the ’019 Patent (under any sub-section of 35 U.S.C. § 271) because they do not meet the (1) “wherein the positive electrode contains, as an active material, at least two lithium-containing transition metal oxides having different average particle sizes, wherein said at least two lithium-containing transition metal oxides having different average particle sizes have different compositions of elements between them,” and (2) “said lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (1): LixM1 yM2 zM3 vO2 (1) … x, y, z and v are numbers satisfying the equations

respectively: 0.97≦x<1.02, 0.8≦y<1.02, 0.002≦z≦0.05, and 0≦v≦0.05" limitations, as required by the claims of the '019 Patent. The allegations in this paragraph are exemplary and do not preclude ATL from contending that the claims are not infringed for additional reasons.

41. ATL has never had any intent to cause its customers or anyone else to infringe the '019 Patent.

42. An actual and justiciable controversy therefore exists between ATL and Maxell regarding whether any of the Accused ATL Products have infringed any of the asserted claims of the '019 Patent. A judicial declaration is necessary to determine the parties' respective rights regarding the '019 Patent.

43. ATL seeks a judgment declaring that the Accused ATL Products do not directly or indirectly infringe any asserted claims of the '019 Patent, either literally or under the doctrine of equivalents under 35 U.S.C. § 271 (or any sub-section thereof).

44. ATL further seeks and is entitled to a declaratory judgment that its customers do not and have not infringed under 35 U.S.C. § 271 (or any sub-section thereof) any claim of the '019 Patent by using the Accused ATL Products (or any other ATL Products).

COUNT III - DECLARATORY JUDGMENT OF NONINFRINGEMENT OF U.S. PATENT NO. 9,077,035

45. ATL realleges and incorporates paragraphs 1 to 42 as if fully set forth herein.

46. Maxell Holdings, Ltd. is the owner of the '035 Patent, entitled "Nonaqueous secondary battery and method of using the same." The '035 Patent issued on July 7, 2015. A true and correct copy of the '035 Patent is attached as Exhibit 3.

47. Maxell provided ATL with a claim chart purporting to demonstrate how each and every element of claim 1 of the '035 Patent is met by the Accused ATL Products and accusing ATL's customers of infringement. By way of example, ATL products do not infringe the '035

Patent (under any sub-section of 35 U.S.C. § 271) because they do not meet the (1) “a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, wherein the positive electrode comprises, as active materials, at least two lithium-containing transition metal oxides having different average particle sizes” and (2) “the lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (1): LixM1 yM2 zM3 vO2 (1) … x, y, z and v are numbers satisfying the equations respectively: 0.97≦x<1.02, 0.8≦y<1.02, 0.002≦z≦0.05, and 0≦v≦0.05” limitations, as required by the claims of the ’035 Patent. The allegations in this paragraph are exemplary and do not preclude ATL from contending that the claims are not infringed for additional reasons.

48. ATL has never had any intent to cause its customers or anyone else to infringe the ’035 Patent.

49. An actual and justiciable controversy therefore exists between ATL and Maxell regarding whether any of the Accused ATL Products have infringed any of the asserted claims of the ’035 Patent. A judicial declaration is necessary to determine the parties’ respective rights regarding the ’035 Patent.

50. ATL seeks a judgment declaring that the Accused ATL Products do not directly or indirectly infringe any asserted claims of the ’035 Patent, either literally or under the doctrine of equivalents under 35 U.S.C. § 271 (or any sub-section thereof).

51. ATL further seeks and is entitled to a declaratory judgment that its customers do not and have not infringed under 35 U.S.C. § 271 (or any sub-section thereof) any claim of the ’035 Patent by using the Accused ATL Products (or any other ATL Products).

COUNT IV - DECLARATORY JUDGMENT OF NONINFRINGEMENT OF U.S. PATENT NO. 9,166,251

52. ATL realleges and incorporates paragraphs 1 to 49 as if fully set forth herein.

53. Maxell Holdings, Ltd. is the owner of the ’251 Patent, entitled “Battery separator and nonaqueous electrolyte battery.” The ’251 Patent issued on October 20, 2015. A true and correct copy of the ’251 Patent is attached as Exhibit 4.

54. Maxell provided ATL with a claim chart purporting to demonstrate how each and every element of claim 1 of the ’251 Patent is met by Accused ATL Products and accusing ATL’s customers of infringement. By way of example, ATL products do not infringe the ’251 Patent (under any sub-section of 35 U.S.C. § 271) because they do not meet the limitation of “the thermoplastic resin constitutes a shutdown layer formed of a heat-shrinkable microporous film” as required by the claims of the ’251 Patent. The allegations in this paragraph are exemplary and do not preclude ATL from contending that the claims are not infringed for additional reasons.

55. ATL has never had any intent to cause its customers or anyone else to infringe the ’251 Patent.

56. An actual and justiciable controversy therefore exists between ATL and Maxell regarding whether any of the Accused ATL Products have infringed any of the asserted claims of the ’251 Patent. A judicial declaration is necessary to determine the parties’ respective rights regarding the ’251 Patent.

57. ATL seeks a judgment declaring that the Accused ATL Products do not directly or indirectly infringe any asserted claims of the ’251 Patent, either literally or under the doctrine of equivalents under 35 U.S.C. § 271 (or any sub-section thereof).

58. ATL further seeks and is entitled to a declaratory judgment that its customers do not and have not infringed under 35 U.S.C. § 271 (or any sub-section thereof) any claim of the

’251 Patent by using the Accused ATL Products (or any other ATL Products).

DEMAND FOR JURY TRIAL

Plaintiff, under Rule 38 of the Federal Rules of Civil Procedure, requests a trial by jury of any issues so triable by right.

REQUEST FOR RELIEF

WHEREFORE, ATL respectfully requests the Court to enter judgment in its favor and against the Defendants as follows:

1. That neither ATL nor its products have infringed or do infringe under 35 U.S.C. § 271 (or any sub-section thereof) any claim of the Maxell LIB Patents;

2. That ATL’s customers’ products and/or services have not infringed and do not infringe under 35 U.S.C. § 271 (or any sub-section thereof) any claim of the Maxell LIB Patents based on their purported use of ATL’s products;

3. Enjoining Defendants and their officers, employees or agents from (a) alleging that ATL or its customers infringe the Maxell LIB Patents; (b) taking any action to suggest that ATL or its customers require a license from Defendants for use of the Maxell LIB Patents; or (c) pursuing or continuing to pursue infringement actions against ATL’s customers on the basis of those customers’ use of ATL’s products;

4. Declaring this to be an exceptional case within the meaning of 35 U.S.C. § 285;

5. Awarding costs and reasonable attorneys’ fees incurred in connection with this action; and

6. For such other and further relief as the Court deems just and proper.

DATED: May 3, 2021

Respectfully submitted,

/s/ *Becky L. Caruso*
Becky L. Caruso (local counsel)

GREENBERG TRAURIG LLP
500 Campus Drive, Suite 400
Florham Park, NJ 07932
Tel: (973) 360-7900
carusob@gtlaw.com

GREENBERG TRAURIG LLP
L. Howard Chen (admitted *pro hac vice*)
Harold H. Davis (admitted *pro hac vice*)
Yang Liu (admitted *pro hac vice*)
Four Embarcadero Center, Suite 3000
San Francisco, CA 94111
(415) 655-1300
chenh@gtlaw.com
davish@gtlaw.com
liuyan@gtlaw.com

Rose Cordero-Prey (admitted *pro hac vice*)
MetLife Building
200 Park Avenue
New York, NY 10166
(212) 801-9200
preyr@gtlaw.com

Vishesh Narayen (admitted *pro hac vice*)
101 East Kennedy Boulevard, Suite 1900
Tampa, FL 33602
(813) 318-5700
narayenv@gtlaw.com

ATTORNEYS FOR PLAINTIFF
AMPEREX TECHNOLOGY LIMITED

Exhibit 1

US008691446B2

(12) **United States Patent**
Sakata et al.

(10) **Patent No.: US 8,691,446 B2**
(45) **Date of Patent: Apr. 8, 2014**

(54) **NONAQUEOUS SECONDARY BATTERY AND METHOD OF USING THE SAME**

(75) Inventors: **Hideo Sakata**, Ibaraki (JP); **Fusaji Kita**, Ibaraki (JP); **Kumiko Ishizuka**, Ibaraki (JP)

(73) Assignee: **Hitachi Maxell, Ltd.**, Ibaraki-shi, Osaka (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 765 days.

(21) Appl. No.: **11/976,566**

(22) Filed: **Oct. 25, 2007**

(65) **Prior Publication Data**

US 2008/0102369 A1 May 1, 2008

(30) **Foreign Application Priority Data**

Oct. 26, 2006 (JP) 2006-290637

(51) **Int. Cl.**

H01M 4/50	(2010.01)
H01M 4/52	(2010.01)
H01M 4/525	(2010.01)
H01M 6/16	(2006.01)

(52) **U.S. Cl.**
USPC **429/231.95**; 429/339; 429/231.3; 429/231.5; 429/223; 429/224

(58) **Field of Classification Search**
USPC 429/188, 326, 330, 331, 332, 200, 339, 429/307, 245, 231, 231.5, 231.95, 223, 224, 429/231.3
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,302,518	A	11/1981	Goodenough et al.	
4,668,595	A	5/1987	Yoshino et al.	
5,147,738	A	9/1992	Toyoguchi et al.	
2002/0037456	A1	3/2002	Hosoya	
2003/0068555	A1 *	4/2003	Naruoka	429/231.4
2004/0013946	A1	1/2004	Abe et al.	
2005/0164082	A1 *	7/2005	Kishi et al.	429/188
2005/0266315	A1	12/2005	Sato et al.	
2006/0024584	A1 *	2/2006	Kim et al.	429/326
2006/0035144	A1	2/2006	Shimizu et al.	
2006/0115730	A1 *	6/2006	Taniguchi et al.	429/217
2006/0134521	A1 *	6/2006	Shima	429/231.1
2006/0194118	A1	8/2006	Yew et al.	
2006/0263690	A1 *	11/2006	Suhara et al.	429/231.3

FOREIGN PATENT DOCUMENTS

CN	1776938 A	5/2006

(Continued)

OTHER PUBLICATIONS

Machine translation of JP 2001-176511, Honbo et al., Jun. 2001.*

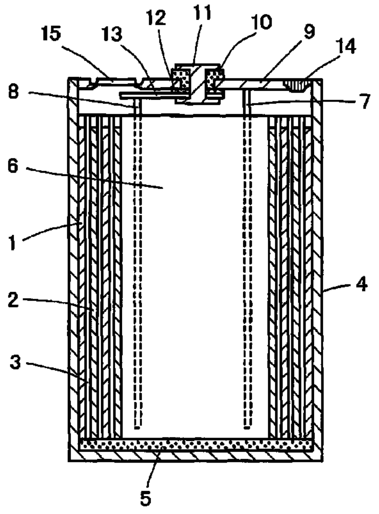
(Continued)

Primary Examiner — Kenneth Douyette
(74) *Attorney, Agent, or Firm* — Birch, Stewart, Kolasch & Birch, LLP

(57) **ABSTRACT**

A nonaqueous secondary battery having a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, in which the positive electrode contains, as an active material, a lithium-containing transition metal oxide containing a metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, the positive electrode mixture layer has a density of 3.5 g/cm^3 or larger, and the nonaqueous electrolyte contains a compound having two or more nitrile groups in the molecule.

5 Claims, 2 Drawing Sheets



(56) References Cited

FOREIGN PATENT DOCUMENTS

JP	55-136131	A		10/1980	
JP	3-201368	A		9/1991	
JP	4-171659	A		6/1992	
JP	7-176302	A		7/1995	
JP	7-176322	A		7/1995	
JP	2001-167763	A		6/2001	
JP	2001-176511	A		6/2001	
JP	2001176511	A	*	6/2001	.... H01M 4/58
JP	2001-319652	A		11/2001	
JP	2002-216745	A		8/2002	
JP	2002-270238	A		9/2002	
JP	2003-217582	A		7/2003	
JP	2004-179146	A		6/2004	
JP	2004-296098	A		10/2004	
JP	2005050582	A	*	2/2005	.... H01M 4/02
JP	2005-339970	A		12/2005	
JP	2006-73513	A		3/2006	
JP	2006-164742	A		6/2006	
JP	2006-245001	A		9/2006	
WO	WO 2005/069423	A1		7/2005	
WO	WO 2005/117198	A1		12/2005	
WO	WO 2006/091019	A1		8/2006	
WO	2007-042302	A		2/2007	
WO	WO-2004/030125	A1	*	4/2008	.... H01M 4/58

OTHER PUBLICATIONS

Machine Translation of: JP 2005/050582 A, Kikuchi, Kazuhiro, Feb. 2005.*

Chinese Office Action for Application No. 200710180385.4, dated Feb. 10, 2011.

Submission of Publications for Application No. 2006-290637, dated Mar. 14, 2011.

A Japanese Office Action, dated Oct. 11, 2011, for Japanese Application No. 2006-290637.

Japanese Office Action, dated May 17, 2013, for Japanese Patent Application No. 2011-261150.

* cited by examiner

Fig. 1A

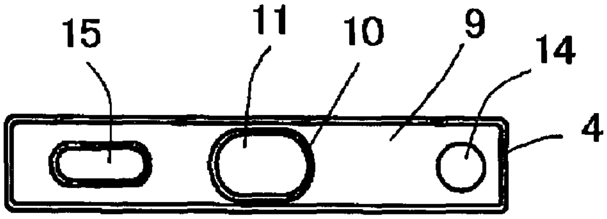


Fig. 1B

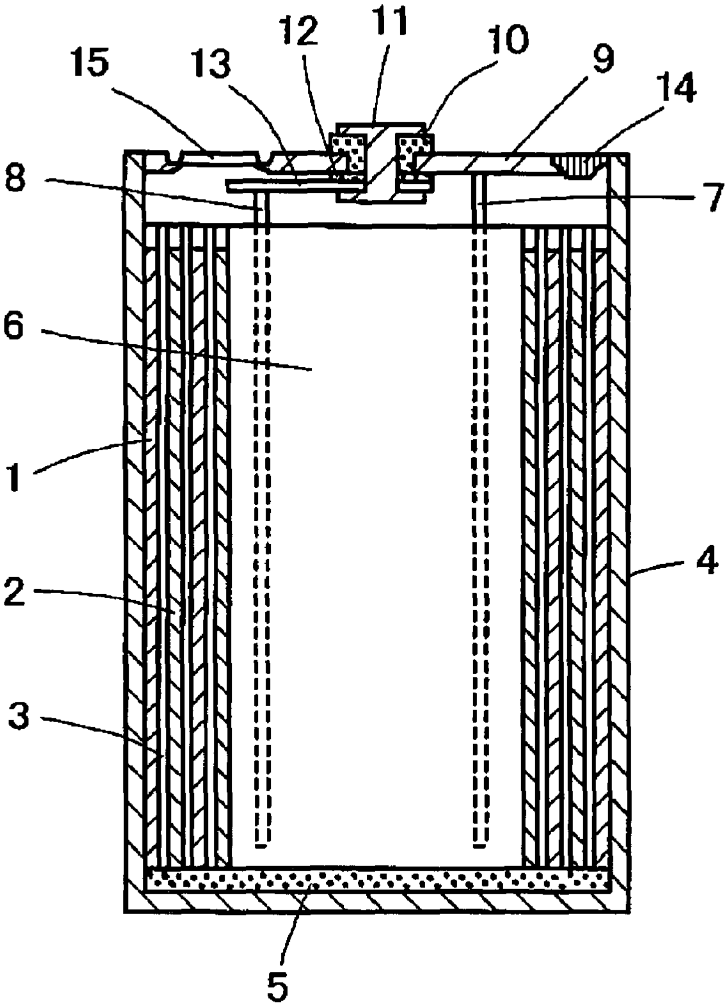
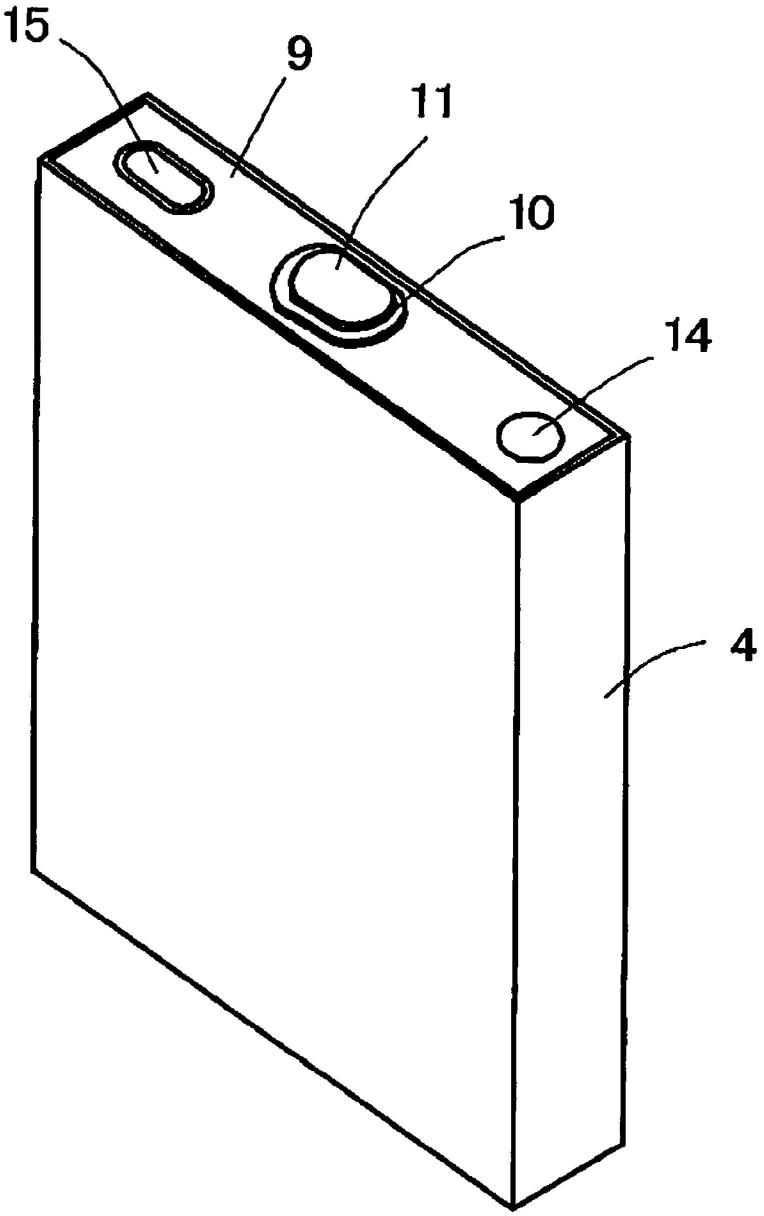


Fig. 2



NONAQUEOUS SECONDARY BATTERY AND METHOD OF USING THE SAME

FILED OF THE INVENTION

The present invention relates to a nonaqueous secondary battery having a high capacity, good charge-discharge cycle characteristics and high reliability such as safety.

RELATED ART

In recent years, the secondary battery is an indispensable, important device as a power source of a personal computer or a cellular phone, or a power source for an electric vehicle or an electric power storage.

In particular, in applications for a mobile communication device such as a portable computer and a personal digital assistant, the battery is required to be made smaller and to trim-weight. Under the current circumstances, however, the system of the battery is not easily made compact or lightweight, since an electric power consumed by a back light of a liquid crystal display panel or consumed to control the drawing of graphics is large, or the capacity of a secondary battery is not sufficiently large. In particular, a personal computer is progressively multi-functionalized by mounting a digital versatile disc (DVD) drive and so on. Thus, the power consumption thereof tends to increase. For this reason, it is highly required to increase the electric capacity of a secondary battery, in particular, the discharge capacity, when the voltage of a single battery is 3.3 V or higher.

Attention is paid to electric vehicles, which discharge no exhaust gas and make less noise in association with the increase of global environmental problems. Recently, parallel hybrid electric vehicles (HEV), which adopt a system of storing regenerative energy generated at the time of braking in a battery and making effective use of the energy, or using an electric energy stored in a battery at the time of engine starting to increase the efficiency of the engine system, have gained popularity. However, since the electric capacity of the currently used battery is small, a plurality of batteries should be used to generate a sufficient voltage. For this reason, problems such that a space in the vehicle should be made smaller and that the stability of the vehicle body deteriorates arise.

Among secondary batteries, a lithium secondary battery using a nonaqueous electrolyte attracts attention, since it generates a high voltage, has a lightweight and is expected to achieve a high energy density. In particular, a lithium secondary battery disclosed in JP-A-55-136131, in which a lithium-containing transition metal oxide, for example, $LiCoO_2$, is used as a positive electrode active material, and metal lithium is used as a negative electrode active material, is expected to attain a high energy density, since it has an electromotive force of 4 V or higher.

However, at present, in the case of a $LiCoO_2$ based secondary battery which uses $LiCoO_2$ as a positive electrode active material and a carbonaceous material such as graphite as a negative electrode active material, a charge final voltage thereof is usually 4.2 V or less. According to this charging condition, the charge capacity is only about 60% of the theoretical capacity of $LiCoO_2$. The electric capacity may be increased by increasing the charge final voltage to higher than 4.2 V. However, with the increase of the charge capacity, the crystalline structure of $LiCoO_2$ decays so that the charge-discharge cycle life may be shortened, or the crystalline structure of $LiCoO_2$ may be destabilized. Accordingly, the thermal stability of the battery deteriorates.

To solve such a problem, many attempts have been made to add a different metal element to $LiCoO_2$ (cf. JP-A-4-171659, JP-A-3-201368, JP-A-7-176302 and JP-A-2001-167763).

In addition, attempts have been made to use a battery in a high-voltage range of 4.2 V or higher (cf. JP-A-2004-296098, JP-A-2001-176511 and JP-A-2002-270238).

In years to come, a secondary battery will be required to have a higher capacity and also better reliability than the conventional batteries. In general, the battery capacity can be greatly improved by raising the content of an active material in electrodes or by increasing an electrode density, in particular, the density of a positive electrode mixture layer. However, according to such capacity-increasing measures, the reliability of the battery including storage characteristics gradually decreases.

Accordingly, in order to meet requirements for the increase of the electric capacity, it is highly desired to provide a battery which uses a material that generates a higher electromotive force (voltage range) than $LiCoO_2$ and has a stable crystalline structure capable of being stably and reversibly charged and discharged, and which further satisfies reliability such that the safety of the conventional batteries can be maintained and the battery does not expand during storage when the density of the positive electrode mixture layer is increased.

When the discharge final voltage of a conventional battery comprising $LiCoO_2$ as a positive electrode active material is made higher than 3.2 V, the battery cannot be completely discharged since the voltage in the final stage of the discharge significantly falls. Thus, an electric quantity efficiency of discharge relative to charging remarkably decreases. Since the complete discharge cannot be attained, the crystalline structure of $LiCoO_2$ easily decays, and thus the charge-discharge cycle life is shortened. This phenomenon remarkably appears in the above-mentioned high voltage range.

Under a charging condition that the final voltage at full charging is set to 4.2 V or higher in the conventional battery, apart from shortening of the charge-discharge cycle life or the decrease of the thermal stability caused by the decay of the crystalline structure of the positive electrode active material, the electrolytic solution (a solvent) is oxidatively decomposed due to the increase of the active sites in the positive electrode active material, whereby a passivation film is formed on the surface of the positive electrode and thus the internal resistance of the battery increases so that the load characteristic may deteriorate.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a nonaqueous secondary battery having a high capacity, good charge-discharge cycle characteristics and high storage characteristics.

Accordingly, the present invention provides a nonaqueous secondary battery comprising: a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, wherein the positive electrode contains, as an active material, at least one lithium-containing transition metal oxide comprising at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, the positive electrode mixture layer has a density of at least 3.5 g/cm^3, and the nonaqueous electrolyte contains a compound having at least two nitrile groups in the molecule.

The nonaqueous secondary battery of the present invention can be charged at a high voltage and thus has a large capacity, since the positive electrode mixture layer has a density of a specific value or larger so as to increase the filled amount of the positive electrode active material in the positive electrode mixture layer, and a lithium-containing transition metal oxide comprising a specific metal element, which is highly stable in a charged state at a high voltage, is used as a positive electrode active material.

Furthermore, since the positive electrode active material used in the nonaqueous secondary battery of the present invention has good stability, the decay of the active material is suppressed when the charging and discharging of the battery are repeated. Thereby, the nonaqueous secondary battery has good charge-discharge cycle characteristics.

In addition, the nonaqueous electrolyte used in the nonaqueous secondary battery of the present invention contains a compound having at least two nitrile groups in the molecule. Such a nitrile compound acts on the surface of the positive electrode and functions to prevent the direct contact of the positive electrode and the nonaqueous electrolyte. Thus, the reaction of the positive electrode and the nonaqueous electrolyte is suppressed, whereby the generation of a gas in the battery by such a reaction is prevented. Accordingly, the suppression of the reaction of the positive electrode and the nonaqueous electrolyte and the use of the positive electrode active material having high stability synergistically function to prevent the expansion of the battery during the storage of the charged battery at a high temperature and thus to improve the storage characteristics of the battery.

Consequently, the nonaqueous secondary battery of the present invention has good charge-discharge cycle characteristics and good storage characteristics. The nonaqueous secondary battery of the present invention can be charged at a high positive electrode voltage in a range of 4.35 to 4.6 V with reference to the potential of lithium, and thus it can be used in applications which require a high output.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1**A and **1**B schematically show one example of the nonaqueous secondary battery of the present invention. FIG. **1**A is a plan view thereof and FIG. **1**B is a partial vertical section thereof.

FIG. **2** shows a perspective view of the nonaqueous secondary battery illustrated in FIGS. **1**A and **1**B.

DETAILED DESCRIPTION OF THE INVENTION

The nonaqueous secondary battery of the present invention may have such a configuration that a laminate electrode body having a positive electrode with a positive electrode mixture layer and a negative electrode which are laminated each other with inserting a separator between them, or a wound electrode body in which the laminate electrode body is wound is enclosed within a housing together with a nonaqueous electrolyte.

In the nonaqueous secondary battery of the present invention, the nonaqueous electrolyte is preferably a nonaqueous solvent-base electrolytic solution comprising an electrolyte salt such as a lithium salt dissolved in a nonaqueous solvent such as an organic solvent, from the viewpoint of electric characteristics or handling easiness. A polymer electrolyte or a gel electrolyte may be used without any problem.

The solvent in the nonaqueous electrolytic solution is not particularly limited, and examples thereof include acyclic esters such as dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, and methyl propyl carbonate; cyclic esters having a high dielectric constant, such as ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate; and mixed solvents comprising an acyclic ester and a cyclic ester. Mixed solvents each comprising an acyclic ester as a main solvent and a cyclic ester are particularly suitable.

Apart form the esters exemplified above, the following solvents may also be used: acyclic phosphoric acid triesters such as trimethyl phosphate; ethers such as 1,2-dimethoxyethane, 1,3-dioxolane, tetrahydrofuran, 2-methyl-tetrahydrofuran and diethyl ether; nitriles and dinitriles; isocyanates; and halogen-containing solvents. Furthermore, amine or imide organic solvents may be used.

Examples of the electrolyte salt to be dissolved in the solvent during the preparation of the nonaqueous electrolytic solution include $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiSbF_6$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiCF_3CO_2$, $Li_2C_2F_4(SO_3)_2$, $LiN(RfSO_2)(Rf'SO_2)$, $LiC(RfSO_2)_3$, $LiC_nF_{2n+1}SO_3$ wherein $n \geq 2$, and $LiN(RfOSO_2)_2$ wherein Rf and Rf' each represent a fluoroalkyl group. They may be used alone or in combination of two or more thereof. Among these electrolyte salts, particularly preferred are fluorine-containing organic lithium salts having 2 or more carbon atoms, since such lithium salts have a large anionic property and further ion separation easily occurs so that the salts are easily dissolved in the above-mentioned solvents. The concentration of the electrolyte salt in the nonaqueous electrolytic solution is not particularly limited, and it is preferably 0.3 mol/L or more, more preferably 0.4 mol/L or more, while it is preferably 1.7 mol/L or less, more preferably 1.5 mol/L or less.

According to the present invention, the nonaqueous electrolyte should contain a compound having at least two nitrile groups in the molecule.

The nitrile compound used according to the present invention can form a protective film on the surface of the positive electrode active material during charging, in particular, initial charging, of the battery, and the protective film suppresses the direct contact of the positive electrode and the nonaqueous electrolyte. Therefore, the battery of the present invention comprising the nonaqueous electrolyte containing the compound having at least two nitrile groups in the molecule can prevent the generation of a gas in the battery due to the reaction of the positive electrode and the nonaqueous electrolyte, when it is stored at a high temperature of, for example, about 85° C., in a charged state, since the protective film formed of the nitrile compound prevents the positive electrode and the nonaqueous electrolyte from direct contact and in turn prevents the reaction therebetween. The gas generated by the reaction of the positive electrode and the nonaqueous electrolyte in the battery causes the expansion of the battery resulting in the decrease of the battery characteristics due to the increase of the distance between the positive and negative electrodes. However, the battery of the present invention can suppress the expansion of the battery caused by the gas during storage and thus has good storage characteristics.

The compound having at least two nitrile groups in the molecule may be one having two nitrile groups in the molecule, one having three nitrile groups in the molecule, etc. Among them, a dinitrile compound, that is, a compound having two nitrile groups in the molecule is preferable since it has a better property to form the protective film and thus to prevent the reaction of the positive electrode and the nonaqueous electrolyte. The dinitrile compound is preferably a compound of the formula: NC—R—CN wherein R is a linear or branched hydrocarbon group having 1 to 10 carbon atoms, preferably a linear or branched alkylene group having 1 to 10 carbon atoms.

Specific examples of the dinitrile compound include malononitrile, succinonitrile, glutaronitrile, adiponitrile, 1,4-dicyanoheptane, 1,5-dicyanopentane, 1,6-dicyanohexane, 1,7-dicyanoheptane, 2,6-dicyanoheptane, 1,8-dicyanooctane, 2,7-dicyanooctane, 1,9-dicyanononane, 2,8-dicyanononane, 1,10-dicyanodecane, 1,6-dicyanodecane, 2,4-dimethylglutaronitrile, etc.

The nonaqueous electrolyte containing the nitrile compound may be prepared by any method. For example, the nitrile compound and the electrolyte salt are dissolved in the solvent described above by a conventional method.

The amount of the nitrile compound is preferably at least 0.005% by weight, more preferably at least 0.01% by weight, still more preferably at least 0.05% by weight, based on the whole weight of the nonaqueous electrolyte, from the viewpoint of effectively utilizing the effects of the addition of the nitrile compound. However, when the amount of the nitrile compound in the electrolyte is too large, the charge-discharge cycle characteristics of the battery tends to decrease although the storage characteristics of the battery is improve. Thus, the amount of the nitrile compound is preferably 1% or less, more preferably 0.75% by weight or less, still more preferably 0.5% by weight or less, based on the whole weight of the nonaqueous electrolyte.

Besides the nitrile compound, the nonaqueous electrolytic solution may contain other additive or additives. A preferred example of the additive is a nonionic aromatic compound. Specific examples thereof include aromatic compounds having an alkyl group bonded to an aromatic ring (e.g., cyclohexylbenzene, isopropylbenzene, tert-butylbenzene, tert-amylbenzene, octylbenzene, toluene and xylene); aromatic compounds having a halogen group bonded to an aromatic ring (e.g., fluorobenzene, difluorobenzene, trifluorobenzene and chlorobenzene); aromatic compounds having an alkoxy group bonded to an aromatic ring (e.g., anisole, fluoroanisole, dimethoxybenzene and diethoxybenzene); aromatic carboxylic acid esters such as phthalic acid esters (e.g., dibutyl phthalate and di-2-ethylhexyl phthalate) and benzoic acid esters; carbonic acid esters having a phenyl group (e.g., methylphenyl carbonate, butylphenyl carbonate and diphenyl carbonate); phenyl propionate; and biphenyl. Among them, the compounds having an alkyl group bonded to an aromatic ring (alkaryl compounds) are preferred, and cyclohexylbenzene is particularly preferred.

The aromatic compounds exemplified above can also form a film on the surface of the active material in the positive electrode or the negative electrode in the battery. These aromatic compounds may be used alone, while more advantageous effects can be attained by the use of two or more of the aromatic compounds together. Particularly advantageous effects can be attained on the improvement of the safety of the battery by the use of the alkaryl compound together with an aromatic compound, which can be oxidized at a lower voltage than the alkaryl compound, such as biphenyl.

The method for adding the aromatic compound in the nonaqueous electrolytic solution is not particularly limited. In general, the aromatic compound is added to the nonaqueous electrolytic solution prior to the fabrication of the battery.

The content of the aromatic compound in the nonaqueous electrolytic solution is preferably 4% by weight or more from the viewpoint of the safety, and it is preferably 10% by weight or less from the viewpoint of the load characteristic. When two or more aromatic compounds are used together, the total amount thereof is within the above-mentioned range. When the alkaryl (alkylaryl) compound and the aromatic compound which can be oxidized at a lower voltage that the alkaryl compound are used in combination, the content of the alkaryl compound in the nonaqueous electrolytic solution is preferably 0.5% by weight or more, more preferably 2% by weight or more, while it is preferably 8% by weight or less, more preferably 5% by weight or less. The content of the aromatic compound that can be oxidized at a lower voltage than the alkaryl compound in the nonaqueous electrolytic solution is preferably 0.1% by weight or more, more preferably 0.2% by weight or more, while it is preferably 1% by weight or less, more preferably 0.5% by weight or less.

Furthermore, a surface protecting coating can be formed on the surface of the positive electrode active material in the step of initial charging of the battery, when the nonaqueous electrolytic solution contains at least one compound selected from the group consisting of halogen-containing organic solvents (e.g., halogen-containing carbonates), organic sulfur compounds, fluorine-containing organic lithium salts, phosphorus-containing organic solvents, silicon-containing organic solvents, nitrogen-containing organic solvents other than the compounds having at least two nitrile groups in the molecule, etc. In particular, the fluorine-containing organic compounds such as fluorine-containing carbonate esters, the organic sulfur compounds and the fluorine-containing organic lithium salts are preferred. Specific examples thereof include F-DPC [$C_2F_5CH_2O(C{=}O)OCH_2C_2F_5$], F-DEC [$CF_3CH_2O(C{=}O)OCH_2CF_3$], HFE7100 ($C_4F_9OCH_3$), butyl sulfate ($C_4H_9OSO_2OC_4H_9$), methylethylene sulfate [$(\text{—}OCH(CH_3)CH_2O\text{—})SO_2$], butyl sulfate ($C_4H_9SO_2C_4H_9$), a polymer imide salt ($[\text{—}N(Li)SO_2OCH_2(CF_2)_4CH_2OSO_2\text{—}]_n$ wherein n is from 2 to 100), $(C_2F_5SO_2)_2NLi$, and $[(CF_3)_2CHOSO_2]_2NLi$.

Such additives may be used alone. It is particularly preferable to use a fluorine-containing organic solvent together with a fluorine-containing organic lithium salt. The amount of such an additive added is preferably 0.1% by weight or more, more preferably 2% by weight or more, particularly preferably 5% by weight or more, while it is preferably 30% by weight or less, more preferably 10% by weight or less, each based on the whole weight of the nonaqueous electrolytic solution. When the amount of the additive is too large, the electric characteristics of the battery may deteriorate. When the amount is too small, a good coating may hardly be formed.

When the battery comprising the nonaqueous electrolytic solution containing the above-mentioned additive(s) is charged, particularly at a high voltage, a surface protecting coating that contains fluorine or sulfur atoms is formed on the positive electrode active material surface. This surface protecting coating may contain either fluorine atoms or sulfur atoms. Preferably, the coating contains both of fluorine atoms and sulfur atoms.

The amount of the sulfur atoms in the surface protecting coating formed on the positive electrode active material surface is preferably 0.5 atomic % or more, more preferably 1 atomic % or more, particularly preferably 3 atomic % or more. However, when the amount of the sulfur atoms in the positive electrode active material surface is too large, the discharge characteristic of the battery tends to decrease. Thus, the amount is preferably 20 atomic % or less, more preferably 10 atomic % or less, particularly preferably 6 atomic % or less.

The amount of the fluorine atoms in the surface protecting coating formed on the positive electrode active material surface is preferably 15 atomic % or more, more preferably 20 atomic % or more, particularly preferably 25 atomic % or more. However, when the amount of the fluorine atoms in the positive electrode active material surface is too large, the discharge characteristic of the battery tends to fall. Thus, the amount of the fluorine atoms is preferably 50 atomic % or less, more preferably 40 atomic % or less, particularly preferably 30 atomic % or less.

In order to improve the charge-discharge cycle characteristic of the battery, preferably, the nonaqueous electrolytic solution contains at least one carbonate compound selected from the group consisting of vinylene carbonates, such as (—OCH═CHO—)C═O, (—OCH═C(CH_3)O—) C═O and (—OC(CH_3)═C(CH_3)O—)C═O, and derivatives thereof; cyclic carbonate esters having a vinyl group such as vinylethylene carbonate (—OCH_2—CH(—CH═CH_2)O—) C═O); and fluorine-substituted ethylene carbonates, such as (—OCH_2—CHFO—)C═O and (—OCHF—CHFO—) C═O. The addition amount thereof is preferably 0.1% by weight or more, more preferably 0.5% by weight or more, particularly preferably 2% by weight or more based on the whole weight of the nonaqueous electrolytic solution. When the addition amount thereof is too large, the load characteristic of the battery tends to decrease. Thus, the addition amount is preferably 10% by weight or less, more preferably 5% by weight or less, particularly preferably 3% by weight or less based on the whole weight of the nonaqueous electrolytic solution.

In the present invention, the nonaqueous electrolyte may be a gel-form polymer electrolyte besides the nonaqueous electrolytic solution described above. The gel-form polymer electrolyte corresponds to a product obtained by the gelation of the nonaqueous electrolytic solution with a gelling agent. For the gelation of the nonaqueous electrolytic solution, the following gelling agents may be used: a linear polymer such as polyvinylidene fluoride, polyethylene oxide or polyacrylonitrile, or a copolymer thereof; or a polyfunctional monomer which can be polymerized by irradiation with actinic rays such as ultraviolet rays or electron beams (e.g., an acrylate having 4 or more functionalities such as pentaerythritol tetraacrylate, ditrimethylolpropane tetraacrylate, ethoxylated pentaerythritol tetraacrylate, dipentaerythritol hydroxypentaacrylate, or dipentaerythritol hexaacrylate; or a methacrylate having 4 or more functionalities, which are analogous to the above acrylates. In the case of the monomer, the monomer itself does not cause the gelling of the electrolytic solution, but the polymer formed from the monomer acts as a gelling agent.

When a polyfunctional monomer is used to gel the electrolytic solution as described above, a polymerization initiator may optionally be used. Examples of the polymerization initiator include benzoyls, benzoin alkyl ethers, benzophenones, benzoylphenylphosphine oxides, acetophenones, thioxanthones and anthraquinones. As a sensitizer for the polymerization initiator, an alkylamine or an aminoester may be used.

In the present invention, the nonaqueous electrolyte may be a solid electrolyte besides the nonaqueous electrolytic solution or the gel-form polymer electrolyte. The solid electrolyte may be an inorganic solid electrolyte or an organic solid electrolyte.

The positive electrode according to the present invention may have a structure such that the positive electrode mixture layer containing the positive electrode active material is formed on one or both of the surfaces of an electrode collector.

The positive electrode mixture layer according to the present invention may have a density of 3.5 g/cm^3 or more, more preferably 3.6 g/cm^3 or more, particularly preferably 3.8 g/cm^3 or more. With such a density, the capacity of the battery can be increased. However, when the density of the positive electrode mixture layer is too high, the wettability with the nonaqueous electrolyte, which will be explained later, decreases. Thus, the density is preferably 4.6 g/cm^3 or less, more preferably 4.4 g/cm^3 or less, particularly preferably 4.2 g/cm^3 or less.

Herein, the density of the positive electrode mixture layer may be obtained by the following measuring method: The positive electrode is cut to form a sample piece having a predetermined area, the sample piece is weighed with an electronic balance having a minimum scale of 1 mg, and then the weight of the current collector is subtracted from the weight of the sample piece to calculate the weight of the positive electrode mixture layer. The total thickness of the positive electrode is measured at ten points with a micrometer having a minimum scale of 1 μm. Then, the thickness of the current collector is subtracted from the resultant individual thicknesses, and the thicknesses of the positive electrode mixture layer measured at ten points are averaged. From the averaged thicknesses of the positive electrode mixture layer and the surface area, the volume of the positive electrode mixture layer is calculated. Finally, the weight of the positive electrode mixture layer is divided by the volume thereof to obtain the density of the positive electrode mixture layer.

The positive electrode active material contained in the positive electrode mixture layer comprises a lithium-containing transition metal oxide comprising at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn. The use of the lithium-containing transition metal oxide can improve the charge-discharge cycle characteristics of the battery, since it has good stability, in particular, in the charged state at a high voltage, so that the decay of the compound is prevented when the charge-discharge cycle is repeated. Since the lithium-containing transition metal oxide has good stability, it can improve the storage characteristics and the reliability such as safety of the battery.

The positive electrode active material preferably has a particle size frequency peak in a particle size range larger than a midpoint d_M between d_{10} and d_{90} in a particle size distribution curve, which obtained by a method for measuring an average particle size described below. To obtain a positive electrode active material having such a particle size distribution, preferably, at least two lithium-containing transition metal oxides having different average particle sizes are used. When a lithium-containing transition metal oxide having a larger average particle size and one having a smaller average particle size are used in combination, the particles of the latter infill the gaps among the particles of the former. Thus, the positive electrode mixture layer having a large density as described above can be easily formed.

The "average particle size" of the lithium-containing transition metal oxide(s) used herein means a 50% diameter value (d_{50}), that is, an median diameter, read from an integral fraction curve based on volumes, which is obtained by integrating the volumes of the particles from a smaller particle size measured by a MICROTRAC particle size analyzer (HRA 9320 available from NIKKISO Co., Ltd.). Analogously, d_{10} and d_{90} means a 10% diameter value and a 90% diameter value, respectively.

The mixture of "at least two lithium-containing transition metal oxides having different average particle sizes" preferably has a particle size frequency peak in a particle size range larger than a midpoint d_M between d_{10} and d_{90} in a particle size distribution curve, as described above. Hereinafter, a particle size corresponding to the particle size frequency peak is expressed by "d_p". In a preferred embodiment, the ratio of d_p to d_M (d_p/d_M) is at least 1.05, more preferably at least 1.2, most preferably at least 1.3. Furthermore, the ratio of d_p to d_M is preferably 1.6 or less, more preferably 1.5 or less, most preferably 1.45 or less. In a more preferred embodiment, the lithium-containing transition metal oxide mixture has at least two peaks in the particle size distribution curve. When the lithium-containing transition metal oxides have the same

d_p/d_M of 1.3, the lithium-containing transition metal oxide mixture having at least two peaks in the particle size distribution curve can increase the density of the positive electrode mixture layer by 0.1 g/cm^3 or more. When the particle size distribution curve has two or more peaks, it can be divided into a distribution curve corresponding to particles having a larger particle size and a distribution curve corresponding particles having a smaller particle size by a common peak separation method and then an average particle size (d_{50}) of the respective lithium-containing transition metal oxide and a mixing ratio of the lithium-containing transition metal oxides having the different average particle sizes can be calculated from the particle sizes and the cumulative volumes of the particles.

When the average particle size of the lithium-containing transition metal oxide having the largest average particle size (hereinafter referred to as "positive electrode active material (A)") is represented by A, and that of the lithium-containing transition metal oxide having the smallest average particle size (hereinafter referred to as "positive electrode active material (B)") is expressed by B, the ratio of B to A (i.e., B/A) is preferably from 0.15 to 0.6. When the average particle sizes of the two positive electrode active materials (A) and (B) have such a ratio B/A, the density of the positive electrode mixture layer can be easily increased.

The positive electrode active material (A) preferably has an average particle size of 5 μm or more, more preferably 8 μm or more, particularly preferably 11 μm or more. When the average particle size of the positive electrode active material (A) is too small, the density of the positive electrode mixture layer may hardly be increased. When the average particle size is too large, the battery characteristic tends to decrease. Thus, the average particle size is preferably 25 μm or less, more preferably 20 μm or less, particularly preferably 18 μm or less.

The positive electrode active material (B) preferably has an average particle size of 10 μm or less, more preferably 7 μm or less, particularly preferably 5 μm or less. When the average particle size of the positive electrode active material (B) is too large, the positive electrode active material (B) does not easily fill the gaps between the particles of the lithium-containing transition metal oxide having a relatively large particle size in the positive electrode mixture layer, so that the density of this layer may hardly be increased. When the average particle size is too small, the volume of voids among the small particles increases so that the density of the positive electrode mixture layer may not be increased. Thus, the average particle size of the positive electrode active material (B) is preferably 2 μm or more, more preferably 3 μm or more, particularly preferably 4 μm or more.

The positive electrode active materials according to the present invention may contain only two lithium-containing transition metal oxides having different average particle sizes, for example, the positive electrode active materials (A) and (B) as descried above, while the positive electrode active materials may contain three or more, for example, three, four or five lithium-containing transition metal oxides having different average particle sizes, for example, the positive electrode active materials (A) and (B) and one or more lithium-containing transition metal oxides having an average particle size between those of the positive electrode active materials (A) and (B).

The content of the positive electrode active material (B) having the smallest average particle size in the lithium-containing transition metal oxides contained in the positive electrode is preferably 5% by weight or more, more preferably 10% by weight or more, particularly preferably 20% by weight or more. When the positive electrode active material (B) is contained in an amount of the above-mentioned range, the gaps between the particles of the lithium-containing transition metal oxide having a relatively large particle size are easily filled therewith so that the density of the positive electrode mixture layer is increased. When the content of the positive electrode active material (B) is too large, the density of the positive electrode mixture layer is hardly be increased. Thus, the content of the positive electrode active material (B) is preferably 60% by weight or less, more preferably 50% by weight or less, particularly preferably 40% by weight or less.

Accordingly, when the lithium-containing transition metal oxides contained in the positive electrode are only the positive electrode active materials (A) and (B), the content of the positive electrode active material (A) is preferably 40% by weight or more, more preferably 50% by weight or more, particularly preferably 60% by weight or more of the oxides, while it is preferably 95% by weight or less, more preferably 90% by weight or less, particularly preferably 80% by weight or less.

Among the lithium-containing transition metal oxides contained in the positive electrode, the positive electrode active material (B) having the smallest average particle size has the above-mentioned average particle size. Such a lithium-containing transition metal oxide having a relatively small particle size has low stability, for example, in a state that the battery is charged at a high voltage, so that the oxide may damage the reliability including the safety of the battery.

When two or more lithium-containing transition metal oxides having the different average particle sizes are used, a lithium-containing transition metal oxide comprising at least one metal element M^2 selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn is preferably used at least as the positive electrode active material (B) which is the lithium-containing transition metal oxide having the smallest average particle size, since the lithium-containing transition metal oxide comprising the metal element M^2 has the improved stability and thus surely increases the charge-discharge cycle characteristics of the battery and also improves the storage characteristics and the reliability including the safety of the battery.

When two or more lithium-containing transition metal oxides having the different average particle sizes are used, the positive electrode active material (B) having the smallest average particle size preferably comprises the metal element M^2. More preferably, the lithium-containing transition metal oxide other than the positive electrode active material (B), for example, the positive electrode active material (A) having the largest average particle size or the lithium-containing transition metal oxide having the average particle size between those of the positive electrode active materials (A) and (B), comprises the metal element M^2. When the lithium-containing transition metal oxide other than the positive electrode active material (B) comprises the metal element M^2, the reliability including the safety of the battery can be further improved, since such a lithium-containing transition metal oxide has the improved stability, in particular, the stability in a state that the battery is charged at a high voltage as described above.

The positive electrode active material (B) is preferably a lithium-containing transition metal oxide represented by the following formula (1):

$$Li_xM^1_yM^2_zM^3_vO_2 \quad (1)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, M^3 represents an element other than Li, M^1 and M^2, and x, y, z and v are numbers satisfying the following equations respectively: $0.97 \leq x \leq 1.02$, $0.8 \leq y < 1.02$, $0.002 \leq z \leq 0.05$, and $0 \leq v \leq 0.05$. z is preferably at least 0.004, more preferably at least 0.006, while it is preferably less than 0.02, more preferably less than 0.01. When z is too small, the charge-discharge characteristics or the safety of the battery may not sufficiently be improved. When z is too large, the electric characteristics of the battery tend to deteriorate.

Each of the lithium-containing transition metal oxides other than the positive electrode active material (B) such as the positive electrode active material (A) is preferably a lithium-containing transition metal oxide represented by the following formula (2):

$$Li_aM^1_bM^2_cM^3_dO_2 \quad (2)$$

wherein M^1, M^2 and M^3 are the same as defined in the formula (1), and a, b, c and d are numbers satisfying the following equations respectively: $0.97 \leq a < 1.02$, $0.8 \leq b < 1.02$, $0 \leq c \leq 0.02$, and $0 \leq d \leq 0.02$.

M^1, M^2 and M^3 are selected from the same elements as in the formula (1), but the elements selected or the constituting element ratios selected in the individual positive electrode active materials having different average particle sizes may differ from each other. For example, in the positive electrode active material (B), Mg, Ti and Al may be selected, while in the positive electrode active material (A), Mg and Ti may be selected. As explained in this example, however, among the elements M^2, preferably at least one common element is selected, more preferably at least two common elements are selected, and particularly preferably at least three common elements are selected.

In the case of the positive electrode active material (A), "c" is preferably 0.0002 or more, more preferably 0.001 or more, and it is preferably less than 0.005, more preferably less than 0.0025, and "d" is preferably 0.0002 or more, more preferably 0.001 or more and it is preferably less than 0.005, more preferably less than 0.0025 for the following reason: the particle size of the positive electrode active material (A) is relatively large; thus, when the amount of M^2 and the like added to the material (A) is relatively small, advantageous effects can be attained; but when the amount is too large, the electrical characteristics of the battery tends to decrease.

The transition metal element in the lithium-containing transition metal oxide is preferably mainly Co and/or Ni. For example, the total amount of Co and Ni is preferably 50% by mole or more based on all the transition metal elements contained in the lithium-containing transition metal oxides.

Preferably, the proportion of Co in the lithium-containing transition metal oxide is higher, since the density of the positive electrode mixture layer can be made higher. In the formulae (1) and (2), the proportion of Co in the transition metal element M^1 is preferably 30% by mole or more, more preferably 65% by mole or more, particularly preferably 95% by mole or more.

The values of x in the formula (1) and a in the formula (2) may vary as the battery is charged or discharged. Nevertheless, when the battery is an as-produced one, x and a are each preferably 0.97, more preferably 0.98 or more, particularly preferably 0.99 or more, while x and a are each preferably less than 1.02, more preferably 1.01 or less, particularly preferably 1.00 or less.

The values of y in the formula (1) and b in the formula (2) are each preferably 0.98 or more, more preferably 0.98 or more, particularly preferably 0.99 or more, and they are each preferably less than 1.02, more preferably less than 1.01, particularly preferably less than 1.0.

Each of the positive electrode active material (B) represented by the formula (1), and the lithium-containing transition metal oxides other than the positive electrode active material (B) which are represented by the formula (2) preferably contains Mg as the element M^2, since the safety of the battery is more effectively improved. In addition, each of them comprises Mg and also at least one metal element M^2 selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn. In this case, the stability of those lithium-containing transition metal oxides is further improved in a state that the battery is charged at a high voltage.

In the positive electrode active material (B), the content of Mg is preferably at least 0.1% by mole, more preferably at least 0.15% by mole, particularly preferably at least 0.2% by mole, based on the amount of the metal element M^1, from the view point of more effectively attaining the effects of Mg.

When the positive electrode active material (B) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.05% by mole, more preferably at least 0.08% by mole, particularly preferably at least 0.1% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (B) contains Al and/or Sn, the total content thereof is preferably 0.1% by mole or more, more preferably 0.15% by mole or more, particularly preferably 0.2% by mole or more based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements.

When the content of Mg is too large in the positive electrode active material (B), the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 2% by mole, more preferably less than 1% by mole, particularly preferably 0.5% by mole, most preferably 0.3% by mole.

When the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (B), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.5% by mole, more preferably less than 0.25% by mole, particularly preferably less than 0.15% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 1% by mole, more preferably less than 0.5% by mole, particularly preferably less than 0.3% by mole based on the content of M^1.

In the positive electrode active material (A), the content of Mg is preferably at least 0.01% by mole, more preferably at least 0.05% by mole, particularly preferably at least 0.07% by mole, based on the amount of the metal element M^1, from the view point of more effectively attaining the effects of Mg.

When the positive electrode active material (A) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.005% by mole, more preferably at least 0.008% by mole, particularly preferably at least 0.01% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (A) contains Al and/or Sn, the total content thereof is preferably 0.01% by mole or more, more preferably 0.05% by mole or more, particularly preferably 0.07% by mole or more based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements.

Also, when the content of Mg is too large in the positive electrode active material (A), the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 0.5% by mole, more preferably less than 0.2% by mole, particularly preferably 0.1% by mole.

Also, when the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (A), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.3% by mole, more preferably less than 0.1% by mole, particularly preferably less than 0.05% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 0.5% by mole, more preferably less than 0.2% by mole, particularly preferably less than 0.1% by mole based on the content of M^1.

Furthermore, when the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B) is used, the content of Mg in the other metal oxide is preferably at least 0.01% by mole, more preferably at least 0.05% by mole, particularly preferably at least 0.07% by mole, based on the amount of the metal element M^1, from the view point of more effectively attaining the effects of Mg.

When the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.005% by mole, more preferably at least 0.008% by mole, particularly preferably at least 0.01% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (A) contains Al and/or Sn, the total content thereof is preferably 0.01% by mole or more, more preferably 0.05% by mole or more, particularly preferably 0.07% by mole or more based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements.

However, again in the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B), when the content of Mg is too large, the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 2% by mole, more preferably less than 1% by mole, particularly preferably 0.5% by mole, most preferably 0.3% by mole, each based on the content of M^1.

Again, in the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B), when the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (A), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.5% by mole, more preferably less than 0.25% by mole, particularly preferably less than 0.15% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 1% by mole, more preferably less than 0.5% by mole, particularly preferably less than 0.3% by mole based on the content of M^1.

A method for including the metal element M^2 in the positive electrode active material (B) or the other lithium-containing transition metal oxide(s) is not particularly limited. For example, the element M^2 may be present on the particles of the metal oxide, may be evenly present as a solid solution inside the metal oxides, or may be unevenly present inside the metal oxides with having a density distribution. Furthermore, the element M^2 may form a compound which in turn forms a layer on the particle surfaces. Preferably, the element M^2 is evenly present as a solid solution.

In the formulae (1) and (2) representing the positive electrode active material (B) and the other lithium-containing transition metal oxide(s), respectively, the element M^3 is an element other than Li, M^1 and M^2. The positive electrode active material (B) and the other lithium-containing transition metal oxides may each contain the M^3 in an amount such that the advantageous effects of the present invention are not impaired, or they may contain no M^3.

Examples of the element M^3 include alkali metals other than Li (e.g., Na, K and Rb), alkaline earth metals other than Mg (e.g., Be, Ca, Sr and Ba), Group IIIa metals (e.g., Sc, Y, La), Group IVa metals other than Ti and Zr (e.g., Hf), Group Va metals other than Nb (e.g., V and Ta), Group VIa metals (e.g., Cr, Mo and W), Group VIIb metals other than Mn (e.g., Tc and Re), Group VIII metals other than Co and Ni (e.g., Fe, Ru, and Rh), Group Ib metals (e.g., Cu, Ag and Au), Group IIIb metals other than Zn and Al (e.g., B, Ca and In), Group IVb metals other than Sn and Pb (e.g., Si), P and Bi.

The metal element M^2 contributes to an improvement in the stability of the lithium-containing transition metal oxides. However, when the content thereof is too large, a function of storing and releasing Li ions is impaired so that the battery characteristics may be decreased. Since the positive electrode active material (B) having the smallest average particle size has the particularly small particle size and decreased stability, it is preferable that the content of the element M^2, which is a stabilizing element, is somewhat high. In addition, since the positive electrode active material (B) has the small particle size and in turn the large surface area, it exhibits a high activity. Thus, the presence of the element M^2 in the material (B) has less influence on the function of storing and releasing Li ions.

In contrast, the lithium-containing transition metal oxides having relatively large particle sizes, that is, the lithium-containing transition metal oxides other than the positive electrode active material (B), have better stability than the positive electrode active material (B). Therefore, the former metal oxides have less necessity to contain the element M^2 than the positive electrode active material (B). Furthermore, their function of storing and releasing Li ions is easily impaired by the presence of the element M^2 since the materials have the smaller surface area and the lower activity than the positive electrode active material (B).

Accordingly, it is preferable that the content of the metal element M^2 in the positive electrode active material (B) is larger than that in the lithium-containing transition metal oxide(s) other than the positive electrode active material (B).

That is, z in the formula (1) is preferably larger than c in the formula (2) ($z>c$). In particular, z is at least 1.5 times, more preferably at least 2 times, particularly preferably at least 3 times larger than c. When z is much larger than c, the load characteristics of the battery tend to decrease. Thus, z is preferably less than 5 times as large as c^1, more preferably less than 4 times as large as c, particularly preferably less than 3.5 times as large as c.

When the three or more lithium-containing transition metal oxides having the different average particle sizes are contained in the positive electrode, there is no especial limitation on the relationship of the element M^2 content between the positive electrode active material (A) having the largest average particle size and the other lithium-containing transition metal oxides. Thus, the former may contain a larger amount of the element M^2 than the latter, and vise versa, or the element M^2 contents in the former and the latter may be the same. In a more preferable embodiment, a metal oxide having a smaller average particle size contains a larger amount of the element M^2. In particular, when the three lithium-containing transition metal oxides having different average particle sizes are used, the element M^2 content in the positive electrode active material (B) having the smallest average particle size is largest, that in lithium-containing transition metal oxide having the average particle size between those of the active materials (A) and (B) is second largest, and that in the positive electrode active material (A) having the largest average particle size is smallest.

When two or more lithium-containing transition metal oxides are used, the oxides having different average particle sizes may have the same composition of elements, or different compositions of elements between them. When the lithium-containing transition metal oxides according to the present invention are the above-mentioned positive electrode active materials (A) and (B), the following combination may be used: a combination of the positive electrode active material (A) consisting of $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$, and the positive electrode active material (B) consisting of $LiCo_{0.334}Ni_{0.33}Mn_{0.33}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$.

The positive electrode active material, namely, the lithium-containing transition metal oxide used according to the present invention is formed through a certain synthesizing process and a certain battery producing process. For example, for the preparation of lithium-containing transition metal oxides which contain Co as the transition metal element M^1 and have different average particle sizes, firstly, a solution of an alkali such as NaOH is dropwise added to an acidic aqueous solution containing Co to precipitate $Co(OH)_2$. In order to homogeneously precipitate $Co(OH)_2$, Co may be coprecipitated with a different element, and then the coprecipitated material is calcined to obtain CO_3O_4. The particle size of the precipitates can be adjusted by controlling the period for forming the precipitates. The particle size of CO_3O_4 after calcination is also controlled by the particle size of the precipitate at this time.

When the positive electrode active material is synthesized, conditions such as a mixing condition, calcination temperature, calcination atmosphere, calcination time, starting materials, and also battery fabrication conditions are suitably selected. With regard to the mixing condition in the synthesis of the positive electrode active material, preferably, for example, ethanol or water is added to the powdery starting materials, and then mixed in a planetary ball mill for 0.5 hour or longer. More preferably, ethanol and water are mixed at a volume ratio of 50:50, and the mixture is agitated in a planetary ball mill for 20 hours or longer. Through this mixing step, the powdery starting materials are sufficiently comminuted and mixed to prepare a homogeneous dispersion. The dispersion is dried with a spray drier or the like while keeping homogeneity. The calcination temperature is preferably from 750 to 1,050° C., more preferably from 950 to 1,030° C. The calcination atmosphere is preferably an air. The calcination time is preferably from 10 to 60 hours, more preferably from 20 to 40 hours.

In the preparation of the positive electrode active material, Li_2CO_3 is preferably used as a lithium source. As the sources of other metal such as Mg, Ti, Ge, Zr, Nb, Al and Sn, preferred are nitrates or hydroxides of these metals, or oxides thereof having a particle size of 1 μm or less. It is preferable to use the coprecipitate of the hydroxides since the different elements are uniformly distributed in the active material.

The contents of the metal elements in the positive electrode active materials are measured by the ICP atomic emission spectroscopy or the like. The content of lithium can be measured by an atomic absorption analysis. In the state of a positive electrode, it is difficult to separately measure the contents of the metal elements in each of the positive electrode active material having a larger particle size and one having a smaller particle size. Therefore, the contents or content ratios of the metal elements of the positive electrode active material having different particle sizes may be measured with an electron prove microanalyzer using a mixture of positive electrode active materials having a known mixing ratio as a standard sample. Alternatively, the positive electrode is treated with a suitable solvent such as N-methyl-2-pyrrolidone (NMP) to separate the active material particles from the positive electrode and settled out in the solvent, followed by washing and drying. Then, the particle size distribution of the recovered particles is measured and the peak-separation of the particle size distribution curve is carried out. When the inclusion of two or more particles having different particle sized is confirmed, the particles are classified into a larger one and a smaller one, and the contents of the metal elements in each particle group are measured by the ICP atomic emission spectroscopy.

Herein, the contents of the metal elements in the positive electrode active material may be measured by the ICP atomic emission spectroscopy as follows: about 5 g of the active material is precisely weighed and charged in a 200 ml beaker. Then, 100 ml of aqua regia is added, and the mixture is concentrated by heating to a liquid volume of about 20 to 25 ml. After cooling, the mixture is filtrated through a quantitative filter paper (No. 5B available from Advantec MFS, Inc.) to separate the solids. The filtrate and washing liquid are charged in a 100 ml measuring flask and diluted to a specific volume. Then, the contents of the metal elements in the solution are measured with a sequential type ICP analyzer (IPIS 1000 manufactured by Nippon Jarrel-Ash Co., Ltd.).

When the content (I) of at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn in the transition metal oxide having the smallest average particle size and a content (II) of the same metal element as one with which the content (I) in the lithium-containing transition metal oxide other than one having the smallest average particle size are measured by the ICP atomic emission spectroscopy described above, the ratio of the content (I) to the content (II) corresponds to the relationship between z in the formula (I) and c in the formula (2). The ratio of the content (I) to the content (II) is preferably at least 1.5, more preferably at least 2, particularly preferably at least 3. Since the load characteristics of the battery tend to decrease when z is much larger than c, the ratio of the content (I) to the content (II) is preferably less than 5, more preferably less than 4, particularly preferably less than 3.5.

The positive electrode used in the present invention is formed by, for example, a method described below. Firstly, if necessary, an electric conductive aid (e.g., graphite, carbon black, acetylene black, etc.) is added to the lithium-containing transition metal oxide used as a positive electrode active material. Furthermore, to the mixture, a binder (e.g., polyvinylidene fluoride, poly tetrafluoroethylene, etc.) is added to prepare a positive electrode mixture. A solvent is used to formulate this positive electrode mixture in the form of a paste. The binder may be mixed with the positive electrode active material and the like after the binder is dissolved in a solvent. In this way, the paste containing the positive electrode mixture is prepared. The resultant paste is applied to a positive electrode current collector made of an aluminum foil or the like, and then dried to form a positive electrode mixture layer. If necessary, the layer is pressed to obtain a positive electrode. When the positive electrode active material comprises two or more lithium-containing transition metal oxides having the different average particle sizes, for example, the positive electrode active materials (A) and (B), they are mixed at a predetermined ratio, and then the electric conductive aid and the binder are added to the mixture to prepare a positive electrode mixture, which is used in the subsequent steps. However, the method for producing the positive electrode is not limited to the above-mentioned method, and may be any other method.

The thickness of the positive electrode mixture layer is preferably from 30 to 200 μm, and the thickness of the current collector used in the positive electrode is preferably from 8 to 20 μm.

In the positive electrode mixture layer, the content of the lithium-containing transition metal oxides as the active materials is preferably 96% by weight or more, more preferably 97% by weight or more, particularly preferably 97.5% by weight or more, while it is preferably 99% by weight or less, more preferably 98% by weight or less. The content of the binder in the positive electrode mixture layer is preferably 1% by weight or more, more preferably 1.3% by weight or more, particularly preferably 1.5% by weight or more, while it is preferably 4% by weight or less, more preferably 3% by weight or less, particularly preferably 2% by weight or less. The content of the electric conductive aid in the positive electrode mixture layer is preferably 1% by weight or more, more preferably 1.1% by weight or more, particularly preferably 1.2% by weight or more, while it is preferably 3% by weight or less, more preferably 2% by weight or less, particularly preferably 1.5% by weight or less.

When the content of the active material in the positive electrode mixture layer is too small, the capacity cannot be increased and also the density of the positive electrode mixture layer cannot be increased. When this content is too large, the resistance may increase or the formability of the positive electrode may be impaired. When the binder content in the positive electrode mixture layer is too large, the capacity may hardly be increased. When this content is too small, the adhesion of the layer to the current collector decreases so that the powder may drop off from the electrode. Thus, the above-mentioned preferable ranges are desirable. Furthermore, when the content of the electric conductive aid in the positive electrode mixture layer is too large, the density of the positive electrode mixture layer may not be made sufficiently high so that the capacity may hardly be increased. When this content is too small, the sufficient electric conduction through the positive electrode mixture layer is not attained so that the charge-discharge cycle characteristic or the load characteristic of the battery may deteriorated.

It is essential for the nonaqueous secondary battery of the present invention to have the nonaqueous electrolyte and the positive electrode, which are explained above, and thus there is no specific limitation on other elements or structure of the battery. The battery of the present invention may adopt various elements and structures, which are commonly adopted in the conventional nonaqueous secondary batteries in the state of art.

The negative electrode active material in the negative electrode may be any material that can be doped and de-doped with Li ions. Examples thereof are carbonaceous materials such as graphite, pyrolytic carbons, cokes, glassy carbons, burned bodies of organic polymers, mesocarbon microbeads, carbon fibers and activated carbon. In addition, the following materials can also be used as the negative electrode active material: alloys of Si, Sn, In or the like, oxides of Si, Sn or the like that can be charged and discharged at a low voltage near a voltage at which Li can be charged and discharged, and nitrides of Li and Co such as $Li_{2.6}Co_{0.4}N$. Graphite can be partially substituted with a metal, a metal oxide or the like that can be alloyed with Li. When graphite is used as the negative electrode active material, the voltage when the battery is fully charged can be regarded as about 0.1 V with reference to the potential of lithium, and therefore the voltage of the positive electrode can be conveniently calculated as a voltage obtained by adding 0.1 V to the battery voltage. Consequently, the charge voltage of the positive electrode is easily controlled.

Preferably, graphite has such a form in that a lattice spacing d_{002} of the (002) planes is 0.338 nm or less, since the negative electrode or a negative electrode mixture layer, which will be explained later, has a higher density as the crystallinity is higher. However, when the lattice spacing d_{002} is too large, the high density negative electrode may decrease the discharge characteristic or the load characteristic of the battery. Thus, the lattice spacing d_{002} is preferably 0.335 nm or more, more preferably 0.3355 nm or more.

The crystal size of the graphite in the c axis direction (Lc) is preferably 70 nm or more, more preferably 80 nm or more, particularly preferably 90 nm or more. As the Lc is larger, the charging curve becomes flat so that the voltage of the positive electrode is easily controlled and also the capacity can be made large. When the Lc is too large, the battery capacity tends to decrease with the high-density negative electrode. Thus, the Lc is preferably less than 200 nm.

Furthermore, the specific surface area of the graphite is preferably 0.5 m^2/g or more, more preferably 1 m^2/g or more, particularly preferably 2 m^2/g or more, while it is preferably 6 m^2/g or less, more preferably 5 m^2/g or less. Unless the specific surface area of the graphite is somewhat large, the characteristics tend to decrease. When the specific surface area is too large, the graphite easily reacts with the electrolyte and such a reaction may have influences on the properties of the battery.

The graphite used in the negative electrode is preferably made of natural graphite. More preferred is a mixture of two or more graphite materials having different surface crystallinity to achieve the high density of the negative electrode. Since natural graphite is inexpensive and achieves a high capacity, the negative electrode with a high cost performance can be produced. Usually, when natural graphite is used, the battery capacity is easily decreased as the density of the negative electrode is increased. However, the decrease in the battery capacity can be suppressed by mixing the natural graphite with a graphite having a reduced surface crystallinity by a surface treatment.

The surface crystallinity of specific graphite can be determined by the Raman spectrum analysis. When the R value of the Raman spectrum ($R=I_{1350}/I_{1580}$, that is, the ratio of the Raman intensity around 1350 cm^{-1} to that around 1580 cm^{-1}) is 0.01 or more, where the Raman spectrum is measured with graphite which has been excited with an argon laser having a wavelength of 514.5 nm, the surface crystallinity of the specific graphite is slightly lower than that of natural graphite. Thus, with the graphite having a surface crystallinity decreased by the surface treatment, the R value is preferably 0.01 or more, more preferably 0.1 or more, while it is preferably 0.5 or less, more preferably 0.3 or less. The content of the graphite having a surface crystallinity decreased by surface treatment is preferably 100% by weight of the whole graphite in order to increase the density of the negative electrode. However, in order to prevent the decrease of the battery capacity, the content of such graphite is preferably 50% by weight or more, more preferably 70% by weight or more, particularly preferably 85% by weight or more of the whole graphite.

When the average particle size of the graphite is too small, an irreversible capacity increases. Thus, the average particle size of the graphite is preferably 5 μm or more, more preferably 12 μm or more, particularly preferably 18 μm or more. From the viewpoint of the increase of the capacity of the negative electrode, the average particle size of the graphite is 30 μm or less, more preferably 25 μm or less, particularly preferably 20 μm or less.

The negative electrode may be produced by the following method, for example: The negative electrode active material and an optional a binder and/or other additives are mixed to prepare a negative electrode mixture, and the mixture is dispersed in a solvent to prepare a paste. Preferably, the binder is dissolved in a solvent prior to mixing with the negative electrode active material, and then mixed with the negative electrode active material and so on. The paste containing the negative electrode mixture is applied to a negative electrode current collector made of a copper foil or the like, and then dried to form a negative electrode mixture layer. The layer is pressed to obtain a negative electrode. However, the method for producing the negative electrode is not limited to the above-mentioned method, and may be any other method.

The density of the negative electrode mixture layer after pressing is preferably 1.70 g/cm^3 or more, more preferably 1.75 g/cm^3 or more. Based on the theoretical density of graphite, the upper limit of the density of the negative electrode mixture layer formed using graphite is 2.1 to 2.2 g/cm^3. The density of the negative electrode mixture layer is preferably 2.0 g/cm^3 or less, more preferably 1.9 g/cm^3 or less from the viewpoint of the affinity with the nonaqueous electrolyte. It is preferable to press the negative electrode plural times since the negative electrode can be uniformly pressed.

The binder used in the negative electrode is not particularly limited. For the increase of the content of the active material to increase the capacity, the amount of the binder is preferably made as small as possible. To this end, the binder is preferably a mixture of an aqueous resin which can be dissolved or dispersed, and a rubbery polymer, since the use of only a small amount of the aqueous resin can contribute to the dispersion of the graphite and thus prevents the delamination of the negative electrode mixture layer from the current collector caused by the expansion and contraction of the electrode in the charge-discharge cycles.

Examples of the aqueous resins include cellulose resins such as carboxymethylcellulose, and hydroxypropylcellulose, and polyvinylpyrrolidone, polyepichlorohydrin, polyvinylpyridine, polyvinyl alcohol, polyether resins such as polyethylene oxide and polyethylene glycol, etc. Examples of the rubbery polymers include latex, butyl rubber, fluororubber, styrene-butadiene rubber, nitrile-butadiene copolymer rubber, ethylene-propylene-diene copolymer (EPDM), polybutadiene, etc. From the viewpoint of the dispersibility of the graphite particles and the prevention of delamination of the layer, it is preferable to use a cellulose ether compound such as carboxymethylcellulose together with a butadiene copolymer rubber such as a styrene-butadiene rubber. It is particularly preferable to use carboxymethylcellulose together with a butadiene copolymer rubber such as a styrene-butadiene copolymer rubber or a nitrile-butadiene-copolymer rubber. The cellulose ether compound such as carboxymethylcellulose mainly has a thickening effect on the paste containing the negative electrode mixture, while the rubbery polymer such as the styrene-butadiene copolymer rubber has a binding effect on the negative electrode mixture. When the cellulose ether compound such as carboxymethylcellulose and the rubbery polymer such as the styrene-butadiene copolymer rubber are used in combination, the weight of the former to the latter is preferably from 1:1 to 1:15.

The thickness of the negative electrode mixture layer is preferably from 40 to 200 μm. The thickness of the current collector used in the negative electrode is preferably from 5 to 30 μm.

In the negative electrode mixture layer, the content of the binder or binders is preferably 1.5% by weight or more, more preferably 1.8% by weight or more, particularly preferably 2.0% by weight or more of the layer, while it is preferably less than 5% by weight, less than 3% by weight, less than 2.5% by weight. When the amount of the binder in the negative electrode mixture layer is too large, the discharge capacity of the battery may decrease. When the amount is too small, the adhesion between the particles decreases. The content of the negative electrode active material in the negative electrode mixture layer is preferably more than 95% by weight and 98.5% by weight or less.

In the present invention, a separator used in the present invention preferably has a thickness of 5 μm or more, more preferably 10 μm or more, particularly preferably 12 μm or more, while it is preferably less than 25 μm, more preferably less than 20 μm, particularly preferably less than 18 μm, from the viewpoint of imparting the directionality of the tensile strength to the separator, keeping good insulating properties and reducing the thermal shrinkage of the separator. The gas permeability of the separator is preferably 500 second/100-mL or less, more preferably 300 second/100-mL or less, particularly preferably 120 second/100-mL or less. As the gas permeability of the separator is smaller, the load characteristic is made better but an inside short-circuit is more easily caused. Thus, the gas permeability is preferably 50 second/100-mL or more. Here, a gas permeability is measured according to JIS P8117. As the thermal shrinkage factor of the separator in the transverse direction (TD) is smaller, an inside short-circuit is less easily caused when the temperature of the battery rises. Thus, the thermal shrinkage factor in TD of the separator is as small as possible. The thermal shrinkage factor in TD is preferably 10% or less, more preferably 5% or less. In order to restrain the thermal shrinkage of the separator, it is preferable to thermally treat the separator in advance at a temperature of about 100 to 125° C. The separator having such a thermal shrinkage factor is preferably combined with the positive electrode materials according to the present invention to fabricate a battery, since the behaviors of the battery at high temperature become stable.

The thermal shrinkage factor in TD of the separator means the shrinkage factor of a portion thereof that most largely shrinks in TD when the separator having a size of 30 mm square is allowed to stand at 105° C. for 8 hours.

With regard to the strength of the separator, a tensile strength in the machine direction (MD) is preferably 6.8×10^7 N/m^2 or more, more preferably 9.8×10^7 N/m or more. The tensile strength in TD is preferably smaller than that in MD. The ratio of the tensile strength in TD to that in MD (tensile strength in TD/tensile strength in MD) is preferably 0.95 or less, more preferably 0.9 or less, while it is preferably 0.1 or more. The transverse direction means a direction perpendicular to the direction in which the film resin for the production of the separator is wound up, that is, the machine direction.

The puncture strength of the separator is preferably 2.0 N or more, more preferably 2.5 N or more. As this value is higher, the battery is less easily short-circuited. Usually, however, the upper limit thereof is substantially determined by the material of the separator. In the case of a separator made of polyethylene, the upper limit of the puncture strength is about 10 N. Here, a puncture strength is measured by cutting a sample piece of 50 mm×50 mm from a separator, clamping the sample piece with jigs at the edges of 5 mm, puncturing the sample piece with a needle having a tip end with a radius of 0.5 mm at a rate of 2 mm/sec., and measuring a maximum load before the puncture of the sample piece as a puncture strength.

When a conventional nonaqueous secondary battery is charged at a high positive electrode voltage of 4.35 V or higher with reference to the potential of lithium and is discharged to a final voltage higher than 3.2 V, the crystalline structure of the positive electrode active material decays to decrease the capacity or to induce heating of the battery due to the deterioration of the thermal stability. Thus, the battery may not be practically used. When a positive electrode active material to which a different element such as Mg or Ti is added is used, the decrease of the safety or of the capacity over charge-discharge cycles can be suppressed, but the degree of suppression is not sufficient. Moreover, the filling of the positive electrode is insufficient so that the battery easily expands.

In contrast, the battery of the present invention having the structure explained above is a nonaqueous secondary battery which improves the capacity, the charge-discharge cycle characteristic, the safety and the suppression of expansion of the battery (storage characteristics). These advantageous effects can be attained at a usual charging volt (a battery voltage of 4.2 V). Furthermore, when the positive electrode is charged up to a high voltage of 4.35 V with reference to the potential of lithium (i.e., a battery voltage of 4.25 V) and then the discharge of the battery is terminated at a high voltage, that is, a battery voltage of 3.2 V or higher, the crystalline structures of the positive electrode active materials are very stable so that the decrease of the capacity or thermal stability is prevented.

Moreover, the positive electrode active material of any conventional nonaqueous secondary battery generates a low average voltage. Therefore, when a charge-discharge cycle test is repeated under a condition that the discharge final voltage of a unit cell is 4.35 V or higher with reference to the potential of lithium, the positive electrode is doped or dedoped with a large amount of Li ions. This situation is analogous to a case where the battery is subjected to a charge-discharge cycle test under an overcharge condition. Under such a severe condition, any conventional positive electrode active material cannot maintain its crystalline structure so as to cause disadvantages such that the thermal stability declines or the charge-discharge cycle life is shortened. To the contrary, the use of the positive electrode active material according to the battery of the present invention can overcome such disadvantages of the conventional positive electrode active material. Thus, the present invention provides a nonaqueous secondary battery which can be reversibly charged and discharged even at a high voltage, such as a voltage of 4.35 to 4.6 V with reference to the potential of lithium, when the battery is fully charged.

Here, the "fully charged" means that a battery is charged by charging it at a constant current of 0.2 C to a specific voltage and then charging it at a constant voltage at the specific voltage until the total charging time of the constant current charging and the constant voltage charging reaches 8 hours. When the battery of the present invention has a graphite negative electrode (i.e. a negative electrode containing graphite as a negative electrode active material) which has a voltage of 0.1 V with reference to the lithium potential when the battery is fully charged, the charging of the battery to a battery voltage of 4.45 V or higher is assumed as a charging of the battery in which the voltage of the positive electrode is substantially 4.35 V or higher.

The nonaqueous secondary battery of the present invention has characteristics including a high voltage, a high capacity and a high safety. By making use of such characteristics, the nonaqueous secondary battery of the present invention can be used as a power source of a notebook personal computer, a stylus-operated personal computer, a pocket personal computer, a notebook word processor, a pocket word processor, an electronic book player, a cellular phone, a codeless handset, a pager, a portable terminal, a portable copier, an electrical notebook, an electronic calculator, a liquid crystal television set, an electric shaver, an electric power tool, an electronic translating machine, an automobile telephone, a transceiver, a voice input device, a memory card, a backup power source, a tape recorder, a radio, a headphone stereo, a handy printer, a handy cleaner, a portable CD player, a MD player, a portable digital audio player, a video movie, a navigation system, a refrigerator, an air conditioner, a television, a stereo, a water heater, a microwave oven, a dishwasher, a washing machine, a drying machine, a game equipment, a lighting equipment, a toy, a sensor equipment, a load conditioner, a medical machine, an automobile, an electric vehicle, a golf cart, an electrically-powered cart, a security system, a power storing system, or the like. The battery can be used not only for the consumer applications but also for aerospace applications. The capacity-increasing effect of the present invention is enhanced, in particular, in small-sized portable devices. Thus, the battery of the present invention is used in a portable device desirably having a weight of 3 kg or less, more desirably 1 kg or less. The lower limit of the weight of the portable device is not particularly limited. However, the lower limit is desirably a value equal to the weight of the battery, for example, 10 g or more in order to attain the advantageous effects to some degree.

EXAMPLES

The present invention will be described in detail with reference to the following Examples; however, the Examples do not limit the scope of the present invention. Thus, modifications of the examples are encompassed by the scope of the present invention as long as the modifications do not depart from the subject matter of the present invention, which has been described above or will be described hereinafter.

Example 1

Production of Positive Electrode

The lithium-containing positive electrode materials, $LiCu_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm) as a positive electrode active material (A), and $LiCu_{0.994}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm) as a positive electrode active material (B) at a weight ratio of 65:35 were mixed. Then, 97.3 parts by weight of the mixture and 1.5 parts by weight of a carbonaceous material as an electric conductive aid were charged in a volumetric feeder as a device for supplying powder. An amount of a 10 wt. % solution of polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) to be supplied to the feeder was adjusted to control a solid content in the mixture constantly at 94% by weight during kneading. While the amount of the mixed materials supplied in a unit time was controlled to a predetermined amount, the materials were supplied in a biaxial kneading extruder and then kneaded. In this way, a paste containing the positive electrode mixture was prepared.

Separately, the positive electrode active materials (A) and (B) were dissolved in aqua regia and the ratio of the elements contained in the materials (A) and (B) was measured by the ICP atomic emission spectroscopy, the results of which confirmed that they had the above elementary compositions.

The resultant paste was charged in a planetary mixer, and then a 10 wt. % solution of PVDF in NMP, and NMP were added to dilute the paste, thereby adjusting the viscosity of the paste at a level sufficient for application. This diluted paste containing the positive electrode active material mixture was passed through a 70-mesh net to remove large substances. Thereafter, the paste was uniformly applied to both surfaces of a positive electrode current collector made of an aluminum foil with a thickness of 15 μm, and then dried to form film-form positive electrode mixture layers. In the dried positive electrode mixture layers, the weight ratio of the positive electrode active material/the electric conduction aiding agent/PVDF was 97.3:1.5:1.2. Thereafter, the resultant sheet was pressed and cut out in a predetermined size. To the cut piece, a lead member made of aluminum was welded to form a sheet-form positive electrode. The density of the pressed positive electrode mixture layers (the density of the positive electrode) was 3.86 g/cm^3. The thickness of the positive electrode mixture layers (the total thickness of the layers on both the surfaces, i.e., the thickness obtained by subtracting the thickness of the aluminum foil layer of the positive electrode current collector from the total thickness of the positive electrode) was 135 μm.

The particle size distribution of the mixture of the positive electrode active materials (A) and (B) was measured by a MICROTRAC particle size analyzer (HRA 9320 available from NIKKISO Co., Ltd.). In the particle size distribution curve, two peaks were found at an average particle size of about 5 μm and 12 μm, respectively. d_p was larger than d_M and d_p/d_M was 1.4.

In the positive electrode active material (A), the amount of Mg was 0.08% by mole, that of Ti was 0.04% by mole, and that of Al was 0.08% by mole, each based on the amount of Co. An electron prove X-ray microanalyzer (EMPA 1600 manufactured by Shimadzu Corporation) was used to measure the concentration of the metal element M^2 in cross sections of the particles. As a result, no difference in the concentration of each of Mg, Ti and Al was observed between the surface portion and the core portion.

In the positive electrode active material (B), the amount of Mg was 0.24% by mole, that of Ti was 0.12% by mole, and that of Al was 0.24% by mole, each based on the amount of Co. The concentration of the metal element M^2 in the cross sections of the particles was measured in the same manner as in the case of the positive electrode active material (A). As a result, no difference in the concentration of each of Mg, Ti and Al was observed between the surface portion and the core portion.

With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Production of Negative Electrode

As negative electrode active materials, 70 parts by weight of a graphite type carbonaceous material (a) (purity: 99.9% or more, average particle size: 18 μm, d_{002}: 0.3356 nm, size of the crystallite in the c axis direction (Lc): 100 nm, R value of the Raman spectrum: 0.18) and 30 parts by weight of a graphite type carbonaceous material (b) (purity: 99.9% or more, average particle size: 21 μm, d_{002}: 0.3363 nm, size of the crystallite in the c axis direction (Lc): 60 nm, R value of the Raman spectrum: 0.11) were mixed. Then, 98 parts by weight of the graphite mixture, 1 part by weight of carboxymethylcellulose and 1 part by weight of a styrene-butadiene rubber were mixed in the presence of water to prepare a paste containing negative electrode mixture. This paste was uniformly applied to both surfaces of a negative electrode current collector made of a strip-form copper foil having a thickness of 10 μm, and then dried to form negative electrode mixture layers. The resultant sheet was pressed with a roller until the density of the negative electrode mixture layers became 1.75 g/cm^3. The resultant sheet was then cut out in a predetermined size. Thereafter, a lead member made of nickel was welded to the cut piece to form a sheet-form negative electrode.

Preparation of Nonaqueous Electrolytic Solution

An amount of $LiPF_6$ was dissolved in a mixed solvent of methylethyl carbonate, diethyl carbonate and ethylene carbonate mixed at a volume ratio of 1:3:2 to attain a concentration of 1.4 mol/L. To this solution, 0.2% by weight of succinonitrile and 3% by weight of vinylene carbonate were added to prepare a nonaqueous electrolytic solution.

Production of Nonaqueous Secondary Battery

The positive electrode and the negative electrode were spirally wound with interposing, therebetween, a separator made of a microporous polyethylene film (porosity: 53%, tensile strength in MD: 2.1×10^8 N/m^2, tensile strength in TD: 0.28×10^8 N/m^2, thickness: 16 μm, gas permeability: 80 seconds/100-mL, thermal shrinkage factor after being kept at 105° C. for 8 hours: 3%, puncture strength: 3.5 N (360 g)), to form an electrode body having a spiral structure. Thereafter, the electrode body was pressed to form a flat-shaped electrode body and inserted into a box-shaped battery case made of an aluminum alloy. The positive and negative lead members were welded and a cover plate was laser welded to the edge portion of an opening of the battery case. Then, the nonaqueous electrolytic solution prepared in the above was poured into the battery case through an inlet made in the cover plate. The nonaqueous electrolytic solution was sufficiently infiltrated into the separator and the like. Thereafter, the battery was partially charged, and gas generated during the partial charging was discharged. Then, the inlet was sealed up to make the battery airtight. Thereafter, the battery was charged and aged to yield a rectangular nonaqueous secondary battery having a structure as shown in FIGS. **1**A and **1**B and an external appearance as shown in FIG. **2**, and a width of 34.0 mm, a thickness of 4.0 mm, and a height of 50.0 mm.

Here, the battery shown in FIGS. **1**A, **1**B and **2** will be explained. The positive electrode **1** and the negative electrode **2** are spirally wound with interposing the separator **3** therebetween, as described above, and the spirally wound electrode body is pressed in a flat form to form the electrode laminate **6** having a flat spiral structure. The laminate **6** together with a nonaqueous electrolytic solution is contained in the box-shaped battery case **4**. For simplicity, in FIG. **1**, metal foils as current collectors used to form the positive electrode **1** and the negative electrode **2**, and the electrolytic solution are not depicted.

The battery case **4** is made of an aluminum alloy, and constitutes a main part of the exterior package of the battery. This battery case **4** also functions as a positive electrode terminal. The insulator **5** made of a polytetrafluoroethylene sheet is arranged on the inside bottom of the battery case **4**. The positive electrode lead member **7** and the negative electrode lead member **8** connected to one end of the positive electrode **1** and that of the negative electrode **2**, respectively, are taken out from the electrode laminate **6** having the flat spiral structure. The terminal **11** made of stainless steel is attached to the cover plate **9** made of aluminum for closing the opening of the battery case **4** with interposing the insulation packing **10** made of polypropylene therebetween. The lead plate **13** made of stainless steel is attached to this terminal **11** with interposing the insulator **12** therebetween.

The cover plate **9** is inserted into the opening of the battery case **4**, and their joining portions are welded to each other, thereby closing the opening of the battery case **4** to make the interior of the battery airtight. In the battery shown in FIGS. **2**A and **2**B, the inlet **14** for pouring the electrolytic solution is made in the cover plate **9**, and the inlet **14** is welded and sealed up by, for example, laser welding, with inserting a sealing member (not shown). In this way, the air-tightness of the battery is kept. Accordingly, in the case of the battery shown in FIGS. **2**A, **2**B and **3**, the electrolytic solution pouring inlet **14** is actually composed of the inlet **14** and the sealing member, but the inlet **14** is illustrated as such without a sealing member in order to make the figure simple. The explosion-proof vent **15** is made in the cover plate **9**.

In the battery **1** of Example 1, the positive electrode lead member **7** is directly welded to the cover plate **9**, whereby the combination of the battery case **4** and the cover plate **9** functions as a positive electrode terminal. The negative electrode lead member **9** is welded to the lead plate **13**, and the negative electrode lead member **8** and the terminal **11** are made electrically conductive through the lead plate **13**, whereby the terminal **11** functions as a negative electrode terminal. However, the functions of the positive and negative electrodes may be reversed in accordance with the material of the battery case **4**, etc.

FIG. **2** is a perspective view schematically illustrating the external appearance of the battery shown in FIGS. **1**A and **1**B. FIG. **2** shows that the above-mentioned battery is a rectangular battery. Thus, FIG. **2** schematically shows the battery, and depicts the specific elements out of the constituting elements of the battery.

Example 2

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that glutaronitrile was used in place of succinonitrile.

Example 3

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that adiponitrile was used in place of succinonitrile.

Example 4

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the amount of succinonitrile was changed to 0.5% by weight.

Example 5

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the amount of succinonitrile was changed to 1.0% by weight.

Example 6

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCu_{0.9988}Mg_{0.0008}Ti_{0.004}O_2$ (average particle size: 12 μm), and the positive electrode active material (B) was changed to $LiCu_{0.9964}Mg_{0.0024}Ti_{0.0012}O_2$ (average particle size: 5 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.79 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg and Ti in the positive electrode active material (B) were 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 7

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the weight ratio of the positive electrode active material (A) to the positive electrode active material (B) was changed to 90:10. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.75 g/cm^3.

Example 8

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that a mixture of the positive electrode active material (A) consisting of $LiCu_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm), and the positive electrode active material (B) consisting of $LiCu_{0.994}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm) in a weight ratio of 50:50 was used as a positive electrode active material. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.76 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 9

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Sn_{0.0008}O_2$ (average particle size: 14 μm), and the positive electrode active material (B) was changed to $LiCu_{0.994}Mg_{0.0024}Ti_{0.0012}Sn_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.76 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Sn in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 10

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCu_{0.998}Mg_{0.0008}Zr_{0.0004}Al_{0.0008}O_2$ (average particle size: 13 μm) and the positive electrode active material (B) was changed to $LiCu_{0.994}Mg_{0.0024}Zr_{0.0012}Al_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.8 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Zr and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 11

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCu_{0.998}Mg_{0.0008}Ge_{0.0004}Al_{0.0008}O_2$ (average particle size:

12 μm), and the positive electrode active material (B) was changed to $LiCu_{0.994}Mg_{0.0024}Ge_{0.0012}Al_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.79 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ge and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 12

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.334}Ni_{0.33}Mn_{0.33}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.72 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Comparative Example 1

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that only $LiCu_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm) was used as a positive electrode active material and no succinonitrile was added to the nonaqueous electrolyte. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.7 g/cm^3. This is a comparative example using only a positive electrode active material having a large particle size, that is, the positive electrode active material (A), among the positive electrode active materials used in Example 1 and further no compound having at least two nitrile compound was used.

With the nonaqueous secondary batteries fabricated in Examples 1-12 and Comparative Example 1, the following properties were evaluated:

Discharge Capacity After Charge-Discharge Cycles

Each of the batteries fabricated in Examples and Comparative Example was discharged to 3.0 V at 1 CmA at a room temperature, and charged to 4.2 V at a constant current of 1 C and then at a constant voltage of 4.2 V until the total charge time reached 2.5 hours. Thereafter, the battery was discharged at 0.2 CmA down to 3.0 V. Thereby, a discharge capacity of the battery was measured. Then, the above charge-discharge cycle was repeated five times, and the discharge capacity after the fifth cycle was used to evaluate the discharge capacity after the charge-discharge cycles. The results are shown in Table 1. In Table 1, the discharge capacity after the charge-discharge cycles obtained with each battery is shown as a relative value in relation to the discharge capacity of the battery of Comparative Example 1 after the charge-discharge cycles, which is “100”.

Evaluation of Storage Characteristics

Each of the batteries fabricated in Examples and Comparative Example was charged to 4.2 V at a constant current of 1 C and then at a constant voltage of 4.2 V until the total charge time reached 2.5 hours, followed by discharging at 1 CmA down to 3.0 V. Thereafter, the battery was again charged to 4.2 V at a constant current of 1 C and then at a constant voltage of 4.2 V until the total charge time reached 2.5 hours. Then, the thickness T_b of the battery (before storage) was measured. After the measurement of the thickness, the battery was

stored in a thermostatic chamber kept at 85° C. for 24 hours, removed from the chamber and kept standing at room temperature for 4 hours. Again, the thickness T_a of the battery (after storage) was measured. Using the thicknesses of the battery before and after storage, a rate of change of the battery thickness was calculated according to the following equation:

$$\text{Rate of change }(\%)=[(T_b-T_a)/T_a]\times 100$$

The results are shown in Table 1.

TABLE 1

Example No.	Discharge capacity after charge-discharge cycles	Rate of change of battery thickness
1	102	14.8
2	102	13.2
3	103	11.6
4	101	12.6
5	99	9.8
6	103	15.3
7	102	15.6
8	103	15.2
9	102	15.3
10	103	15.4
11	103	15.6
12	104	17.6
C. 1	100	25.0

As can be seen from the results in Table 1, the nonaqueous secondary batteries of Examples 1-12 according to the present invention had the better discharge capacity, charge-discharge cycle characteristics and storage characteristics than the nonaqueous secondary battery of Comparative Example 1.

The invention claimed is:

1. A nonaqueous secondary battery comprising: a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte,

wherein the positive electrode contains, as an active material, at least two lithium-containing transition metal oxides having different average particle sizes,

wherein said at least two lithium-containing transition metal oxides having different average particle sizes have different compositions of elements between them,

said lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (1):

$$Li_xM^1_yM^2_zM^3_vO_2 \qquad (1)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents Mg and at least one metal element selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn, M^3 represents an element other than Li, M^1 and M^2, and x, y, z and v are numbers satisfying the equations respectively: $0.97 \le x < 1.02$, $0.8 \le y < 1.02$, $0.002 \le z \le 0.05$, and $0 \le v \le 0.05$,

the positive electrode mixture layer has a density of at least 3.5 g/cm^3, and

the nonaqueous electrolyte contains a compound having at least two nitrile groups in the molecule.

2. The nonaqueous secondary battery according to claim **1**, wherein a lithium-containing transition metal oxide other than the lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (2):

$$Li_aM^1_bM^2_cM^3_dO_2 \qquad (2)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, M^3 represents an element other than Li, M^1 and M^2, and a, b, c and d are numbers satisfying the equations respectively: $0.97 \leq a < 1.02$, $0.8 \leq b < 1.02$, $0 \leq c \leq 0.02$, and $0 \leq d \leq 0.02$, and

wherein a composition of elements of the lithium-containing transition metal oxide represented by the formula (2) is different from that of the lithium-containing transition metal oxide represented by the formula (1).

3. A nonaqueous secondary battery comprising: a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte,

wherein the positive electrode contains, as an active material, at least two lithium-containing transition metal oxides having different average particle sizes,

wherein said at least two lithium-containing transition metal oxides having different average particle sizes have different compositions of elements between them,

the positive electrode mixture layer has a density of at least 3.5 g/cm^3,

a lithium-containing transition metal oxide other than a lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (2):

$$Li_aM^1_bM^2_cM^3_dO_2 \qquad (2)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents Mg and at least one metal element selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn, M^3 represents an element other than Li, M^1 and M^2, and a, b, c and d are numbers satisfying the equations respectively: $0.97 \leq a < 1.02$, $0.8 \leq b < 1.02$, $0 \leq c \leq 0.02$, and $0 \leq d \leq 0.02$, and

the nonaqueous electrolyte contains a compound having at least two nitrile groups in the molecule.

4. The nonaqueous secondary battery according to claim **3**, wherein a lithium-containing transition metal oxide having the smallest average particle size among said at least two lithium-containing transition metal oxides is a lithium-containing transition metal oxide represented by the formula (1):

$$Li_xM^1_yM^2_zM^3_vO_2 \qquad (1)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, M^3 represents an element other than Li, M^1 and M^2, and x, y, z and v are numbers satisfying the equations respectively: $0.97 \leq x < 1.02$, $0.8 \leq y < 1.02$, $0.002 \leq z \leq 0.05$, and $0 \leq v \leq 0.05$.

5. The nonaqueous secondary battery according to claim **4**, wherein M^2 in the formula (1) represents Mg and at least one metal element selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn.

* * * * *

Exhibit 2

US009350019B2

(12) **United States Patent**
Sakata et al.

(10) **Patent No.: US 9,350,019 B2**
(45) **Date of Patent: *May 24, 2016**

(54) **NONAQUEOUS SECONDARY BATTERY AND METHOD OF USING THE SAME**

(71) Applicant: **Hitachi Maxell, Ltd.**, Osaka (JP)

(72) Inventors: **Hideo Sakata**, Osaka (JP); **Fusaji Kita**, Osaka (JP); **Kumiko Ishizuka**, Osaka (JP)

(73) Assignee: **HITACHI MAXELL, LTD.**, Ibaraki-shi, Osaka (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 125 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **14/189,628**

(22) Filed: **Feb. 25, 2014**

(65) **Prior Publication Data**

US 2014/0178757 A1 Jun. 26, 2014

Related U.S. Application Data

(62) Division of application No. 11/976,566, filed on Oct. 25, 2007, now Pat. No. 8,691,446.

(30) **Foreign Application Priority Data**

Oct. 26, 2006 (JP) 2006-290637

(51) **Int. Cl.**

H01M 4/60	(2006.01)
H01M 4/505	(2010.01)

(Continued)

(52) **U.S. Cl.**
CPC ***H01M 4/505*** (2013.01); ***H01M 4/13*** (2013.01); ***H01M 4/131*** (2013.01); ***H01M 4/133*** (2013.01);

(Continued)

(58) **Field of Classification Search**
CPC H01M 4/505; H01M 4/60; H01M 4/525
USPC 429/188, 326, 330, 331, 332, 200, 339, 429/307, 245, 231
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,302,518	A	11/1981	Goodenough et al.
4,668,595	A	5/1987	Yoshino et al.

(Continued)

FOREIGN PATENT DOCUMENTS

CN	1776938	A	5/2006
JP	55-136131	A	10/1980

(Continued)

OTHER PUBLICATIONS

A Japanese Office Action, dated Oct. 11, 2011, for Japanese Application No. 2006-290637.

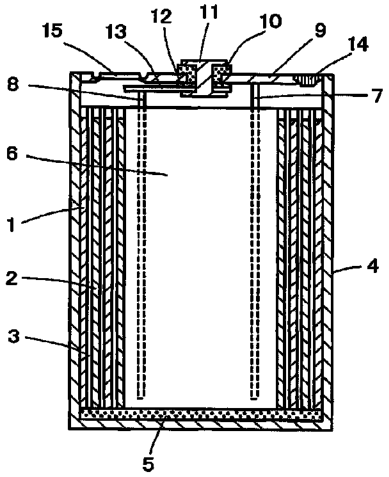
(Continued)

Primary Examiner — Kenneth Douyette
(74) *Attorney, Agent, or Firm* — Birch, Stewart, Kolasch & Birch, LLP

(57) **ABSTRACT**

A nonaqueous secondary battery having a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, in which the positive electrode contains, as an active material, a lithium-containing transition metal oxide containing a metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, the positive electrode mixture layer has a density of 3.5 g/cm^3 or larger, and the nonaqueous electrolyte contains a compound having two or more nitrile groups in the molecule.

5 Claims, 2 Drawing Sheets



(51) **Int. Cl.**

H01M 4/525	(2010.01)
H01M 4/13	(2010.01)
H01M 4/131	(2010.01)
H01M 4/133	(2010.01)
H01M 4/36	(2006.01)
H01M 4/485	(2010.01)
H01M 4/587	(2010.01)
H01M 10/0525	(2010.01)
H01M 10/0567	(2010.01)
H01M 10/42	(2006.01)
H01M 10/0569	(2010.01)
H01M 4/02	(2006.01)

(52) **U.S. Cl.**

CPC ***H01M 4/364*** (2013.01); ***H01M 4/485*** (2013.01); ***H01M 4/525*** (2013.01); ***H01M 4/587*** (2013.01); ***H01M 4/60*** (2013.01); ***H01M 10/0525*** (2013.01); ***H01M 10/0567*** (2013.01); ***H01M 10/4235*** (2013.01); *H01M 10/0569* (2013.01); *H01M 2004/021* (2013.01); *Y02E 60/122* (2013.01); *Y02T 10/7011* (2013.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,147,738	A	9/1992	Toyoguchi
2002/0037456	A1	3/2002	Hosoya
2003/0068555	A1	4/2003	Naruoka
2004/0013946	A1	1/2004	Abe et al.
2005/0164082	A1	7/2005	Kishi et al.
2005/0266315	A1	12/2005	Sato et al.
2006/0024584	A1	2/2006	Kim et al.
2006/0035144	A1	2/2006	Shimizu et al.
2006/0115730	A1	6/2006	Taniguchi et al.
2006/0134521	A1	6/2006	Shima
2006/0194118	A1	8/2006	Yew et al.
2006/0263690	A1	11/2006	Suhara et al.

FOREIGN PATENT DOCUMENTS

JP	3-201368	A	9/1991
JP	4-171659	A	6/1992
JP	7-176302	A	7/1995
JP	7-176322	A	7/1995
JP	2001-167763	A	6/2001
JP	2001-176511	A	6/2001
JP	2004-176511	A	6/2001
JP	2001-319652	A	11/2001
JP	2002-216745	A	8/2002
JP	2002-270238	A	9/2002
JP	2003-217582	A	7/2003
JP	2004-179146	A	6/2004
JP	2004-296098	A	10/2004
JP	2005-050582	A	2/2005
JP	2005-339970	A	12/2005
JP	2006-73513	A	3/2006
JP	2006-164742	A	6/2006
JP	2006-245001	A	9/2006
JP	2007-042302	A	2/2007
WO	WO 2004/030125	A1	4/2004
WO	WO 2005/069423	A1	7/2005
WO	WO 2005/117198	A1	12/2005
WO	WO 2006/091019	A1	8/2006

OTHER PUBLICATIONS

Chinese Office Action for Application No. 200710180385.4, dated Feb. 10, 2011.

Japanese Office Action, dated May 17, 2013, for Japanese Patent Application No. 2011-261150.

Machine Translation of: JP 2005/050582 A, Kikuchi, Kazuhiro, Feb. 2005.

Machine translation of JP 2001-176511, Honbo et al., Jun. 2001.

Submission of Publications for Application No. 2006-290637, dated Mar. 14, 2011.

Fig. 1A

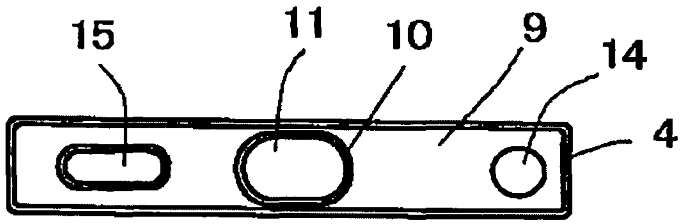


Fig. 1B

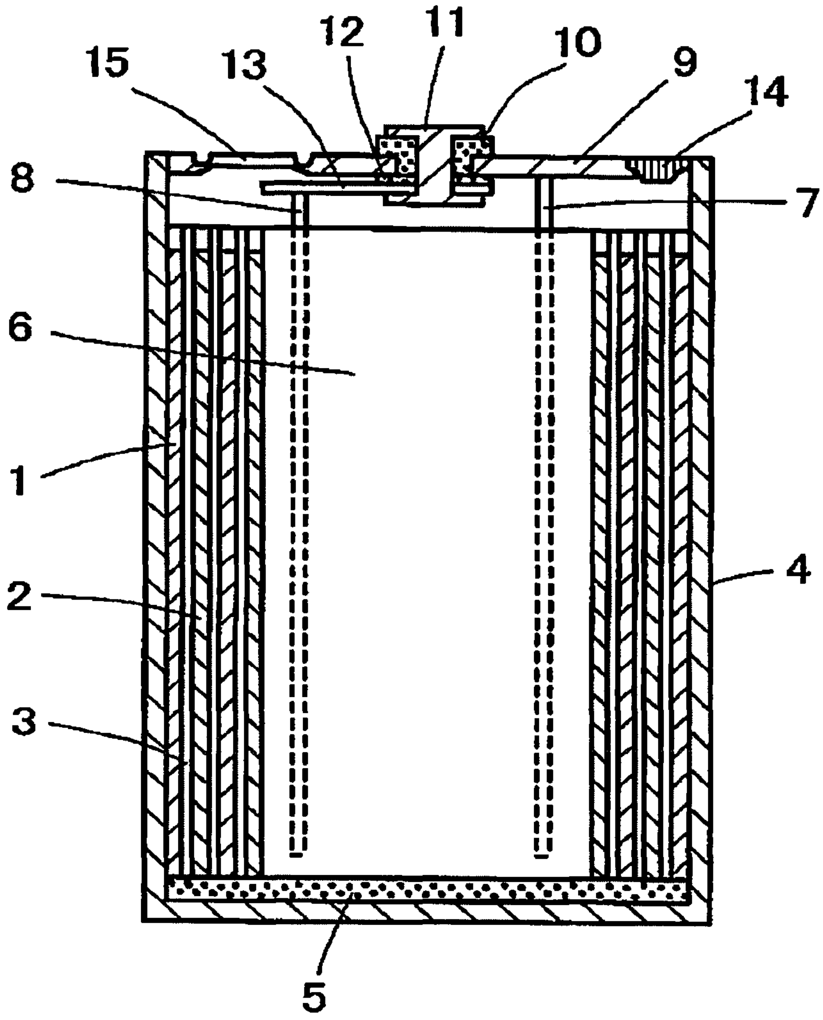
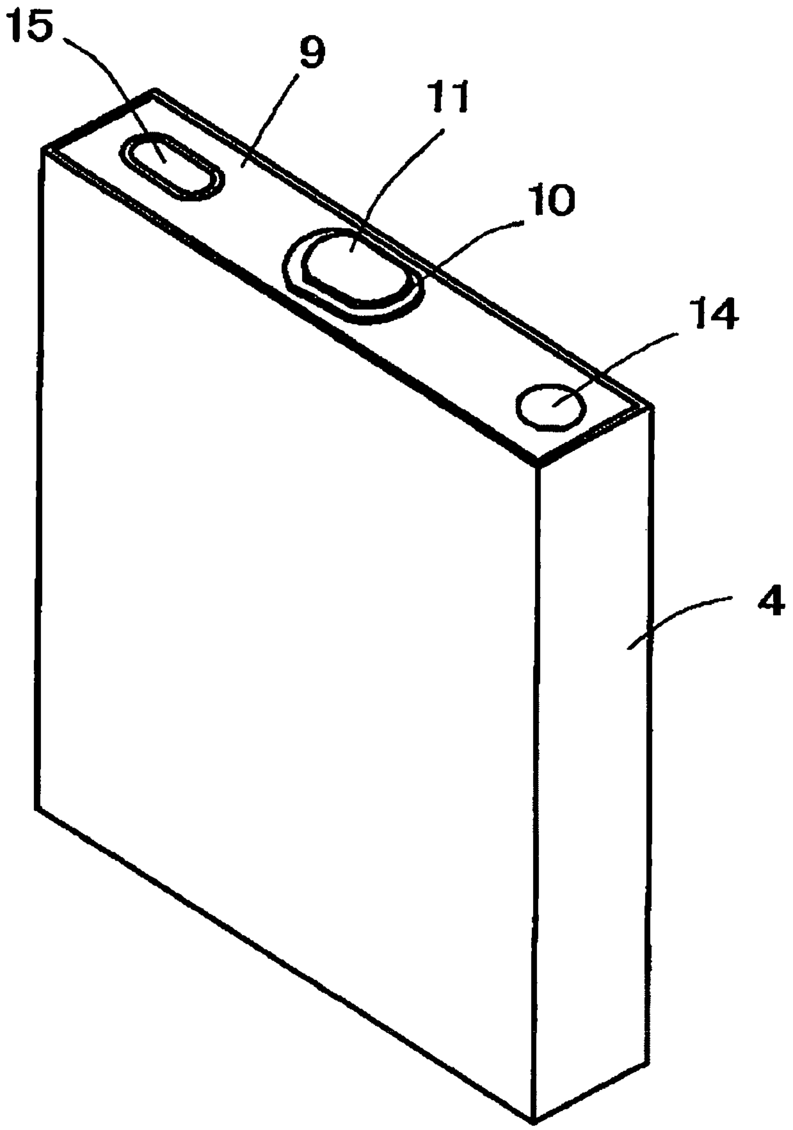


Fig. 2



NONAQUEOUS SECONDARY BATTERY AND METHOD OF USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Divisional of application Ser. No. 11/976,566 filed on Oct. 25, 2007, now U.S. Pat. No. 8,691,446, which claims priority under 35 U.S.C. I19(a) to Patent Application No. 2006-290637 filed in Japan on Oct. 26, 2006. All of the above applications are hereby expressly incorporated by reference into the present application.

FIELD OF THE INVENTION

The present invention relates to a nonaqueous secondary battery having a high capacity, good charge-discharge cycle characteristics and high reliability such as safety.

RELATED ART

In recent years, the secondary battery is an indispensable, important device as a power source of a personal computer or a cellular phone, or a power source for an electric vehicle or an electric power storage.

In particular, in applications for a mobile communication device such as a portable computer and a personal digital assistant, the battery is required to be made smaller and to trim weight. Under the current circumstances, however, the system of the battery is not easily made compact or lightweight, since an electric power consumed by a back light of a liquid crystal display panel or consumed to control the drawing of graphics is large, or the capacity of a secondary battery is not sufficiently large. In particular, a personal computer is progressively multi-functionalized by mounting a digital versatile disc (DVD) drive and so on. Thus, the power consumption thereof tends to increase. For this reason, it is highly required to increase the electric capacity of a secondary battery, in particular, the discharge capacity, when the voltage of a single battery is 3.3 V or higher.

Attention is paid to electric vehicles, which discharge no exhaust gas and make less noise in association with the increase of global environmental problems. Recently, parallel hybrid electric vehicles (HEV), which adopt a system of storing regenerative energy generated at the time of braking in a battery and making effective use of the energy, or using an electric energy stored in a battery at the time of engine starting to increase the efficiency of the engine system, have gained popularity. However, since the electric capacity of the currently used battery is small, a plurality of batteries should be used to generate a sufficient voltage. For this reason, problems such that a space in the vehicle should be made smaller and that the stability of the vehicle body deteriorates arise.

Among secondary batteries, a lithium secondary battery using a nonaqueous electrolyte attracts attention, since it generates a high voltage, has a lightweight and is expected to achieve a high energy density. In particular, a lithium secondary battery disclosed in JP-A-55-136131, in which a lithium-containing transition metal oxide, for example, $LiCoO_2$, is used as a positive electrode active material, and metal lithium is used as a negative electrode active material, is expected to attain a high energy density, since it has an electromotive force of 4 V or higher.

However, at present, in the case of a $LiCoO_2$ based secondary battery which uses $LiCoO_2$ as a positive electrode active material and a carbonaceous material such as graphite as a negative electrode active material, a charge final voltage thereof is usually 4.2 V or less. According to this charging condition, the charge capacity is only about 60% of the theoretical capacity of $LiCoO_2$. The electric capacity may be increased by increasing the charge final voltage to higher than 4.2 V. However, with the increase of the charge capacity, the crystalline structure of $LiCoO_2$ decays so that the charge-discharge cycle life may be shortened, or the crystalline structure of $LiCoO_2$ may be destabilized. Accordingly, the thermal stability of the battery deteriorates.

To solve such a problem, many attempts have been made to add a different metal element to $LiCoO_2$ (cf. JP-A-4-171659, JP-A-3-201368, JP-A-7-176302 and JP-A-2001-167763).

In addition, attempts have been made to use a battery in a high-voltage range of 4.2 V or higher (cf. JP-A-2004-296098, JP-A-2001-176511 and JP-A-2002-270238).

In years to come, a secondary battery will be required to have a higher capacity and also better reliability than the conventional batteries. In general, the battery capacity can be greatly improved by raising the content of an active material in electrodes or by increasing an electrode density, in particular, the density of a positive electrode mixture layer. However, according to such capacity-increasing measures, the reliability of the battery including storage characteristics gradually decreases.

Accordingly, in order to meet requirements for the increase of the electric capacity, it is highly desired to provide a battery which uses a material that generates a higher electromotive force (voltage range) than $LiCoO_2$ and has a stable crystalline structure capable of being stably and reversibly charged and discharged, and which further satisfies reliability such that the safety of the conventional batteries can be maintained and the battery does not expand during storage when the density of the positive electrode mixture layer is increased.

When the discharge final voltage of a conventional battery comprising $LiCoO_2$ as a positive electrode active material is made higher than 3.2 V, the battery cannot be completely discharged since the voltage in the final stage of the discharge significantly falls. Thus, an electric quantity efficiency of discharge relative to charging remarkably decreases. Since the complete discharge cannot be attained, the crystalline structure of $LiCoO_2$ easily decays, and thus the charge-discharge cycle life is shortened. This phenomenon remarkably appears in the above-mentioned high voltage range.

Under a charging condition that the final voltage at full charging is set to 4.2 V or higher in the conventional battery, apart from shortening of the charge-discharge cycle life or the decrease of the thermal stability caused by the decay of the crystalline structure of the positive electrode active material, the electrolytic solution (a solvent) is oxidatively decomposed due to the increase of the active sites in the positive electrode active material, whereby a passivation film is formed on the surface of the positive electrode and thus the internal resistance of the battery increases so that the load characteristic may deteriorate.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a nonaqueous secondary battery having a high capacity, good charge-discharge cycle characteristics and high storage characteristics.

Accordingly, the present invention provides a nonaqueous secondary battery comprising: a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, wherein the positive electrode contains, as an active material, at least one lithium-containing transition metal oxide comprising at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, the positive electrode mixture layer has a density of at least 3.5 g/cm^3, and the nonaqueous electrolyte contains a compound having at least two nitrile groups in the molecule.

The nonaqueous secondary battery of the present invention can be charged at a high voltage and thus has a large capacity, since the positive electrode mixture layer has a density of a specific value or larger so as to increase the filled amount of the positive electrode active material in the positive electrode mixture layer, and a lithium-containing transition metal oxide comprising a specific metal element, which is highly stable in a charged state at a high voltage, is used as a positive electrode active material.

Furthermore, since the positive electrode active material used in the nonaqueous secondary battery of the present invention has good stability, the decay of the active material is suppressed when the charging and discharging of the battery are repeated. Thereby, the nonaqueous secondary battery has good charge-discharge cycle characteristics.

In addition, the nonaqueous electrolyte used in the nonaqueous secondary battery of the present invention contains a compound having at least two nitrile groups in the molecule. Such a nitrile compound acts on the surface of the positive electrode and functions to prevent the direct contact of the positive electrode and the nonaqueous electrolyte. Thus, the reaction of the positive electrode and the nonaqueous electrolyte is suppressed, whereby the generation of a gas in the battery by such a reaction is prevented. Accordingly, the suppression of the reaction of the positive electrode and the nonaqueous electrolyte and the use of the positive electrode active material having high stability synergistically function to prevent the expansion of the battery during the storage of the charged battery at a high temperature and thus to improve the storage characteristics of the battery.

Consequently, the nonaqueous secondary battery of the present invention has good charge-discharge cycle characteristics and good storage characteristics. The nonaqueous secondary battery of the present invention can be charged at a high positive electrode voltage in a range of 4.35 to 4.6 V with reference to the potential of lithium, and thus it can be used in applications which require a high output.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1**A and **1**B schematically show one example of the nonaqueous secondary battery of the present invention. FIG. **1**A is a plan view thereof and FIG. **1**B is a partial vertical section thereof.

FIG. **2** shows a perspective view of the nonaqueous secondary battery illustrated in FIGS. **1**A and **1**B.

DETAILED DESCRIPTION OF THE INVENTION

The nonaqueous secondary battery of the present invention may have such a configuration that a laminate electrode body having a positive electrode with a positive electrode mixture layer and a negative electrode which are laminated each other with inserting a separator between them, or a wound electrode body in which the laminate electrode body is wound is enclosed within a housing together with a nonaqueous electrolyte.

In the nonaqueous secondary battery of the present invention, the nonaqueous electrolyte is preferably a nonaqueous solvent-base electrolytic solution comprising an electrolyte salt such as a lithium salt dissolved in a nonaqueous solvent such as an organic solvent, from the viewpoint of electric

characteristics or handling easiness. A polymer electrolyte or a gel electrolyte may be used without any problem.

The solvent in the nonaqueous electrolytic solution is not particularly limited, and examples thereof include acyclic esters such as dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, and methyl propyl carbonate; cyclic esters having a high dielectric constant, such as ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate; and mixed solvents comprising an acyclic ester and a cyclic ester. Mixed solvents each comprising an acyclic ester as a main solvent and a cyclic ester are particularly suitable.

Apart form the esters exemplified above, the following solvents may also be used: acyclic phosphoric acid triesters such as trimethyl phosphate; ethers such as 1,2-dimethoxyethane, 1,3-dioxolane, tetrahydrofuran, 2-methyl-tetrahydrofuran and diethyl ether; nitriles and dinitriles; isocyanates; and halogen-containing solvents. Furthermore, amine or imide organic solvents may be used.

Examples of the electrolyte salt to be dissolved in the solvent during the preparation of the nonaqueous electrolytic solution include $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiSbF_6$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiCF_3CO_2$, $Li_2C_2F_4(SO_3)_2$, $LiN(RfSO_2)(Rf'SO_2)$, $LiC(RfSO_2)_3$, $LiC_nF_{2n+1}SO_3$ wherein $n \geq 2$, and $LiN(RfOSO_2)_2$ wherein Rf and Rf' each represent a fluoroalkyl group. They may be used alone or in combination of two or more thereof. Among these electrolyte salts, particularly preferred are fluorine-containing organic lithium salts having 2 or more carbon atoms, since such lithium salts have a large anionic property and further ion separation easily occurs so that the salts are easily dissolved in the above-mentioned solvents. The concentration of the electrolyte salt in the nonaqueous electrolytic solution is not particularly limited, and it is preferably 0.3 mol/L or more, more preferably 0.4 mol/L or more, while it is preferably 1.7 mol/L or less, more preferably 1.5 mol/L or less.

According to the present invention, the nonaqueous electrolyte should contain a compound having at least two nitrile groups in the molecule.

The nitrile compound used according to the present invention can form a protective film on the surface of the positive electrode active material during charging, in particular, initial charging, of the battery, and the protective film suppresses the direct contact of the positive electrode and the nonaqueous electrolyte. Therefore, the battery of the present invention comprising the nonaqueous electrolyte containing the compound having at least two nitrile groups in the molecule can prevent the generation of a gas in the battery due to the reaction of the positive electrode and the nonaqueous electrolyte, when it is stored at a high temperature of, for example, about 85° C., in a charged state, since the protective film formed of the nitrile compound prevents the positive electrode and the nonaqueous electrolyte from direct contact and in turn prevents the reaction therebetween. The gas generated by the reaction of the positive electrode and the nonaqueous electrolyte in the battery causes the expansion of the battery resulting in the decrease of the battery characteristics due to the increase of the distance between the positive and negative electrodes. However, the battery of the present invention can suppress the expansion of the battery caused by the gas during storage and thus has good storage characteristics.

The compound having at least two nitrile groups in the molecule may be one having two nitrile groups in the molecule, one having three nitrile groups in the molecule, etc. Among them, a dinitrile compound, that is, a compound having two nitrile groups in the molecule is preferable since it has a better property to form the protective film and thus to prevent the reaction of the positive electrode and the nonaqueous electrolyte. The dinitrile compound is preferably a compound of the formula: NC—R—CN wherein R is a linear or branched hydrocarbon group having 1 to 10 carbon atoms, preferably a linear or branched alkylene group having 1 to 10 carbon atoms.

Specific examples of the dinitrile compound include malononitrile, succinonitrile, glutaronitrile, adiponitrile, 1,4-dicyanoheptane, 1,5-dicyanopentane, 1,6-dicyanohexane, 1,7-dicyanoheptane, 2,6-dicyanoheptane, 1,8-dicyanooctane, 2,7-dicyanooctane, 1,9-dicyanononane, 2,8-dicyanononane, 1,10-dicyanodecane, 1,6-dicyanodecane, 2,4-dimethylglutaronitrile, etc.

The nonaqueous electrolyte containing the nitrile compound may be prepared by any method. For example, the nitrile compound and the electrolyte salt are dissolved in the solvent described above by a conventional method.

The amount of the nitrile compound is preferably at least 0.005% by weight, more preferably at least 0.01% by weight, still more preferably at least 0.05% by weight, based on the whole weight of the nonaqueous electrolyte, from the viewpoint of effectively utilizing the effects of the addition of the nitrile compound. However, when the amount of the nitrile compound in the electrolyte is too large, the charge-discharge cycle characteristics of the battery tends to decrease although the storage characteristics of the battery is improve. Thus, the amount of the nitrile compound is preferably 1% or less, more preferably 0.75% by weight or less, still more preferably 0.5% by weight or less, based on the whole weight of the nonaqueous electrolyte.

Besides the nitrile compound, the nonaqueous electrolytic solution may contain other additive or additives. A preferred example of the additive is a nonionic aromatic compound. Specific examples thereof include aromatic compounds having an alkyl group bonded to an aromatic ring (e.g., cyclohexylbenzene, isopropylbenzene, tert-butylbenzene, tert-amylbenzene, octylbenzene, toluene and xylene); aromatic compounds having a halogen group bonded to an aromatic ring (e.g., fluorobenzene, difluorobenzene, trifluorobenzene and chlorobenzene); aromatic compounds having an alkoxy group bonded to an aromatic ring (e.g., anisole, fluoroanisole, dimethoxybenzene and diethoxybenzene); aromatic carboxylic acid esters such as phthalic acid esters (e.g., dibutyl phthalate and di-2-ethylhexyl phthalate) and benzoic acid esters; carbonic acid esters having a phenyl group (e.g., methylphenyl carbonate, butylphenyl carbonate and diphenyl carbonate); phenyl propionate; and biphenyl. Among them, the compounds having an alkyl group bonded to an aromatic ring (alkaryl compounds) are preferred, and cyclohexylbenzene is particularly preferred.

The aromatic compounds exemplified above can also form a film on the surface of the active material in the positive electrode or the negative electrode in the battery. These aromatic compounds may be used alone, while more advantageous effects can be attained by the use of two or more of the aromatic compounds together. Particularly advantageous effects can be attained on the improvement of the safety of the battery by the use of the alkaryl compound together with an aromatic compound, which can be oxidized at a lower voltage than the alkaryl compound, such as biphenyl.

The method for adding the aromatic compound in the nonaqueous electrolytic solution is not particularly limited. In general, the aromatic compound is added to the nonaqueous electrolytic solution prior to the fabrication of the battery.

The content of the aromatic compound in the nonaqueous electrolytic solution is preferably 4% by weight or more from the viewpoint of the safety, and it is preferably 10% by weight or less from the viewpoint of the load characteristic. When two or more aromatic compounds are used together, the total amount thereof is within the above-mentioned range. When the alkaryl (alkylaryl) compound and the aromatic compound which can be oxidized at a lower voltage that the alkaryl compound are used in combination, the content of the alkaryl compound in the nonaqueous electrolytic solution is preferably 0.5% by weight or more, more preferably 2% by weight or more, while it is preferably 8% by weight or less, more preferably 5% by weight or less. The content of the aromatic compound that can be oxidized at a lower voltage than the alkaryl compound in the nonaqueous electrolytic solution is preferably 0.1% by weight or more, more preferably 0.2% by weight or more, while it is preferably 1% by weight or less, more preferably 0.5% by weight or less.

Furthermore, a surface protecting coating can be formed on the surface of the positive electrode active material in the step of initial charging of the battery, when the nonaqueous electrolytic solution contains at least one compound selected from the group consisting of halogen-containing organic solvents (e.g., halogen-containing carbonates), organic sulfur compounds, fluorine-containing organic lithium salts, phosphorus-containing organic solvents, silicon-containing organic solvents, nitrogen-containing organic solvents other than the compounds having at least two nitrile groups in the molecule, etc. In particular, the fluorine-containing organic compounds such as fluorine-containing carbonate esters, the organic sulfur compounds and the fluorine-containing organic lithium salts are preferred. Specific examples thereof include F-DPC $[C_2F_5CH_2O(C{=}O)OCH_2C_2F_5]$, F-DEC $[CF_3CH_2O(C{=}O)OCH_2CF_3]$, HFE7100 $(C_4F_9OCH_3)$, butyl sulfate $(C_4H_9OSO_2OC_4H_9)$, methylethylene sulfate $[(\text{—}OCH(CH_3)CH_2O\text{—})SO_2]$, butyl sulfate $(C_4H_9SO_2C_4H_9)$, a polymer imide salt $([\text{—}N(Li)SO_2OCH_2(CF_2)_4CH_2OSO_2\text{-}]_n$ wherein n is from 2 to 100), $(C_2F_5SO_2)_2NLi$, and $[(CF_3)_2CHOSO_2]_2NLi$.

Such additives may be used alone. It is particularly preferable to use a fluorine-containing organic solvent together with a fluorine-containing organic lithium salt. The amount of such an additive added is preferably 0.1% by weight or more, more preferably 2% by weight or more, particularly preferably 5% by weight or more, while it is preferably 30% by weight or less, more preferably 10% by weight or less, each based on the whole weight of the nonaqueous electrolytic solution. When the amount of the additive is too large, the electric characteristics of the battery may deteriorate. When the amount is too small, a good coating may hardly be formed.

When the battery comprising the nonaqueous electrolytic solution containing the above-mentioned additive(s) is charged, particularly at a high voltage, a surface protecting coating that contains fluorine or sulfur atoms is formed on the positive electrode active material surface. This surface protecting coating may contain either fluorine atoms or sulfur atoms. Preferably, the coating contains both of fluorine atoms and sulfur atoms.

The amount of the sulfur atoms in the surface protecting coating formed on the positive electrode active material surface is preferably 0.5 atomic % or more, more preferably 1 atomic % or more, particularly preferably 3 atomic % or more. However, when the amount of the sulfur atoms in the positive electrode active material surface is too large, the discharge characteristic of the battery tends to decrease. Thus, the amount is preferably 20 atomic % or less, more preferably 10 atomic % or less, particularly preferably 6 atomic % or less.

The amount of the fluorine atoms in the surface protecting coating formed on the positive electrode active material surface is preferably 15 atomic % or more, more preferably 20 atomic % or more, particularly preferably 25 atomic % or more. However, when the amount of the fluorine atoms in the positive electrode active material surface is too large, the discharge characteristic of the battery tends to fall. Thus, the amount of the fluorine atoms is preferably 50 atomic % or less, more preferably 40 atomic % or less, particularly preferably 30 atomic % or less.

In order to improve the charge-discharge cycle characteristic of the battery, preferably, the nonaqueous electrolytic solution contains at least one carbonate compound selected from the group consisting of vinylene carbonates, such as $(—OCH{=}CHO—)C{=}O$, $(—OCH{=}C(CH_3)O—)C{=}O$ and $(—OC(CH_3){=}C(CH_3)O—)C{=}O$, and derivatives thereof; cyclic carbonate esters having a vinyl group such as vinylethylene carbonate $(—OCH_2—CH(—CH{=}CH_2)O—)C{=}O)$; and fluorine-substituted ethylene carbonates, such as $(—OCH_2—CHFO—)C{=}O$ and $(—OCHF—CHFO—)C{=}O$. The addition amount thereof is preferably 0.1% by weight or more, more preferably 0.5% by weight or more, particularly preferably 2% by weight or more based on the whole weight of the nonaqueous electrolytic solution. When the addition amount thereof is too large, the load characteristic of the battery tends to decrease. Thus, the addition amount is preferably 10% by weight or less, more preferably 5% by weight or less, particularly preferably 3% by weight or less based on the whole weight of the nonaqueous electrolytic solution.

In the present invention, the nonaqueous electrolyte may be a gel-form polymer electrolyte besides the nonaqueous electrolytic solution described above. The gel-form polymer electrolyte corresponds to a product obtained by the gelation of the nonaqueous electrolytic solution with a gelling agent. For the gelation of the nonaqueous electrolytic solution, the following gelling agents may be used: a linear polymer such as polyvinylidene fluoride, polyethylene oxide or polyacrylonitrile, or a copolymer thereof; or a polyfunctional monomer which can be polymerized by irradiation with actinic rays such as ultraviolet rays or electron beams (e.g., an acrylate having 4 or more functionalities such as pentaerythritol tetraacrylate, ditrimethylolpropane tetraacrylate, ethoxylated pentaerythritol tetraacrylate, dipentaerythritol hydroxypentaacrylate, or dipentaerythritol hexaacrylate; or a methacrylate having 4 or more functionalities, which are analogous to the above acrylates. In the case of the monomer, the monomer itself does not cause the gelling of the electrolytic solution, but the polymer formed from the monomer acts as a gelling agent.

When a polyfunctional monomer is used to gel the electrolytic solution as described above, a polymerization initiator may optionally be used. Examples of the polymerization initiator include benzoyls, benzoin alkyl ethers, benzophenones, benzoylphenylphosphine oxides, acetophenones, thioxanthones and anthraquinones. As a sensitizer for the polymerization initiator, an alkylamine or an aminoester may be used.

In the present invention, the nonaqueous electrolyte may be a solid electrolyte besides the nonaqueous electrolytic solution or the gel-form polymer electrolyte. The solid electrolyte may be an inorganic solid electrolyte or an organic solid electrolyte.

The positive electrode according to the present invention may have a structure such that the positive electrode mixture layer containing the positive electrode active material is formed on one or both of the surfaces of an electrode collector.

The positive electrode mixture layer according to the present invention may have a density of 3.5 g/cm^3 or more, more preferably 3.6 g/cm^3 or more, particularly preferably 3.8 g/cm^3 or more. With such a density, the capacity of the battery can be increased. However, when the density of the positive electrode mixture layer is too high, the wettability with the nonaqueous electrolyte, which will be explained later, decreases. Thus, the density is preferably 4.6 g/cm^3 or less, more preferably 4.4 g/cm^3 or less, particularly preferably 4.2 g/cm^3 or less.

Herein, the density of the positive electrode mixture layer may be obtained by the following measuring method: The positive electrode is cut to form a sample piece having a predetermined area, the sample piece is weighed with an electronic balance having a minimum scale of 1 mg, and then the weight of the current collector is subtracted from the weight of the sample piece to calculate the weight of the positive electrode mixture layer. The total thickness of the positive electrode is measured at ten points with a micrometer having a minimum scale of 1 μm. Then, the thickness of the current collector is subtracted from the resultant individual thicknesses, and the thicknesses of the positive electrode mixture layer measured at ten points are averaged. From the averaged thicknesses of the positive electrode mixture layer and the surface area, the volume of the positive electrode mixture layer is calculated. Finally, the weight of the positive electrode mixture layer is divided by the volume thereof to obtain the density of the positive electrode mixture layer.

The positive electrode active material contained in the positive electrode mixture layer comprises a lithium-containing transition metal oxide comprising at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn. The use of the lithium-containing transition metal oxide can improve the charge-discharge cycle characteristics of the battery, since it has good stability, in particular, in the charged state at a high voltage, so that the decay of the compound is prevented when the charge-discharge cycle is repeated. Since the lithium-containing transition metal oxide has good stability, it can improve the storage characteristics and the reliability such as safety of the battery.

The positive electrode active material preferably has a particle size frequency peak in a particle size range larger than a midpoint d_M between d_{10} and d_{90} in a particle size distribution curve, which obtained by a method for measuring an average particle size described below. To obtain a positive electrode active material having such a particle size distribution, preferably, at least two lithium-containing transition metal oxides having different average particle sizes are used. When a lithium-containing transition metal oxide having a larger average particle size and one having a smaller average particle size are used in combination, the particles of the latter infill the gaps among the particles of the former. Thus, the positive electrode mixture layer having a large density as described above can be easily formed.

The "average particle size" of the lithium-containing transition metal oxide(s) used herein means a 50% diameter value (d_{50}), that is, an median diameter, read from an integral fraction curve based on volumes, which is obtained by integrating the volumes of the particles from a smaller particle size measured by a MICROTRAC particle size analyzer (HRA 9320 available from NIKKISO Co., Ltd.). Analogously, d_{10} and d_{90} means a 10% diameter value and a 90% diameter value, respectively.

The mixture of "at least two lithium-containing transition metal oxides having different average particle sizes" preferably has a particle size frequency peak in a particle size range larger than a midpoint d_M between d_{10} and d_{90} in a particle size distribution curve, as described above. Hereinafter, a particle size corresponding to the particle size frequency peak is expressed by “d_r”. In a preferred embodiment, the ratio of d_p to d_M (d_p/d_M) is at least 1.05, more preferably at least 1.2, most preferably at least 1.3. Furthermore, the ratio of d_p to d_M is preferably 1.6 or less, more preferably 1.5 or less, most preferably 1.45 or less. In a more preferred embodiment, the lithium-containing transition metal oxide mixture has at least two peaks in the particle size distribution curve. When the lithium-containing transition metal oxides have the same d_p/d_M of 1.3, the lithium-containing transition metal oxide mixture having at least two peaks in the particle size distribution curve can increase the density of the positive electrode mixture layer by 0.1 g/cm^3 or more. When the particle size distribution curve has two or more peaks, it can be divided into a distribution curve corresponding to particles having a larger particle size and a distribution curve corresponding particles having a smaller particle size by a common peak separation method and then an average particle size (d_{50}) of the respective lithium-containing transition metal oxide and a mixing ratio of the lithium-containing transition metal oxides having the different average particle sizes can be calculated from the particle sizes and the cumulative volumes of the particles.

When the average particle size of the lithium-containing transition metal oxide having the largest average particle size (hereinafter referred to as “positive electrode active material (A)”) is represented by A, and that of the lithium-containing transition metal oxide having the smallest average particle size (hereinafter referred to as “positive electrode active material (B)”) is expressed by B, the ratio of B to A (i.e., B/A) is preferably from 0.15 to 0.6. When the average particle sizes of the two positive electrode active materials (A) and (B) have such a ratio B/A, the density of the positive electrode mixture layer can be easily increased.

The positive electrode active material (A) preferably has an average particle size of 5 μm or more, more preferably 8 μm or more, particularly preferably 11 μm or more. When the average particle size of the positive electrode active material (A) is too small, the density of the positive electrode mixture layer may hardly be increased. When the average particle size is too large, the battery characteristic tends to decrease. Thus, the average particle size is preferably 25 μm or less, more preferably 20 μm or less, particularly preferably 18 μm or less.

The positive electrode active material (B) preferably has an average particle size of 10 μm or less, more preferably 7 μm or less, particularly preferably 5 μm or less. When the average particle size of the positive electrode active material (B) is too large, the positive electrode active material (B) does not easily fill the gaps between the particles of the lithium-containing transition metal oxide having a relatively large particle size in the positive electrode mixture layer, so that the density of this layer may hardly be increased. When the average particle size is too small, the volume of voids among the small particles increases so that the density of the positive electrode mixture layer may not be increased. Thus, the average particle size of the positive electrode active material (B) is preferably 2 μm or more, more preferably 3 μm or more, particularly preferably 4 μm or more.

The positive electrode active materials according to the present invention may contain only two lithium-containing transition metal oxides having different average particle sizes, for example, the positive electrode active materials (A) and (B) as descried above, while the positive electrode active materials may contain three or more, for example, three, four or five lithium-containing transition metal oxides having different average particle sizes, for example, the positive electrode active materials (A) and (B) and one or more lithium-containing transition metal oxides having an average particle size between those of the positive electrode active materials (A) and (B).

The content of the positive electrode active material (B) having the smallest average particle size in the lithium-containing transition metal oxides contained in the positive electrode is preferably 5% by weight or more, more preferably 10% by weight or more, particularly preferably 20% by weight or more. When the positive electrode active material (B) is contained in an amount of the above-mentioned range, the gaps between the particles of the lithium-containing transition metal oxide having a relatively large particle size are easily filled therewith so that the density of the positive electrode mixture layer is increased. When the content of the positive electrode active material (B) is too large, the density of the positive electrode mixture layer is hardly be increased. Thus, the content of the positive electrode active material (B) is preferably 60% by weight or less, more preferably 50% by weight or less, particularly preferably 40% by weight or less.

Accordingly, when the lithium-containing transition metal oxides contained in the positive electrode are only the positive electrode active materials (A) and (B), the content of the positive electrode active material (A) is preferably 40% by weight or more, more preferably 50% by weight or more, particularly preferably 60% by weight or more of the oxides, while it is preferably 95% by weight or less, more preferably 90% by weight or less, particularly preferably 80% by weight or less.

Among the lithium-containing transition metal oxides contained in the positive electrode, the positive electrode active material (B) having the smallest average particle size has the above-mentioned average particle size. Such a lithium-containing transition metal oxide having a relatively small particle size has low stability, for example, in a state that the battery is charged at a high voltage, so that the oxide may damage the reliability including the safety of the battery.

When two or more lithium-containing transition metal oxides having the different average particle sizes are used, a lithium-containing transition metal oxide comprising at least one metal element M^2 selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn is preferably used at least as the positive electrode active material (B) which is the lithium-containing transition metal oxide having the smallest average particle size, since the lithium-containing transition metal oxide comprising the metal element M^2 has the improved stability and thus surely increases the charge-discharge cycle characteristics of the battery and also improves the storage characteristics and the reliability including the safety of the battery.

When two or more lithium-containing transition metal oxides having the different average particle sizes are used, the positive electrode active material (B) having the smallest average particle size preferably comprises the metal element M^2. More preferably, the lithium-containing transition metal oxide other than the positive electrode active material (B), for example, the positive electrode active material (A) having the largest average particle size or the lithium-containing transition metal oxide having the average particle size between those of the positive electrode active materials (A) and (B), comprises the metal element M^2. When the lithium-containing transition metal oxide other than the positive electrode active material (B) comprises the metal element M^2, the reliability including the safety of the battery can be further improved, since such a lithium-containing transition metal oxide has the improved stability, in particular, the stability in a state that the battery is charged at a high voltage as described above.

The positive electrode active material (B) is preferably a lithium-containing transition metal oxide represented by the following formula (1):

$$Li_xM^1_yM^2_zM^3_vO_2 \quad (1)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, M^3 represents an element other than Li, M^1 and M^2, and x, y, z and v are numbers satisfying the following equations respectively: $0.97 \leq x < 1.02$, $0.8 \leq y < 1.02$, $0.002 \leq z \leq 0.05$, and $0 \leq v \leq 0.05$. z is preferably at least 0.004, more preferably at least 0.006, while it is preferably less than 0.02, more preferably less than 0.01. When z is too small, the charge-discharge characteristics or the safety of the battery may not sufficiently be improved. When z is too large, the electric characteristics of the battery tend to deteriorate.

Each of the lithium-containing transition metal oxides other than the positive electrode active material (B) such as the positive electrode active material (A) is preferably a lithium-containing transition metal oxide represented by the following formula (2):

$$Li_aM^1_bM^2_cM^3_dO_2 \quad (2)$$

wherein M^1, M^2 and M^3 are the same as defined in the formula (1), and a, b, c and d are numbers satisfying the following equations respectively: $0.97 \leq a < 1.02$, $0.8 \leq b < 1.02$, $0 \leq c \leq 0.02$, and $0 \leq d \leq 0.02$.

M^1, M^2 and M^3 are selected from the same elements as in the formula (1), but the elements selected or the constituting element ratios selected in the individual positive electrode active materials having different average particle sizes may differ from each other. For example, in the positive electrode active material (B), Mg, Ti and Al may be selected, while in the positive electrode active material (A), Mg and Ti may be selected. As explained in this example, however, among the elements M^2, preferably at least one common element is selected, more preferably at least two common elements are selected, and particularly preferably at least three common elements are selected.

In the case of the positive electrode active material (A), "c" is preferably 0.0002 or more, more preferably 0.001 or more, and it is preferably less than 0.005, more preferably less than 0.0025, and "d" is preferably 0.0002 or more, more preferably 0.001 or more and it is preferably less than 0.005, more preferably less than 0.0025 for the following reason: the particle size of the positive electrode active material (A) is relatively large; thus, when the amount of M^2 and the like added to the material (A) is relatively small, advantageous effects can be attained; but when the amount is too large, the electrical characteristics of the battery tends to decrease.

The transition metal element in the lithium-containing transition metal oxide is preferably mainly Co and/or Ni. For example, the total amount of Co and Ni is preferably 50% by mole or more based on all the transition metal elements contained in the lithium-containing transition metal oxides.

Preferably, the proportion of Co in the lithium-containing transition metal oxide is higher, since the density of the positive electrode mixture layer can be made higher. In the formulae (1) and (2), the proportion of Co in the transition metal element M^1 is preferably 30% by mole or more, more preferably 65% by mole or more, particularly preferably 95% by mole or more.

The values of x in the formula (1) and a in the formula (2) may vary as the battery is charged or discharged. Nevertheless, when the battery is an as-produced one, x and a are each preferably 0.97, more preferably 0.98 or more, particularly preferably 0.99 or more, while x and a are each preferably less than 1.02, more preferably 1.01 or less, particularly preferably 1.00 or less.

The values of y in the formula (1) and b in the formula (2) are each preferably 0.98 or more, more preferably 0.98 or more, particularly preferably 0.99 or more, and they are each preferably less than 1.02, more preferably less than 1.01, particularly preferably less than 1.0.

Each of the positive electrode active material (B) represented by the formula (1), and the lithium-containing transition metal oxides other than the positive electrode active material (B) which are represented by the formula (2) preferably contains Mg as the element M^2, since the safety of the battery is more effectively improved. In addition, each of them comprises Mg and also at least one metal element M^2 selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn. In this case, the stability of those lithium-containing transition metal oxides is further improved in a state that the battery is charged at a high voltage.

In the positive electrode active material (B), the content of Mg is preferably at least 0.1% by mole, more preferably at least 0.15% by mole, particularly preferably at least 0.2% by mole, based on the amount of the metal element M', from the view point of more effectively attaining the effects of Mg.

When the positive electrode active material (B) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.05% by mole, more preferably at least 0.08% by mole, particularly preferably at least 0.1% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (B) contains Al and/or Sn, the total content thereof is preferably 0.1% by mole or more, more preferably 0.15% by mole or more, particularly preferably 0.2% by mole or more based on the content of M', from the viewpoint of more effectively attaining the effects of the use of these metal elements.

When the content of Mg is too large in the positive electrode active material (B), the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 2% by mole, more preferably less than 1% by mole, particularly preferably 0.5% by mole, most preferably 0.3% by mole.

When the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (B), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.5% by mole, more preferably less than 0.25% by mole, particularly preferably less than 0.15% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 1% by mole, more preferably less than 0.5% by mole, particularly preferably less than 0.3% by mole based on the content of M^1.

In the positive electrode active material (A), the content of Mg is preferably at least 0.01% by mole, more preferably at least 0.05% by mole, particularly preferably at least 0.07% by mole, based on the amount of the metal element M^1, from the view point of more effectively attaining the effects of Mg.

When the positive electrode active material (A) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.005% by mole, more preferably at least 0.008% by mole, particularly preferably at least 0.01% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (A) contains Al and/or Sn, the total content thereof is preferably 0.01% by mole or more, more preferably 0.05% by mole or more, particularly preferably 0.07% by mole or more based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements.

Also, when the content of Mg is too large in the positive electrode active material (A), the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 0.5% by mole, more preferably less than 0.2% by mole, particularly preferably 0.1% by mole.

Also, when the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (A), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.3% by mole, more preferably less than 0.1% by mole, particularly preferably less than 0.05% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 0.5% by mole, more preferably less than 0.2% by mole, particularly preferably less than 0.1% by mole based on the content of M^1.

Furthermore, when the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B) is used, the content of Mg in the other metal oxide is preferably at least 0.01% by mole, more preferably at least 0.05% by mole, particularly preferably at least 0.07% by mole, based on the amount of the metal element M^1, from the view point of more effectively attaining the effects of Mg.

When the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.005% by mole, more preferably at least 0.008% by mole, particularly preferably at least 0.01% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (A) contains Al and/or Sn, the total content thereof is preferably 0.01% by mole or more, more preferably 0.05% by mole or more, particularly preferably 0.07% by mole or more based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements.

However, again in the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B), when the content of Mg is too large, the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 2% by mole, more preferably less than 1% by mole, particularly preferably 0.5% by mole, most preferably 0.3% by mole, each based on the content of M^1.

Again, in the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B), when the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (A), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.5% by mole, more preferably less than 0.25% by mole, particularly preferably less than 0.15% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 1% by mole, more preferably less than 0.5% by mole, particularly preferably less than 0.3% by mole based on the content of M^1.

A method for including the metal element M^2 in the positive electrode active material (B) or the other lithium-containing transition metal oxide(s) is not particularly limited. For example, the element M^2 may be present on the particles of the metal oxide, may be evenly present as a solid solution inside the metal oxides, or may be unevenly present inside the metal oxides with having a density distribution. Furthermore, the element M^2 may form a compound which in turn forms a layer on the particle surfaces. Preferably, the element M^2 is evenly present as a solid solution.

In the formulae (1) and (2) representing the positive electrode active material (B) and the other lithium-containing transition metal oxide(s), respectively, the element M^3 is an element other than Li, M^1 and M^2. The positive electrode active material (B) and the other lithium-containing transition metal oxides may each contain the M^3 in an amount such that the advantageous effects of the present invention are not impaired, or they may contain no M^3.

Examples of the element M^3 include alkali metals other than Li (e.g., Na, K and Rb), alkaline earth metals other than Mg (e.g., Be, Ca, Sr and Ba), Group Ma metals (e.g., Sc, Y, La), Group IVa metals other than Ti and Zr (e.g., Hf), Group Va metals other than Nb (e.g., V and Ta), Group VIa metals (e.g., Cr, Mo and W), Group VIIb metals other than Mn (e.g., Tc and Re), Group VIII metals other than Co and Ni (e.g., Fe, Ru, and Rh), Group Ib metals (e.g., Cu, Ag and Au), Group IIIb metals other than Zn and Al (e.g., B, Ca and In), Group IVb metals other than Sn and Pb (e.g., Si), P and Bi.

The metal element M^2 contributes to an improvement in the stability of the lithium-containing transition metal oxides. However, when the content thereof is too large, a function of storing and releasing Li ions is impaired so that the battery characteristics may be decreased. Since the positive electrode active material (B) having the smallest average particle size has the particularly small particle size and decreased stability, it is preferable that the content of the element M^2, which is a stabilizing element, is somewhat high. In addition, since the positive electrode active material (B) has the small particle size and in turn the large surface area, it exhibits a high activity. Thus, the presence of the element M^2 in the material (B) has less influence on the function of storing and releasing Li ions.

In contrast, the lithium-containing transition metal oxides having relatively large particle sizes, that is, the lithium-containing transition metal oxides other than the positive electrode active material (B), have better stability than the positive electrode active material (B). Therefore, the former metal oxides have less necessity to contain the element M^2 than the positive electrode active material (B). Furthermore, their function of storing and releasing Li ions is easily impaired by the presence of the element M^2 since the materials have the smaller surface area and the lower activity than the positive electrode active material (B).

Accordingly, it is preferable that the content of the metal element M^2 in the positive electrode active material (B) is larger than that in the lithium-containing transition metal oxide(s) other than the positive electrode active material (B).

That is, z in the formula (1) is preferably larger than c in the formula (2) ($z>c$). In particular, z is at least 1.5 times, more preferably at least 2 times, particularly preferably at least 3 times larger than c. When z is much larger than c, the load characteristics of the battery tend to decrease. Thus, z is preferably less than 5 times as large as c^1, more preferably less than 4 times as large as c, particularly preferably less than 3.5 times as large as c.

When the three or more lithium-containing transition metal oxides having the different average particle sizes are contained in the positive electrode, there is no especial limitation on the relationship of the element M^2 content between the positive electrode active material (A) having the largest average particle size and the other lithium-containing transition metal oxides. Thus, the former may contain a larger amount of the element M^2 than the latter, and vise versa, or the element M^2 contents in the former and the latter may be the same. In a more preferable embodiment, a metal oxide having a smaller average particle size contains a larger amount of the element M^2. In particular, when the three lithium-containing transition metal oxides having different average particle sizes are used, the element M^2 content in the positive electrode active material (B) having the smallest average particle size is largest, that in lithium-containing transition metal oxide having the average particle size between those of the active materials (A) and (B) is second largest, and that in the positive electrode active material (A) having the largest average particle size is smallest.

When two or more lithium-containing transition metal oxides are used, the oxides having different average particle sizes may have the same composition of elements, or different compositions of elements between them. When the lithium-containing transition metal oxides according to the present invention are the above-mentioned positive electrode active materials (A) and (B), the following combination may be used: a combination of the positive electrode active material (A) consisting of $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$, and the positive electrode active material (B) consisting of $LiCo_{0.334}Ni_{0.33}Mn_{0.33}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$.

The positive electrode active material, namely, the lithium-containing transition metal oxide used according to the present invention is formed through a certain synthesizing process and a certain battery producing process. For example, for the preparation of lithium-containing transition metal oxides which contain Co as the transition metal element M^1 and have different average particle sizes, firstly, a solution of an alkali such as NaOH is dropwise added to an acidic aqueous solution containing Co to precipitate $Co(OH)_2$. In order to homogeneously precipitate $Co(OH)_2$, Co may be coprecipitated with a different element, and then the coprecipitated material is calcined to obtain Co_3O_4. The particle size of the precipitates can be adjusted by controlling the period for forming the precipitates. The particle size of Co_3O_4 after calcination is also controlled by the particle size of the precipitate at this time.

When the positive electrode active material is synthesized, conditions such as a mixing condition, calcination temperature, calcination atmosphere, calcination time, starting materials, and also battery fabrication conditions are suitably selected. With regard to the mixing condition in the synthesis of the positive electrode active material, preferably, for example, ethanol or water is added to the powdery starting materials, and then mixed in a planetary ball mill for 0.5 hour or longer. More preferably, ethanol and water are mixed at a volume ratio of 50:50, and the mixture is agitated in a planetary ball mill for 20 hours or longer. Through this mixing step, the powdery starting materials are sufficiently comminuted and mixed to prepare a homogeneous dispersion. The dispersion is dried with a spray drier or the like while keeping homogeneity. The calcination temperature is preferably from 750 to 1,050° C., more preferably from 950 to 1,030° C. The calcination atmosphere is preferably an air. The calcination time is preferably from 10 to 60 hours, more preferably from 20 to 40 hours.

In the preparation of the positive electrode active material, Li_2CO_3 is preferably used as a lithium source. As the sources of other metal such as Mg, Ti, Ge, Zr, Nb, Al and Sn, preferred are nitrates or hydroxides of these metals, or oxides thereof having a particle size of 1 μm or less. It is preferable to use the coprecipitate of the hydroxides since the different elements are uniformly distributed in the active material.

The contents of the metal elements in the positive electrode active materials are measured by the ICP atomic emission spectroscopy or the like. The content of lithium can be measured by an atomic absorption analysis. In the state of a positive electrode, it is difficult to separately measure the contents of the metal elements in each of the positive electrode active material having a larger particle size and one having a smaller particle size. Therefore, the contents or content ratios of the metal elements of the positive electrode active material having different particle sizes may be measured with an electron prove microanalyzer using a mixture of positive electrode active materials having a known mixing ratio as a standard sample. Alternatively, the positive electrode is treated with a suitable solvent such as N-methyl-2-pyrrolidone (NMP) to separate the active material particles from the positive electrode and settled out in the solvent, followed by washing and drying. Then, the particle size distribution of the recovered particles is measured and the peak-separation of the particle size distribution curve is carried out. When the inclusion of two or more particles having different particle sized is confirmed, the particles are classified into a larger one and a smaller one, and the contents of the metal elements in each particle group are measured by the ICP atomic emission spectroscopy.

Herein, the contents of the metal elements in the positive electrode active material may be measured by the ICP atomic emission spectroscopy as follows: about 5 g of the active material is precisely weighed and charged in a 200 ml beaker. Then, 100 ml of aqua regia is added, and the mixture is concentrated by heating to a liquid volume of about 20 to 25 ml. After cooling, the mixture is filtrated through a quantitative filter paper (No. 5B available from Advantec MFS, Inc.) to separate the solids. The filtrate and washing liquid are charged in a 100 ml measuring flask and diluted to a specific volume. Then, the contents of the metal elements in the solution are measured with a sequential type ICP analyzer (IPIS 1000 manufactured by Nippon Jarrel-Ash Co., Ltd.).

When the content (I) of at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn in the transition metal oxide having the smallest average particle size and a content (II) of the same metal element as one with which the content (I) in the lithium-containing transition metal oxide other than one having the smallest average particle size are measured by the ICP atomic emission spectroscopy described above, the ratio of the content (I) to the content (II) corresponds to the relationship between z in the formula (I) and c in the formula (2). The ratio of the content (I) to the content (II) is preferably at least 1.5, more preferably at least 2, particularly preferably at least 3. Since the load characteristics of the battery tend to decrease when z is much larger than c, the ratio of the content (I) to the content (II) is preferably less than 5, more preferably less than 4, particularly preferably less than 3.5.

The positive electrode used in the present invention is formed by, for example, a method described below. Firstly, if necessary, an electric conductive aid (e.g., graphite, carbon black, acetylene black, etc.) is added to the lithium-containing transition metal oxide used as a positive electrode active material. Furthermore, to the mixture, a binder (e.g., polyvinylidene fluoride, poly tetrafluoroethylene, etc.) is added to prepare a positive electrode mixture. A solvent is used to formulate this positive electrode mixture in the form of a paste. The binder may be mixed with the positive electrode active material and the like after the binder is dissolved in a solvent. In this way, the paste containing the positive electrode mixture is prepared. The resultant paste is applied to a positive electrode current collector made of an aluminum foil or the like, and then dried to form a positive electrode mixture layer. If necessary, the layer is pressed to obtain a positive electrode. When the positive electrode active material comprises two ore more lithium-containing transition metal oxides having the different average particle sizes, for example, the positive electrode active materials (A) and (B), they are mixed at a predetermined ratio, and then the electric conductive aid and the binder are added to the mixture to prepare a positive electrode mixture, which is used in the subsequent steps. However, the method for producing the positive electrode is not limited to the above-mentioned method, and may be any other method.

The thickness of the positive electrode mixture layer is preferably from 30 to 200 μm, and the thickness of the current collector used in the positive electrode is preferably from 8 to 20 μm.

In the positive electrode mixture layer, the content of the lithium-containing transition metal oxides as the active materials is preferably 96% by weight or more, more preferably 97% by weight or more, particularly preferably 97.5% by weight or more, while it is preferably 99% by weight or less, more preferably 98% by weight or less. The content of the binder in the positive electrode mixture layer is preferably 1% by weight or more, more preferably 1.3% by weight or more, particularly preferably 1.5% by weight or more, while it is preferably 4% by weight or less, more preferably 3% by weight or less, particularly preferably 2% by weight or less. The content of the electric conductive aid in the positive electrode mixture layer is preferably 1% by weight or more, more preferably 1.1% by weight or more, particularly preferably 1.2% by weight or more, while it is preferably 3% by weight or less, more preferably 2% by weight or less, particularly preferably 1.5% by weight or less.

When the content of the active material in the positive electrode mixture layer is too small, the capacity cannot be increased and also the density of the positive electrode mixture layer cannot be increased. When this content is too large, the resistance may increase or the formability of the positive electrode may be impaired. When the binder content in the positive electrode mixture layer is too large, the capacity may hardly be increased. When this content is too small, the adhesion of the layer to the current collector decreases so that the powder may drop off from the electrode. Thus, the above-mentioned preferable ranges are desirable. Furthermore, when the content of the electric conductive aid in the positive electrode mixture layer is too large, the density of the positive electrode mixture layer may not be made sufficiently high so that the capacity may hardly be increased. When this content is too small, the sufficient electric conduction through the positive electrode mixture layer is not attained so that the charge-discharge cycle characteristic or the load characteristic of the battery may deteriorated.

It is essential for the nonaqueous secondary battery of the present invention to have the nonaqueous electrolyte and the positive electrode, which are explained above, and thus there is no specific limitation on other elements or structure of the battery. The battery of the present invention may adopt various elements and structures, which are commonly adopted in the conventional nonaqueous secondary batteries in the state of art.

The negative electrode active material in the negative electrode may be any material that can be doped and de-doped with Li ions. Examples thereof are carbonaceous materials such as graphite, pyrolytic carbons, cokes, glassy carbons, burned bodies of organic polymers, mesocarbon microbeads, carbon fibers and activated carbon. In addition, the following materials can also be used as the negative electrode active

material: alloys of Si, Sn, In or the like, oxides of Si, Sn or the like that can be charged and discharged at a low voltage near a voltage at which Li can be charged and discharged, and nitrides of Li and Co such as $Li_{2.6}Co_{0.4}N$. Graphite can be partially substituted with a metal, a metal oxide or the like that can be alloyed with Li. When graphite is used as the negative electrode active material, the voltage when the battery is fully charged can be regarded as about 0.1 V with reference to the potential of lithium, and therefore the voltage of the positive electrode can be conveniently calculated as a voltage obtained by adding 0.1 V to the battery voltage. Consequently, the charge voltage of the positive electrode is easily controlled.

Preferably, graphite has such a form in that a lattice spacing d_{002} of the (002) planes is 0.338 nm or less, since the negative electrode or a negative electrode mixture layer, which will be explained later, has a higher density as the crystallinity is higher. However, when the lattice spacing d_{002} is too large, the high density negative electrode may decrease the discharge characteristic or the load characteristic of the battery. Thus, the lattice spacing d_{002} is preferably 0.335 nm or more, more preferably 0.3355 nm or more.

The crystal size of the graphite in the c axis direction (Lc) is preferably 70 nm or more, more preferably 80 nm or more, particularly preferably 90 nm or more. As the Lc is larger, the charging curve becomes flat so that the voltage of the positive electrode is easily controlled and also the capacity can be made large. When the Lc is too large, the battery capacity tends to decrease with the high-density negative electrode. Thus, the Lc is preferably less than 200 nm.

Furthermore, the specific surface area of the graphite is preferably 0.5 m^2/g or more, more preferably 1 m^2/g or more, particularly preferably 2 m^2/g or more, while it is preferably 6 m^2/g or less, more preferably 5 m^2/g or less. Unless the specific surface area of the graphite is somewhat large, the characteristics tend to decrease. When the specific surface area is too large, the graphite easily reacts with the electrolyte and such a reaction may have influences on the properties of the battery.

The graphite used in the negative electrode is preferably made of natural graphite. More preferred is a mixture of two or more graphite materials having different surface crystallinity to achieve the high density of the negative electrode. Since natural graphite is inexpensive and achieves a high capacity, the negative electrode with a high cost performance can be produced. Usually, when natural graphite is used, the battery capacity is easily decreased as the density of the negative electrode is increased. However, the decrease in the battery capacity can be suppressed by mixing the natural graphite with a graphite having a reduced surface crystallinity by a surface treatment.

The surface crystallinity of specific graphite can be determined by the Raman spectrum analysis. When the R value of the Raman spectrum ($R=I_{1350}/I_{1580}$, that is, the ratio of the Raman intensity around 1350 cm^{-1} to that around 1580 cm^{-1}) is 0.01 or more, where the Raman spectrum is measured with graphite which has been excited with an argon laser having a wavelength of 514.5 nm, the surface crystallinity of the specific graphite is slightly lower than that of natural graphite. Thus, with the graphite having a surface crystallinity decreased by the surface treatment, the R value is preferably 0.01 or more, more preferably 0.1 or more, while it is preferably 0.5 or less, more preferably 0.3 or less. The content of the graphite having a surface crystallinity decreased by surface treatment is preferably 100% by weight of the whole graphite in order to increase the density of the negative electrode. However, in order to prevent the decrease of the battery capacity, the content of such graphite is preferably 50% by weight or more, more preferably 70% by weight or more, particularly preferably 85% by weight or more of the whole graphite.

When the average particle size of the graphite is too small, an irreversible capacity increases. Thus, the average particle size of the graphite is preferably 5 μm or more, more preferably 12 μm or more, particularly preferably 18 μm or more. From the viewpoint of the increase of the capacity of the negative electrode, the average particle size of the graphite is 30 μm or less, more preferably 25 μm or less, particularly preferably 20 μm or less.

The negative electrode may be produced by the following method, for example: The negative electrode active material and an optional a binder and/or other additives are mixed to prepare a negative electrode mixture, and the mixture is dispersed in a solvent to prepare a paste. Preferably, the binder is dissolved in a solvent prior to mixing with the negative electrode active material, and then mixed with the negative electrode active material and so on. The paste containing the negative electrode mixture is applied to a negative electrode current collector made of a copper foil or the like, and then dried to form a negative electrode mixture layer. The layer is pressed to obtain a negative electrode. However, the method for producing the negative electrode is not limited to the above-mentioned method, and may be any other method.

The density of the negative electrode mixture layer after pressing is preferably 1.70 g/cm^3 or more, more preferably 1.75 g/cm^3 or more. Based on the theoretical density of graphite, the upper limit of the density of the negative electrode mixture layer formed using graphite is 2.1 to 2.2 g/cm^3. The density of the negative electrode mixture layer is preferably 2.0 g/cm^3 or less, more preferably 1.9 g/cm^3 or less from the viewpoint of the affinity with the nonaqueous electrolyte. It is preferable to press the negative electrode plural times since the negative electrode can be uniformly pressed.

The binder used in the negative electrode is not particularly limited. For the increase of the content of the active material to increase the capacity, the amount of the binder is preferably made as small as possible. To this end, the binder is preferably a mixture of an aqueous resin which can be dissolved or dispersed, and a rubbery polymer, since the use of only a small amount of the aqueous resin can contribute to the dispersion of the graphite and thus prevents the delamination of the negative electrode mixture layer from the current collector caused by the expansion and contraction of the electrode in the charge-discharge cycles.

Examples of the aqueous resins include cellulose resins such as carboxymethylcellulose, and hydroxypropylcellulose, and polyvinylpyrrolidone, polyepichlorohydrin, polyvinylpyridine, polyvinyl alcohol, polyether resins such as polyethylene oxide and polyethylene glycol, etc. Examples of the rubbery polymers include latex, butyl rubber, fluororubber, styrene-butadiene rubber, nitrile-butadiene copolymer rubber, ethylene-propylene-diene copolymer (EPDM), polybutadiene, etc. From the viewpoint of the dispersibility of the graphite particles and the prevention of delamination of the layer, it is preferable to use a cellulose ether compound such as carboxymethylcellulose together with a butadiene copolymer rubber such as a styrene-butadiene rubber. It is particularly preferable to use carboxymethylcellulose together with a butadiene copolymer rubber such as a styrene-butadiene copolymer rubber or a nitrile-butadiene-copolymer rubber. The cellulose ether compound such as carboxymethylcellulose mainly has a thickening effect on the paste containing the negative electrode mixture, while the rubbery polymer such as the styrene-butadiene copolymer rubber has a binding effect on the negative electrode mixture. When the cellulose ether compound such as carboxymethylcellulose and the rubbery polymer such as the styrene-butadiene copolymer rubber are used in combination, the weight of the former to the latter is preferably from 1:1 to 1:15.

The thickness of the negative electrode mixture layer is preferably from 40 to 200 μm. The thickness of the current collector used in the negative electrode is preferably from 5 to 30 μm.

In the negative electrode mixture layer, the content of the binder or binders is preferably 1.5% by weight or more, more preferably 1.8% by weight or more, particularly preferably 2.0% by weight or more of the layer, while it is preferably less than 5% by weight, less than 3% by weight, less than 2.5% by weight. When the amount of the binder in the negative electrode mixture layer is too large, the discharge capacity of the battery may decrease. When the amount is too small, the adhesion between the particles decreases. The content of the negative electrode active material in the negative electrode mixture layer is preferably more than 95% by weight and 98.5% by weight or less.

In the present invention, a separator used in the present invention preferably has a thickness of 5 μm or more, more preferably 10 μm or more, particularly preferably 12 μm or more, while it is preferably less than 25 μm, more preferably less than 20 μm, particularly preferably less than 18 μm, from the viewpoint of imparting the directionality of the tensile strength to the separator, keeping good insulating properties and reducing the thermal shrinkage of the separator. The gas permeability of the separator is preferably 500 second/100-mL or less, more preferably 300 second/100-mL or less, particularly preferably 120 second/100-mL or less. As the gas permeability of the separator is smaller, the load characteristic is made better but an inside short-circuit is more easily caused. Thus, the gas permeability is preferably 50 second/100-mL or more. Here, a gas permeability is measured according to JIS P8117. As the thermal shrinkage factor of the separator in the transverse direction (TD) is smaller, an inside short-circuit is less easily caused when the temperature of the battery rises. Thus, the thermal shrinkage factor in TD of the separator is as small as possible. The thermal shrinkage factor in TD is preferably 10% or less, more preferably 5% or less. In order to restrain the thermal shrinkage of the separator, it is preferable to thermally treat the separator in advance at a temperature of about 100 to 125° C. The separator having such a thermal shrinkage factor is preferably combined with the positive electrode materials according to the present invention to fabricate a battery, since the behaviors of the battery at high temperature become stable.

The thermal shrinkage factor in TD of the separator means the shrinkage factor of a portion thereof that most largely shrinks in TD when the separator having a size of 30 mm square is allowed to stand at 105° C. for 8 hours.

With regard to the strength of the separator, a tensile strength in the machine direction (MD) is preferably 6.8×10^7 N/m^2 or more, more preferably 9.8×10^7 N/m or more. The tensile strength in TD is preferably smaller than that in MD. The ratio of the tensile strength in TD to that in MD (tensile strength in TD/tensile strength in MD) is preferably 0.95 or less, more preferably 0.9 or less, while it is preferably 0.1 or more. The transverse direction means a direction perpendicular to the direction in which the film resin for the production of the separator is wound up, that is, the machine direction.

The puncture strength of the separator is preferably 2.0 N or more, more preferably 2.5 N or more. As this value is higher, the battery is less easily short-circuited. Usually, however, the upper limit thereof is substantially determined by the material of the separator. In the case of a separator made of polyethylene, the upper limit of the puncture strength is about 10 N. Here, a puncture strength is measured by cutting a sample piece of 50 mm×50 mm from a separator, clamping the sample piece with jigs at the edges of 5 mm, puncturing the sample piece with a needle having a tip end with a radius of 0.5 mm at a rate of 2 mm/sec., and measuring a maximum load before the puncture of the sample piece as a puncture strength.

When a conventional nonaqueous secondary battery is charged at a high positive electrode voltage of 4.35 V or higher with reference to the potential of lithium and is discharged to a final voltage higher than 3.2 V, the crystalline structure of the positive electrode active material decays to decrease the capacity or to induce heating of the battery due to the deterioration of the thermal stability. Thus, the battery may not be practically used. When a positive electrode active material to which a different element such as Mg or Ti is added is used, the decrease of the safety or of the capacity over charge-discharge cycles can be suppressed, but the degree of suppression is not sufficient. Moreover, the filling of the positive electrode is insufficient so that the battery easily expands.

In contrast, the battery of the present invention having the structure explained above is a nonaqueous secondary battery which improves the capacity, the charge-discharge cycle characteristic, the safety and the suppression of expansion of the battery (storage characteristics). These advantageous effects can be attained at a usual charging volt (a battery voltage of 4.2 V). Furthermore, when the positive electrode is charged up to a high voltage of 4.35 V with reference to the potential of lithium (i.e., a battery voltage of 4.25 V) and then the discharge of the battery is terminated at a high voltage, that is, a battery voltage of 3.2 V or higher, the crystalline structures of the positive electrode active materials are very stable so that the decrease of the capacity or thermal stability is prevented.

Moreover, the positive electrode active material of any conventional nonaqueous secondary battery generates a low average voltage. Therefore, when a charge-discharge cycle test is repeated under a condition that the discharge final voltage of a unit cell is 4.35 V or higher with reference to the potential of lithium, the positive electrode is doped or dedoped with a large amount of Li ions. This situation is analogous to a case where the battery is subjected to a charge-discharge cycle test under an overcharge condition. Under such a severe condition, any conventional positive electrode active material cannot maintain its crystalline structure so as to cause disadvantages such that the thermal stability declines or the charge-discharge cycle life is shortened. To the contrary, the use of the positive electrode active material according to the battery of the present invention can overcome such disadvantages of the conventional positive electrode active material. Thus, the present invention provides a nonaqueous secondary battery which can be reversibly charged and discharged even at a high voltage, such as a voltage of 4.35 to 4.6 V with reference to the potential of lithium, when the battery is fully charged.

Here, the "fully charged" means that a battery is charged by charging it at a constant current of 0.2C to a specific voltage and then charging it at a constant voltage at the specific voltage until the total charging time of the constant current charging and the constant voltage charging reaches 8 hours. When the battery of the present invention has a graphite negative electrode (i.e. a negative electrode containing graphite as a negative electrode active material) which has a voltage of 0.1 V with reference to the lithium potential when the battery is fully charged, the charging of the battery to a battery voltage of 4.45 V or higher is assumed as a charging of the battery in which the voltage of the positive electrode is substantially 4.35 V or higher.

The nonaqueous secondary battery of the present invention has characteristics including a high voltage, a high capacity and a high safety. By making use of such characteristics, the nonaqueous secondary battery of the present invention can be used as a power source of a notebook personal computer, a stylus-operated personal computer, a pocket personal computer, a notebook word processor, a pocket word processor, an electronic book player, a cellular phone, a codeless handset, a pager, a portable terminal, a portable copier, an electrical notebook, an electronic calculator, a liquid crystal television set, an electric shaver, an electric power tool, an electronic translating machine, an automobile telephone, a transceiver, a voice input device, a memory card, a backup power source, a tape recorder, a radio, a headphone stereo, a handy printer, a handy cleaner, a portable CD player, a MD player, a portable digital audio player, a video movie, a navigation system, a refrigerator, an air conditioner, a television, a stereo, a water heater, a microwave oven, a dishwasher, a washing machine, a drying machine, a game equipment, a lighting equipment, a toy, a sensor equipment, a load conditioner, a medical machine, an automobile, an electric vehicle, a golf cart, an electrically-powered cart, a security system, a power storing system, or the like. The battery can be used not only for the consumer applications but also for aerospace applications. The capacity-increasing effect of the present invention is enhanced, in particular, in small-sized portable devices. Thus, the battery of the present invention is used in a portable device desirably having a weight of 3 kg or less, more desirably 1 kg or less. The lower limit of the weight of the portable device is not particularly limited. However, the lower limit is desirably a value equal to the weight of the battery, for example, 10 g or more in order to attain the advantageous effects to some degree.

EXAMPLES

The present invention will be described in detail with reference to the following Examples; however, the Examples do not limit the scope of the present invention. Thus, modifications of the examples are encompassed by the scope of the present invention as long as the modifications do not depart from the subject matter of the present invention, which has been described above or will be described hereinafter.

Example 1

Production of Positive Electrode

The lithium-containing positive electrode materials, $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm) as a positive electrode active material (A), and $LiCo_{0.994}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm) as a positive electrode active material (B) at a weight ratio of 65:35 were mixed. Then, 97.3 parts by weight of the mixture and 1.5 parts by weight of a carbonaceous material as an electric conductive aid were charged in a volumetric feeder as a device for supplying powder. An amount of a 10 wt. % solution of polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) to be supplied to the feeder was adjusted to control a solid content in the mixture constantly at 94% by weight during kneading. While the amount of the mixed materials supplied in a unit time was controlled to a predetermined amount, the materials were supplied in a biaxial kneading extruder and then kneaded. In this way, a paste containing the positive electrode mixture was prepared.

Separately, the positive electrode active materials (A) and (B) were dissolved in aqua regia and the ratio of the elements contained in the materials (A) and (B) was measured by the ICP atomic emission spectroscopy, the results of which confirmed that they had the above elementary compositions.

The resultant paste was charged in a planetary mixer, and then a 10 wt. % solution of PVDF in NMP, and NMP were added to dilute the paste, thereby adjusting the viscosity of the paste at a level sufficient for application. This diluted paste containing the positive electrode active material mixture was passed through a **70**-mesh net to remove large substances. Thereafter, the paste was uniformly applied to both surfaces of a positive electrode current collector made of an aluminum foil with a thickness of 15 μm, and then dried to form film-form positive electrode mixture layers. In the dried positive electrode mixture layers, the weight ratio of the positive electrode active material/the electric conduction aiding agent/PVDF was 97.3:1.5:1.2. Thereafter, the resultant sheet was pressed and cut out in a predetermined size. To the cut piece, a lead member made of aluminum was welded to form a sheet-form positive electrode. The density of the pressed positive electrode mixture layers (the density of the positive electrode) was 3.86 g/cm^3. The thickness of the positive electrode mixture layers (the total thickness of the layers on both the surfaces, i.e., the thickness obtained by subtracting the thickness of the aluminum foil layer of the positive electrode current collector from the total thickness of the positive electrode) was 135 μm.

The particle size distribution of the mixture of the positive electrode active materials (A) and (B) was measured by a MICROTRAC particle size analyzer (HRA 9320 available from NIKKISO Co., Ltd.). In the particle size distribution curve, two peaks were found at an average particle size of about 5 μm and 12 μm, respectively. d_p was larger than d_M and d_p/d_M was 1.4.

In the positive electrode active material (A), the amount of Mg was 0.08% by mole, that of Ti was 0.04% by mole, and that of Al was 0.08% by mole, each based on the amount of Co. An electron prove X-ray microanalyzer (EMPA 1600 manufactured by Shimadzu Corporation) was used to measure the concentration of the metal element M^2 in cross sections of the particles. As a result, no difference in the concentration of each of Mg, Ti and Al was observed between the surface portion and the core portion.

In the positive electrode active material (B), the amount of Mg was 0.24% by mole, that of Ti was 0.12% by mole, and that of Al was 0.24% by mole, each based on the amount of Co. The concentration of the metal element M^2 in the cross sections of the particles was measured in the same manner as in the case of the positive electrode active material (A). As a result, no difference in the concentration of each of Mg, Ti and Al was observed between the surface portion and the core portion.

With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Production of Negative Electrode

As negative electrode active materials, 70 parts by weight of a graphite type carbonaceous material (a) (purity: 99.9% or more, average particle size: 18 μm, d_{002}: 0.3356 nm, size of the crystallite in the c axis direction (Lc): 100 nm, R value of the Raman spectrum: 0.18) and 30 parts by weight of a graphite type carbonaceous material (b) (purity: 99.9% or more,

average particle size: 21 μm, d_{002}: 0.3363 nm, size of the crystallite in the c axis direction (Lc): 60 nm, R value of the Raman spectrum: 0.11) were mixed. Then, 98 parts by weight of the graphite mixture, 1 part by weight of carboxymethylcellulose and 1 part by weight of a styrene-butadiene rubber were mixed in the presence of water to prepare a paste containing negative electrode mixture. This paste was uniformly applied to both surfaces of a negative electrode current collector made of a strip-form copper foil having a thickness of 10 μm, and then dried to form negative electrode mixture layers. The resultant sheet was pressed with a roller until the density of the negative electrode mixture layers became 1.75 g/cm^3. The resultant sheet was then cut out in a predetermined size. Thereafter, a lead member made of nickel was welded to the cut piece to form a sheet-form negative electrode.

Preparation of Nonaqueous Electrolytic Solution

An amount of $LiPF_6$ was dissolved in a mixed solvent of methylethyl carbonate, diethyl carbonate and ethylene carbonate mixed at a volume ratio of 1:3:2 to attain a concentration of 1.4 mol/L. To this solution, 0.2% by weight of succinonitrile and 3% by weight of vinylene carbonate were added to prepare a nonaqueous electrolytic solution.

Production of Nonaqueous Secondary Battery

The positive electrode and the negative electrode were spirally wound with interposing, therebetween, a separator made of a microporous polyethylene film (porosity: 53%, tensile strength in MD: 2.1×10^8 N/m^2, tensile strength in TD: 0.28×10^8 N/m^2, thickness: 16 μm, gas permeability: 80 seconds/100-mL, thermal shrinkage factor after being kept at 105° C. for 8 hours: 3%, puncture strength: 3.5 N (360 g)), to form an electrode body having a spiral structure. Thereafter, the electrode body was pressed to form a flat-shaped electrode body and inserted into a box-shaped battery case made of an aluminum alloy. The positive and negative lead members were welded and a cover plate was laser welded to the edge portion of an opening of the battery case. Then, the nonaqueous electrolytic solution prepared in the above was poured into the battery case through an inlet made in the cover plate. The nonaqueous electrolytic solution was sufficiently infiltrated into the separator and the like. Thereafter, the battery was partially charged, and gas generated during the partial charging was discharged. Then, the inlet was sealed up to make the battery airtight. Thereafter, the battery was charged and aged to yield a rectangular nonaqueous secondary battery having a structure as shown in FIGS. **1**A and **1**B and an external appearance as shown in FIG. **2**, and a width of 34.0 mm, a thickness of 4.0 mm, and a height of 50.0 mm.

Here, the battery shown in FIGS. **1**A, **1**B and **2** will be explained. The positive electrode **1** and the negative electrode **2** are spirally wound with interposing the separator **3** therebetween, as described above, and the spirally wound electrode body is pressed in a flat form to form the electrode laminate **6** having a flat spiral structure. The laminate **6** together with a nonaqueous electrolytic solution is contained in the box-shaped battery case **4**. For simplicity, in FIG. **1**, metal foils as current collectors used to form the positive electrode **1** and the negative electrode **2**, and the electrolytic solution are not depicted.

The battery case **4** is made of an aluminum alloy, and constitutes a main part of the exterior package of the battery. This battery case **4** also functions as a positive electrode terminal. The insulator **5** made of a polytetrafluoroethylene sheet is arranged on the inside bottom of the battery case **4**. The positive electrode lead member **7** and the negative electrode lead member **8** connected to one end of the positive electrode **1** and that of the negative electrode **2**, respectively, are taken out from the electrode laminate **6** having the flat spiral structure. The terminal **11** made of stainless steel is attached to the cover plate **9** made of aluminum for closing the opening of the battery case **4** with interposing the insulation packing **10** made of polypropylene therebetween. The lead plate **13** made of stainless steel is attached to this terminal **11** with interposing the insulator **12** therebetween.

The cover plate **9** is inserted into the opening of the battery case **4**, and their joining portions are welded to each other, thereby closing the opening of the battery case **4** to make the interior of the battery airtight. In the battery shown in FIGS. **2**A and **2**B, the inlet **14** for pouring the electrolytic solution is made in the cover plate **9**, and the inlet **14** is welded and sealed up by, for example, laser welding, with inserting a sealing member (not shown). In this way, the air-tightness of the battery is kept. Accordingly, in the case of the battery shown in FIGS. **2**A, **2**B and **3**, the electrolytic solution pouring inlet **14** is actually composed of the inlet **14** and the sealing member, but the inlet **14** is illustrated as such without a sealing member in order to make the figure simple. The explosion-proof vent **15** is made in the cover plate **9**.

In the battery **1** of Example 1, the positive electrode lead member **7** is directly welded to the cover plate **9**, whereby the combination of the battery case **4** and the cover plate **9** functions as a positive electrode terminal. The negative electrode lead member **9** is welded to the lead plate **13**, and the negative electrode lead member **8** and the terminal **11** are made electrically conductive through the lead plate **13**, whereby the terminal **11** functions as a negative electrode terminal. However, the functions of the positive and negative electrodes may be reversed in accordance with the material of the battery case **4**, etc.

FIG. **2** is a perspective view schematically illustrating the external appearance of the battery shown in FIGS. **1**A and **1**B. FIG. **2** shows that the above-mentioned battery is a rectangular battery. Thus, FIG. **2** schematically shows the battery, and depicts the specific elements out of the constituting elements of the battery.

Example 2

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that glutaronitrile was used in place of succinonitrile.

Example 3

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that adiponitrile was used in place of succinonitrile.

Example 4

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the amount of succinonitrile was changed to 0.5% by weight.

Example 5

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the amount of succinonitrile was changed to 1.0% by weight.

Example 6

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to

$LiCo_{0.9988}Mg_{0.0008}Ti_{0.0004}O_2$ (average particle size: 12 μm), and the positive electrode active material (B) was changed to $LiCo_{0.9964}Mg_{0.0024}Ti_{0.0012}O_2$ (average particle size: 5 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.79 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg and Ti in the positive electrode active material (B) were 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 7

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the weight ratio of the positive electrode active material (A) to the positive electrode active material (B) was changed to 90:10. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.75 g/cm^3.

Example 8

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that a mixture of the positive electrode active material (A) consisting of $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm), and the positive electrode active material (B) consisting of $LiCo_{0.9964}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm) in a weight ratio of 50:50 was used as a positive electrode active material. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.76 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 9

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Sn_{0.0008}O_2$ (average particle size: 14 μm), and the positive electrode active material (B) was changed to $LiCo_{0.994}Mg_{0.0024}Ti_{0.0012}Sn_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.76 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Sn in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 10

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.998}Mg_{0.0008}Zr_{0.0004}Al_{0.0008}O_2$ (average particle size: 13 μm), and the positive electrode active material (B) was changed to $LiCo_{0.994}Mg_{0.0024}Zr_{0.0012}Al_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.8 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Zr and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 11

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.998}Mg_{0.0008}Ge_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm), and the positive electrode active material (B) was changed to $LiCo_{0.994}Mg_{0.0024}Ge_{0.0012}Al_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.79 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ge and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 12

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCO_{0.334}Ni_{0.33}Mn_{0.33}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.72 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Comparative Example 1

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that only $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm) was used as a positive electrode active material and no succinonitrile was added to the nonaqueous electrolyte. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.7 g/cm^3. This is a comparative example using only a positive electrode active material having a large particle size, that is, the positive electrode active material (A), among the positive electrode active materials used in Example 1 and further no compound having at least two nitrile compound was used.

With the nonaqueous secondary batteries fabricated in Examples 1-12 and Comparative Example 1, the following properties were evaluated:

Discharge Capacity After Charge-Discharge Cycles

Each of the batteries fabricated in Examples and Comparative Example was discharged to 3.0 V at 1 CmA at a room temperature, and charged to 4.2 V at a constant current of 1 C and then at a constant voltage of 4.2 V until the total charge time reached 2.5 hours. Thereafter, the battery was discharged at 0.2 CmA down to 3.0 V. Thereby, a discharge capacity of the battery was measured. Then, the above charge-discharge cycle was repeated five times, and the discharge capacity after the fifth cycle was used to evaluate the discharge capacity after the charge-discharge cycles. The results are shown in Table 1. In Table 1, the discharge capacity after the charge-discharge cycles obtained with each battery is shown as a relative value in relation to the discharge capacity of the battery of Comparative Example 1 after the charge-discharge cycles, which is "100".

Evaluation of Storage Characteristics

Each of the batteries fabricated in Examples and Comparative Example was charged to 4.2 V at a constant current of 1 C and then at a constant voltage of 4.2 V until the total charge time reached 2.5 hours, followed by discharging at 1 CmA down to 3.0 V. Thereafter, the battery was again charged to 4.2 V at a constant current of 1 C and then at a constant voltage of 4.2 V until the total charge time reached 2.5 hours. Then, the thickness T_b of the battery (before storage) was measured. After the measurement of the thickness, the battery was stored in a thermostatic chamber kept at 85° C. for 24 hours, removed from the chamber and kept standing at room temperature for 4 hours. Again, the thickness T_a of the battery (after storage) was measured. Using the thicknesses of the battery before and after storage, a rate of change of the battery thickness was calculated according to the following equation:

$$\text{Rate of change (\%)}=[(T_b-T_a)/T_a]\times 100$$

The results are shown in Table 1.

TABLE 1

Example No.	Discharge capacity after charge-discharge cycles	Rate of change of battery thickness
1	102	14.8
2	102	13.2
3	103	11.6
4	101	12.6
5	99	9.8
6	103	15.3
7	102	15.6
8	103	15.2
9	102	15.3
10	103	15.4
11	103	15.6
12	104	17.6
C. 1	100	25.0

As can be seen from the results in Table 1, the nonaqueous secondary batteries of Examples 1-12 according to the present invention had the better discharge capacity, charge-discharge cycle characteristics and storage characteristics than the nonaqueous secondary battery of Comparative Example 1.

The invention claimed is:

1. A nonaqueous secondary battery comprising: a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, wherein

the positive electrode contains, as an active material, at least two lithium-containing transition metal oxides having different average particle sizes,

said lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (1):

$$Li_xM^1_yM^2_zM^3_vO_2 \qquad (1)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents Mg, or Mg and at least one metal element selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn, M^3 represents an element other than Li, M^1 and M^2, and x, y, z and v are numbers satisfying the equations respectively: $0.97 \leq x < 1.02$, $0.8 \leq y < 1.02$, $0.002 \leq z \leq 0.05$, and $0 \leq v \leq 0.05$;

a content of Mg in the formula (1) is from 0.15% by mole to less than 2% by mole based on an amount of the metal element M^1;

the positive electrode mixture layer has a density of at least 3.5 g/cm^3; and the nonaqueous electrode mixture contains a compound having at least two nitrile groups in the molecule.

2. The nonaqueous secondary battery according to claim **1**, wherein a lithium-containing transition metal oxide other than the lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (2):

$$Li_aM^4_bM^5_cM^6_dO_2 \qquad (2)$$

wherein M^4 represents at least one transition metal element selected from Co, Ni and Mn, M^5 represents at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, M^6 represents an element other than Li, M^4 and M^5, and a, b, c and d are numbers satisfying the equations respectively: $0.97 \leq a < 1.02$, $0.8 \leq b < 1.02$, $0 \leq c \leq 0.02$, and $0 \leq d \leq 0.02$.

3. The nonaqueous secondary battery according to claim **1**, wherein said at least two lithium-containing transition metal oxides having different average particle sizes have different compositions of elements between them.

4. The nonaqueous secondary battery according to claim **2**, wherein a composition of elements of the lithium-containing transition metal oxide represented by the formula (2) is different from that of the lithium-containing transition metal oxide represented by the formula (1).

5. The nonaqueous secondary battery according to claim **1**, wherein M^2 in the formula (1) represents Mg and at least one metal element selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn.

* * * * *

Exhibit 3

US009077035B2

(12) **United States Patent**
Kita et al.

(10) **Patent No.:** **US 9,077,035 B2**
(45) **Date of Patent:** **Jul. 7, 2015**

---

(54) **NONAQUEOUS SECONDARY BATTERY AND METHOD OF USING THE SAME**

(75) Inventors: **Fusaji Kita**, Ibaraki (JP); **Hideki Tsubata**, Ibaraki (JP); **Hiroyasu Inoue**, Ibaraki (JP)

(73) Assignee: **HITACHI MAXELL, LTD.**, Ibaraki-Shi (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 1224 days.

(21) Appl. No.: **11/723,350**

(22) Filed: **Mar. 16, 2007**

(65) **Prior Publication Data**

US 2007/0224504 A1 Sep. 27, 2007

(30) **Foreign Application Priority Data**

Mar. 20, 2006	(JP)	P2006-077040
Mar. 27, 2006	(JP)	P2006-084980
Mar. 27, 2006	(JP)	P2006-084981
Jan. 17, 2007	(JP)	P2007-007563
Jan. 19, 2007	(JP)	P2007-009860
Jan. 19, 2007	(JP)	P2007-009861

(51) **Int. Cl.**

H01M 4/52	(2010.01)
H01M 4/36	(2006.01)

(Continued)

(52) **U.S. Cl.**

CPC ***H01M 4/52*** (2013.01); ***H01M 4/364*** (2013.01); ***H01M 6/164*** (2013.01); ***H01M 6/168*** (2013.01); *H01M 10/0525* (2013.01); *H01M 2004/028* (2013.01); *H01M 2300/0034* (2013.01); ***H01M 10/0567*** (2013.01); *H01M 4/02* (2013.01); ***H01M 4/131*** (2013.01); ***H01M 4/485*** (2013.01);

(Continued)

(58) **Field of Classification Search**

CPC H01M 4/131; H01M 4/52; H01M 4/364; H01M 6/164; H01M 10/0525; H01M 10/0568; H01M 2004/028; H01M 2300/0028; H01M 2300/0034; H01M 6/168; H01M 10/0569; H01M 10/0567; Y02E 60/122

USPC 429/231.1, 231.3, 231.6, 231.5, 340, 429/341, 50

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,551,744	B1 *	4/2003	Ohzuku et al.	429/223
6,555,268	B1 *	4/2003	Inoue et al.	429/217

(Continued)

FOREIGN PATENT DOCUMENTS

JP	8-227708	A	9/1996
JP	10-112335	A	4/1998

(Continued)

OTHER PUBLICATIONS

English translation for Japanese Office Action, dated Mar. 27, 2012, for Japanese Patent Application No. 2007-009861.

(Continued)

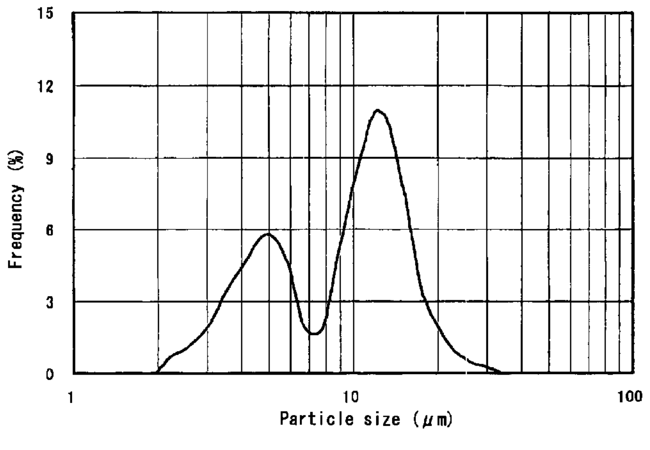
Primary Examiner — Laura Weiner

(74) *Attorney, Agent, or Firm* — Birch, Stewart, Kolasch & Birch, LLP

(57) **ABSTRACT**

A nonaqueous secondary battery containing a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, wherein the positive electrode comprises, as active materials, two or more lithium-containing transition metal oxides having different average particle sizes, and the lithium-containing transition metal oxide having the smallest average particle size contains one or more of Mg, Ti, Zr, Ge, Nb, Al and Sn.

11 Claims, 3 Drawing Sheets



(51) **Int. Cl.**

H01M 6/16	(2006.01)
H01M 10/0567	(2010.01)
H01M 4/131	(2010.01)
H01M 4/485	(2010.01)
H01M 10/0569	(2010.01)
H01M 10/0525	(2010.01)
H01M 4/02	(2006.01)

(52) **U.S. Cl.**
CPC ***H01M 10/0569*** (2013.01); *H01M 2004/021* (2013.01); *Y02E 60/122* (2013.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,737,195	B2 *	5/2004	Kweon et al.	429/231.1
7,122,278	B1 *	10/2006	Nakashima et al.	429/224
2006/0194119	A1 *	8/2006	Son et al.	429/330

FOREIGN PATENT DOCUMENTS

JP	11-54122	A	2/1999
JP	11-86845	A	3/1999
JP	2000-82466	A	3/2000
JP	2002-42890	A	2/2002
JP	2004-63269	A	2/2004
JP	2004-182564	A	7/2004
JP	2004-259675	A	9/2004
JP	2004-349132	A	12/2004
JP	2005-5208	A	1/2005
JP	2005-93238	A	4/2005
JP	2005-285720	A	10/2005
JP	2005-302507	A	10/2005

OTHER PUBLICATIONS

English translation for Japanese Office Action, dated Mar. 27, 2012, for Japanese Patent Application No. 2007-009860.

English translation for Japanese Office Action, dated May 15, 2012, for Japanese Patent Application No. 2007-007563.

Office Action for corresponding Japanese Patent Application No. 2007-007563, issued on May 15, 2012.

Office Action for corresponding Japanese Patent Application No. 2007-009860, issued on Mar. 27, 2012.

Office Action for corresponding Japanese Patent Application No. 2007-009881, issued on Mar. 27, 2012.

Korean Office Action and English translation thereof, dated Jul. 19, 2013, for Patent Application No. 10-2007-0026624.

* cited by examiner

Fig. 1

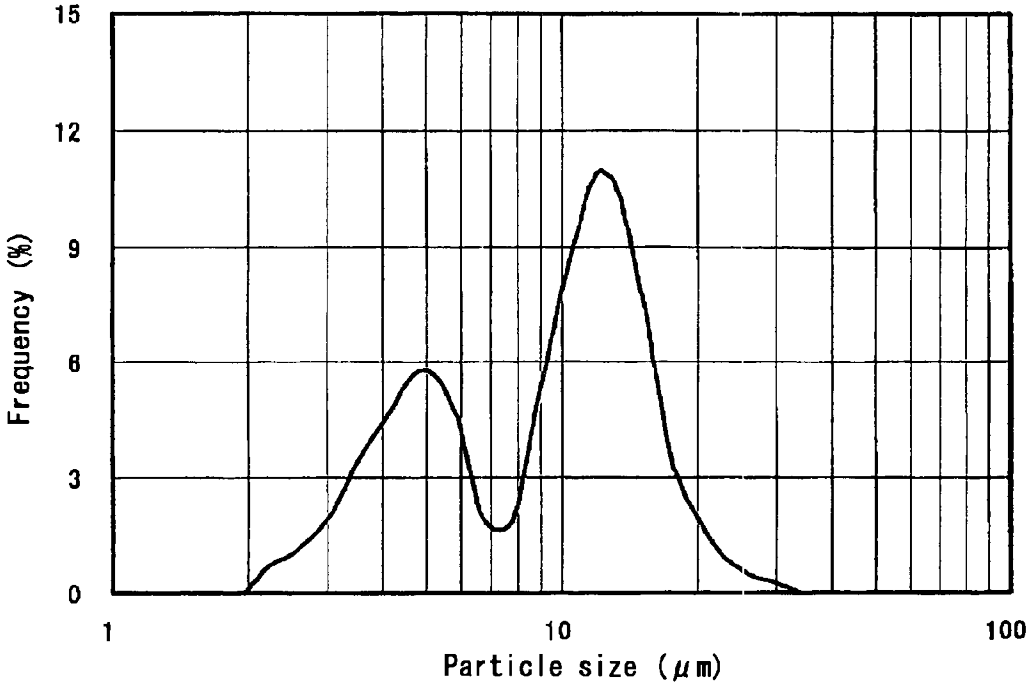


Fig. 2A

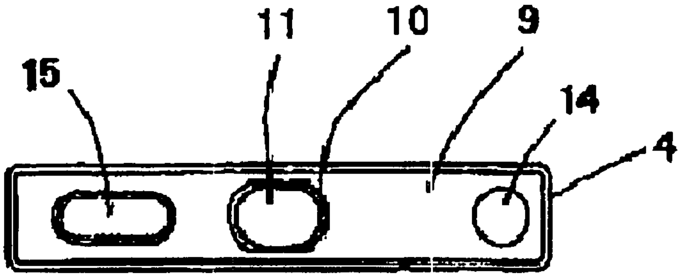


Fig. 2B

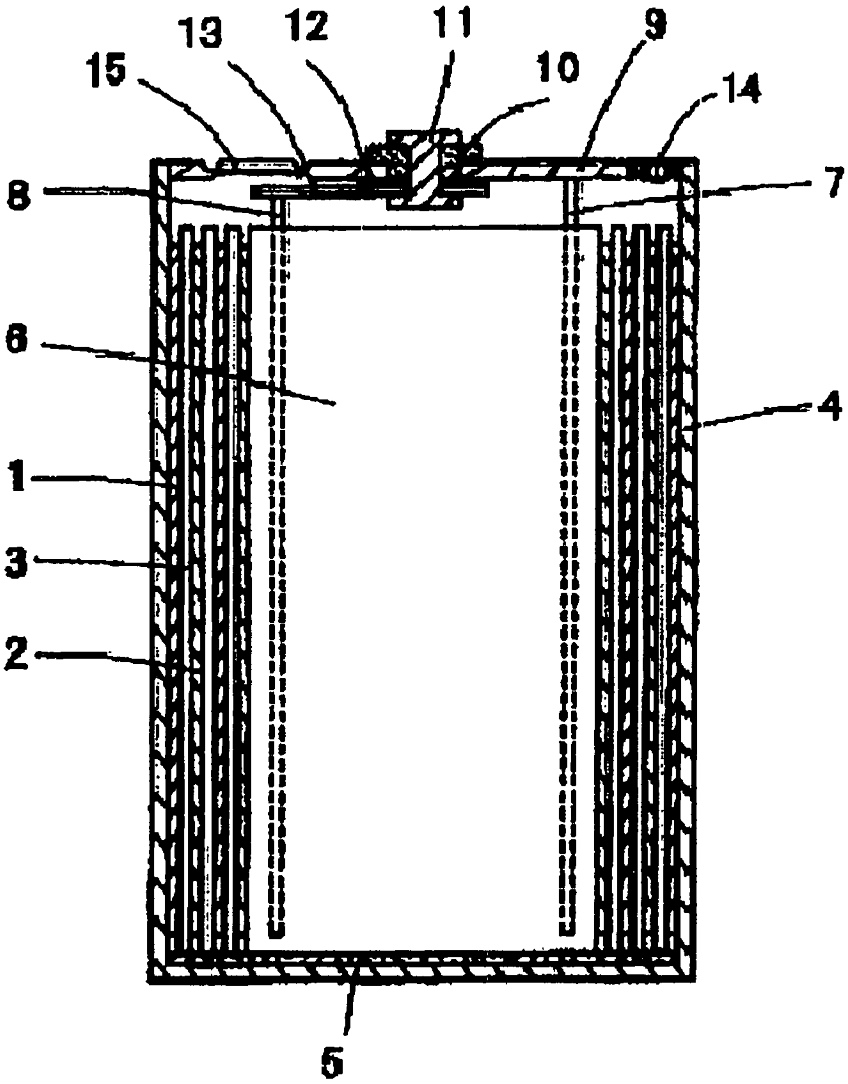
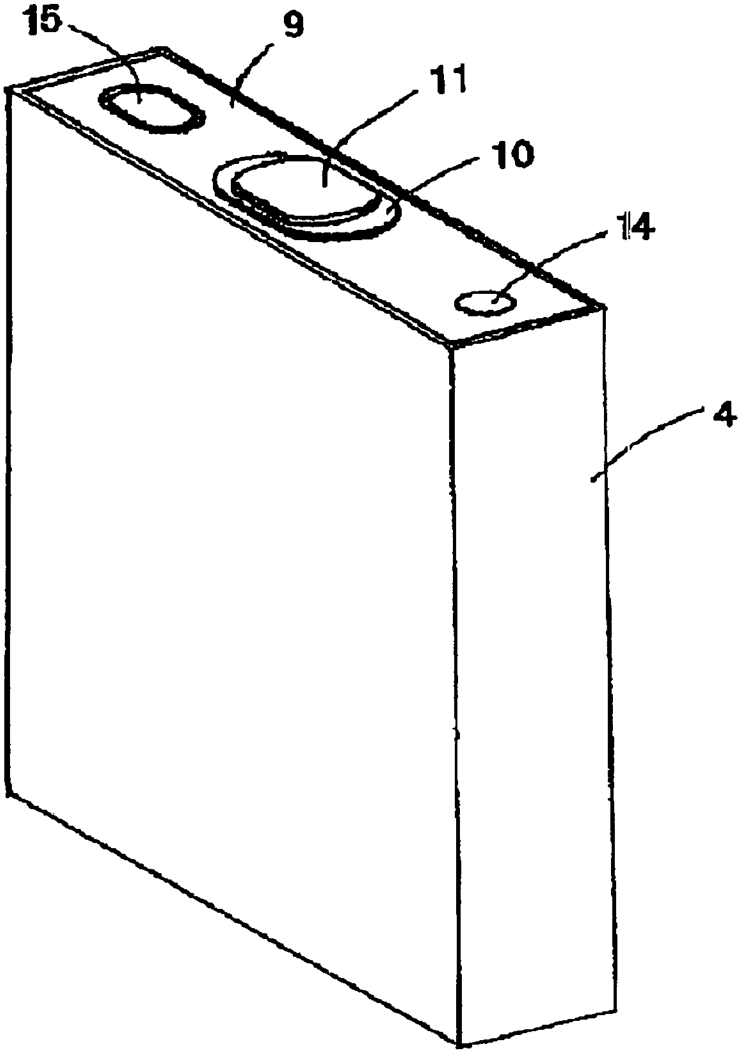


Fig. 3



NONAQUEOUS SECONDARY BATTERY AND METHOD OF USING THE SAME

FILED OF THE INVENTION

The present invention relates to a nonaqueous secondary battery and a method of using the same.

RELATED ART

In recent years, the secondary battery is an indispensable, important device as a power source of a personal computer or a cellular phone, or a power source for an electric vehicle or an electric power storage.

In particular, in applications for a mobile communication device such as a portable computer and a personal digital assistant, the battery is required to be made smaller and to trim weight. Under the current circumstances, however, the system of the battery is not easily made compact or lightweight, since an electric power consumed by a back light of a liquid crystal display panel or consumed to control the drawing of graphics is large, or the capacity of a secondary battery is not sufficiently large. In particular, a personal computer is progressively multi-functionalized by mounting a digital versatile disc (DVD) drive and so on. Thus, the power consumption thereof tends to increase. For this reason, it is highly required to increase the electric capacity of a secondary battery, in particular, the discharge capacity, when the voltage of a single battery is 3.3 V or higher.

Attention is paid to electric vehicles, which discharge no exhaust gas and make less noise in association with the increase of global environmental problems. Recently, hybrid electric vehicles (HEV), which adopt a system of storing regenerative energy generated at the time of braking in a battery and making effective use of the energy, or using an electric energy stored in a battery at the time of engine starting to increase the efficiency of the engine system, have gained popularity. However, since the electric capacity of the currently used battery is small, a plurality of batteries should be used to generate a sufficient voltage. For this reason, problems such that a space in the vehicle should be made smaller and that the stability of the vehicle body deteriorates arise.

Among secondary batteries, a lithium secondary battery using a nonaqueous electrolyte attracts attention, since it generates a high voltage, has a lightweight and is expected to achieve a high energy density. In particular, a lithium secondary battery disclosed in JP-A-55-136131, in which a lithium-containing transition metal oxide, for example, $LiCoO_2$, is used as a positive electrode active material, and metal lithium is used as a negative electrode active material, is expected to attain a high energy density, since it has an electromotive force of 4 V or higher.

However, at present, in the case of a $LiCoO_2$ based secondary battery which uses $LiCoO_2$ as a positive electrode active material and a carbonaceous material such as graphite as a negative electrode active material, a charge final voltage thereof is usually 4.2 V or less. According to this charging condition, the charge capacity is only about 60% of the theoretical capacity of $LiCoO_2$. The electric capacity may be increased by increasing the charge final voltage to higher than 4.2 V. However, with the increase of the charge capacity, the crystalline structure of $LiCoO_2$ decays so that the charge-discharge cycle life may be shortened, or the crystalline structure of $LiCoO_2$ may be destabilized. Accordingly, the thermal stability of the battery deteriorates.

To solve such a problem, many attempts have been made to add a different metal element to $LiCoO_2$ (cf. JP-A-4-171659, JP-A-3-201368, JP-A-7-176302 and JP-A-2001-167763).

In addition, attempts have been made to use a battery in a high-voltage range of 4.2 V or higher (cf. JP-A-2004-296098, JP-A-2001-176511 and JP-A-2002-270238). Also, attempts have been made to use a fluorine-containing organic solvent or a sulfur-containing organic solvent as a solvent of an electrolyte (cf. JP-A-8-37024, JP-A-10-112334, JP-A-10-112335, JP-A-2000-123880, JP-A-6-302336 and JP-A-11-162511).

In years to come, a secondary battery will be required to have a higher capacity and also better reliability including higher safety than the conventional batteries. In general, the battery capacity can be greatly improved by raising the content of an active material in electrodes or by increasing an electrode density, in particular, the density of a positive electrode mixture layer. However, according to such capacity-increasing measures, the safety of the battery gradually decreases.

Accordingly, in order to meet requirements for the increase of the electric capacity, it is highly desired to provide a battery which uses a material that generates a higher electromotive force (voltage range) than $LiCoO_2$ and has a stable crystalline structure capable of being stably and reversibly charged and discharged, and which further satisfies reliability such that the safety of the conventional batteries can be maintained and the battery does not expand when the density of the positive electrode mixture layer is increased.

When the discharge final voltage of a conventional battery comprising $LiCoO_2$ as a positive electrode active material is made higher than 3.2 V, the battery cannot be completely discharged since the voltage in the final stage of the discharge significantly falls. Thus, an electric quantity efficiency of discharge relative to charging remarkably decreases. Since the complete discharge cannot be attained, the crystalline structure of $LiCoO_2$ easily decays, and thus the charge-discharge cycle life is shortened. This phenomenon remarkably appears in the above-mentioned high voltage range.

Under a charging condition that the final voltage at full charging is set to 4.2 V or higher in the conventional battery, apart from shortening of the charge-discharge cycle life or the decrease of the thermal stability caused by the decay of the crystalline structure of the positive electrode active material, the electrolytic solution (a solvent) is oxidatively decomposed due to the increase of the active sites in the positive electrode active material, whereby a passivation film is formed on the surface of the positive electrode and thus the internal resistance of the battery increases so that the load characteristic may deteriorate.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a nonaqueous secondary battery having a high capacity, good charge-discharge cycle characteristics, and high reliability including high safety, and a method of using the same.

Accordingly, the present invention provides a nonaqueous secondary battery comprising: a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, wherein the positive electrode comprises, as active materials, at least two lithium-containing transition metal oxides having different average particle sizes, and at least the lithium-containing transition metal oxide having the smallest average particle size comprises at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn.

Furthermore, the present invention provides a nonaqueous secondary battery comprising: a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte, wherein the positive electrode comprises, as active materials, at least two lithium-containing transition metal oxides having different average particle sizes, the lithium-containing transition metal oxides comprise at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, and a ratio of a content (I) of said at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn in the transition metal oxide having the smallest average particle size to a content (II) of the same metal element as one with which the content (I) is measured, in the lithium-containing transition metal oxide other than one having the smallest average particle size is at least 1.5, where the contents (I) and (II) are measured by an inductively coupled plasma (ICP) atomic emission spectroscopy.

The "average particle size" of the lithium-containing transition metal oxides used herein means a 50% diameter value (d_{50}), that is, an median diameter, read from an integral fraction curve based on volumes, which is obtained by integrating the volumes of the particles from a smaller particle size measured by a MICROTRAC particle size analyzer (HRA 9320 available from NIKKISO Co., Ltd.).

The present invention also provides a method of using a nonaqueous secondary battery according to the present invention comprising the step of charging the battery so that a positive electrode voltage is in a range of 4.35 to 4.6 V with reference to the potential of lithium when the battery is fully charged.

For example, in the method of using the nonaqueous secondary battery according to the present invention, when the nonaqueous secondary battery of the present invention comprises a graphite negative electrode, namely, a negative electrode containing graphite as a negative electrode active material, which has a voltage of 0.1 V with reference to the lithium potential when the battery is fully charged, charging the battery up to a battery voltage of 4.45 V or higher is regarded as charging the battery so as to substantially attain a positive electrode voltage of 4.35 V or higher.

In the method of using the nonaqueous secondary battery according to the present invention, the term "fully charging (charged)" means charging under the following conditions: the battery is charged at a constant current of 0.2 C up to a predetermined voltage and subsequently the battery is charged at a predetermined constant voltage, provided that the total time of the constant current charging and the constant voltage charging is set to 8 hours.

Consequently, the nonaqueous secondary battery of the present invention has a high capacity, good charge-discharge cycle characteristics and high reliability including high safety.

According to the using method of the present invention, the nonaqueous secondary battery of the present invention can be used in applications which require larger power output.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** shows an example of a particle size distribution curve of a positive electrode active material used in the nonaqueous secondary battery according to the present invention.

FIGS. **2**A and **2**B schematically show one example of the nonaqueous secondary battery of the present invention. FIG. **2**A is a plan view thereof and FIG. **2**B is a partial vertical section thereof.

FIG. **3** shows a perspective view of the nonaqueous secondary battery illustrated in FIGS. **2**A and **2**B.

DETAILED DESCRIPTION OF THE INVENTION

The positive electrode used in the nonaqueous secondary battery of the present invention comprises, as the active material, the mixture of at least two lithium-containing transition metal oxides having different average particle sizes. When the lithium-containing transition metal oxide having a larger particle size and one having a smaller particle size are used in combination, gaps between the particles of one having the larger particle size are filled with the particles of one having the smaller particle size. Accordingly, the density of the positive electrode mixture layer is increased and, in turn, the capacity of the battery is increased.

The mixture of "at least two lithium-containing transition metal oxides having different average particle sizes" has three or more inflection points in a particle size distribution curve of the mixture. The particle size distribution curve may have two or more peaks or a shoulder in one or more peaks. In the case of such a particle size distribution curve, firstly, a conventional peak-separating method is applied to separate a distribution of particles having a larger particle size and that of particles having a smaller particle size. Subsequently, from the particle sizes and the integrated volume, the average particle size (d_{50}) of each of the lithium-containing transition metal oxides and the mixing ratio between them can be calculated.

When the average particle size of the lithium-containing transition metal oxide having the largest average particle size (hereinafter referred to as "positive electrode active material (A)") is represented by A, and that of the lithium-containing transition metal oxide having the smallest average particle size (hereinafter referred to as "positive electrode active material (B)") is expressed by B, the ratio of B to A (i.e., B/A) is preferably from 0.15 to 0.6. When the average particle sizes of the two positive electrode active materials (A) and (B) have such a ratio B/A, the density of the positive electrode mixture layer can be easily increased.

The positive electrode active material (A) preferably has an average particle size of 5 μm or more, more preferably 8 μm or more, particularly preferably 11 μm or more. When the average particle size of the positive electrode active material (A) is too small, the density of the positive electrode mixture layer may hardly be increased. When the average particle size is too large, the battery characteristic tends to decrease. Thus, the average particle size is preferably 25 μm or less, more preferably 20 μm or less, particularly preferably 18 μm or less.

The positive electrode active material (B) preferably has an average particle size of 10 μm or less, more preferably 7 μm or less, particularly preferably 5 μm or less. When the average particle size of the positive electrode active material (B) is too large, the positive electrode active material (B) does not easily fill the gaps between the particles of the lithium-containing transition metal oxide having a relatively large particle size in the positive electrode mixture layer, so that the density of this layer may hardly be increased. When the average particle size is too small, the volume of voids among the small particles increases so that the density of the positive electrode mixture layer may not be increased. Thus, the average particle size of the positive electrode active material (B) is preferably 2 μm or more, more preferably 3 μm or more, particularly preferably 4 μm or more.

The positive electrode active materials according to the present invention may contain only two lithium-containing transition metal oxides having different average particle sizes, for example, the positive electrode active materials (A) and (B) as descried above, while the positive electrode active materials may contain three or more, for example, three, four or five lithium-containing transition metal oxides having different average particle sizes, for example, the positive electrode active materials (A) and (B) and one or more lithium-containing transition metal oxides having an average particle size between those of the positive electrode active materials (A) and (B).

The content of the positive electrode active material (B) having the smallest average particle size in the lithium-containing transition metal oxides contained in the positive electrode is preferably 5% by weight or more, more preferably 10% by weight or more, particularly preferably 20% by weight or more. When the positive electrode active material (B) is contained in an amount of the above-mentioned range, the gaps between the particles of the lithium-containing transition metal oxide having a relatively large particle size are easily filled therewith so that the density of the positive electrode mixture layer is increased. When the content of the positive electrode active material (B) is too large, the density of the positive electrode mixture layer is hardly be increased. Thus, the content of the positive electrode active material (B) is preferably 60% by weight or less, more preferably 50% by weight or less, particularly preferably 40% by weight or less.

Accordingly, when the lithium-containing transition metal oxides contained in the positive electrode are only the positive electrode active materials (A) and (B), the content of the positive electrode active material (A) is preferably 40% by weight or more, more preferably 50% by weight or more, particularly preferably 60% by weight or more of the oxides, while it is preferably 95% by weight or less, more preferably 90% by weight or less, particularly preferably 80% by weight or less.

Among the lithium-containing transition metal oxides contained in the positive electrode, the positive electrode active material (B) having the smallest average particle size has the above-mentioned average particle size. Such a lithium-containing transition metal oxide having a relatively small particle size has low stability, for example, in a state that the battery is charged at a high voltage, so that the oxide may damage the reliability including the safety of the battery.

Thus, the present invention uses, as at least the positive electrode active material (B), which is the lithium-containing transition metal oxide having the smallest average particle size, a lithium-containing transition metal oxide comprising at least one metal element M^2 selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, since the lithium-containing transition metal oxide comprising the metal element M^2 has the improved stability, in particular, the stability in a state that the battery is charged at a high voltage, and thus the reliability including the safety of the battery can be improved. Furthermore, because of the improved stability of the lithium-containing transition metal oxide comprising the metal element M^2, the decay of the active material (B) is suppressed, when the charge-discharge cycles are repeated. Thus, the use of such a positive electrode active material (B) increases the charge-discharge cycle characteristics of the battery.

Apart from the positive electrode active material (B), the other lithium-containing transition metal oxide such as the positive electrode active material (A) and/or the lithium-containing transition metal oxide having the average particle size between those of the positive electrode active materials (A) and (B) may preferably comprise the metal element M^2. When the lithium-containing transition metal oxide other than the positive electrode active material (B) comprises the metal element M^2, the reliability including the safety of the battery can be further improved, since such a lithium-containing transition metal oxide has the improved stability, in particular, the stability in a state that the battery is charged at a high voltage as described above.

The positive electrode active material (B) is preferably a lithium-containing transition metal oxide represented by the following formula (1):

$$Li_xM^1_yM^2_zM^3_vO_2 \quad (1)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn, M^3 represents an element other than Li, M^1 and M^2, and x, y, z and v are numbers satisfying the following Equations respectively: $0.97 \leq x < 1.02$, $0.8 \leq y < 1.02$, $0.002 \leq z \leq 0.05$, and $0 \leq v \leq 0.05$. z is preferably at least 0.004, more preferably at least 0.006, while it is preferably less than 0.02, more preferably less than 0.01. When z is too small, the charge-discharge characteristics or the safety of the battery may not sufficiently be improved. When z is too large, the electric characteristics of the battery tend to deteriorate.

Each of the lithium-containing transition metal oxides other than the positive electrode active material (B) such as the positive electrode active material (A) is preferably a lithium-containing transition metal oxide represented by the following formula (2):

$$Li_aM^1_bM^2_cM^3_dO_2 \quad (2)$$

wherein M^1, M^2 and M^3 are the same as defined in the formula (1), and a, b, c and d are numbers satisfying the following equations respectively: $0.97 \leq a < 1.02$, $0.8 \leq b < 1.02$, $0 \leq c \leq 0.02$, and $0 \leq d \leq 0.02$.

M^1, M^2 and M^3 are selected from the same elements as in the formula (1), but the elements selected or the constituting element ratios selected in the individual positive electrode active materials having different average particle sizes may differ from each other. For example, in the positive electrode active material (B), Mg, Ti and Al may be selected, while in the positive electrode active material (A), Mg and Ti may be selected. As explained in this example, however, among the elements M^2, preferably at least one common element is selected, more preferably at least two common elements are selected, and particularly preferably at least three common elements are selected.

In the case of the positive electrode active material (A), "c" is preferably 0.0002 or more, more preferably 0.001 or more, and it is preferably less than 0.005, more preferably less than 0.0025, and "d" is preferably 0.0002 or more, more preferably 0.001 or more and it is preferably less than 0.005, more preferably less than 0.0025 for the following reason: the particle size of the positive electrode active material (A) is relatively large; thus, when the amount of M^2 and the like added to the material (A) is relatively small, advantageous effects can be attained; but when the amount is too large, the electrical characteristics of the battery tends to decrease.

In each of the lithium-containing transition metal oxides used in the present invention, the transition metal element(s) thereof is/are preferably mainly Co and/or Ni. For example, the total amount of Co and Ni is preferably 50% by mole or more based on all the transition metal elements contained in the lithium-containing transition metal oxides.

Preferably, the proportion of Co in the lithium-containing transition metal oxide is higher, since the density of the positive electrode mixture layer can be made higher. In the formulae (1) and (2), the proportion of Co in the transition metal element M^1 is preferably 30% by mole or more, more preferably 65% by mole or more, particularly preferably 95% by mole or more.

The values of x in the formula (1) and a in the formula (2) may vary as the battery is charged or discharged. Nevertheless, when the battery is an as-produced one, x and a are each preferably 0.97, more preferably 0.98 or more, particularly preferably 0.99 or more, while x and a are each preferably less than 1.02, more preferably 1.01 or less, particularly preferably 1.00 or less.

The values of y in the formula (1) and b in the formula (2) are each preferably 0.98 or more, more preferably 0.98 or more, particularly preferably 0.99 or more, and they are each preferably less than 1.02, more preferably less than 1.01, particularly preferably less than 1.0.

Each of the positive electrode active material (B) represented by the formula (1), and the lithium-containing transition metal oxides other than the positive electrode active material (B) which are represented by the formula (2) preferably contains Mg as the element M^2, since the safety of the battery is more effectively improved. In addition, each of them comprises Mg and also at least one metal element M^2 selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn. In this case, the stability of those lithium-containing transition metal oxides is further improved in a state that the battery is charged at a high voltage.

In the positive electrode active material (B), the content of Mg is preferably at least 0.1% by mole, more preferably at least 0.15% by mole, particularly preferably at least 0.2% by mole, based on the amount of the metal element M^1, from the viewpoint of more effectively attaining the effects of Mg.

Herein the content of the metal element M^2 (% by mole) is based on the amount of the metal element M^1 (100% by mole).

When the positive electrode active material (B) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.05% by mole, more preferably at least 0.08% by mole, particularly preferably at least 0.1% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (B) contains Al and/or Sn, the total content thereof is preferably 0.1% by mole or more, more preferably 0.15% by mole or more, particularly preferably 0.2% by mole or more based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements.

When the content of Mg is too large in the positive electrode active material (B), the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 2% by mole, more preferably less than 1% by mole, particularly preferably 0.5% by mole, most preferably 0.3% by mole.

When the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (B), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.5% by mole, more preferably less than 0.25% by mole, particularly preferably less than 0.15% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 1% by mole, more preferably less than 0.5% by mole, particularly preferably less than 0.3% by mole based on the content of M^1.

In the positive electrode active material (A), the content of Mg is preferably at least 0.01% by mole, more preferably at least 0.05% by mole, particularly preferably at least 0.07% by mole, based on the amount of the metal element M^1, from the viewpoint of more effectively attaining the effects of Mg.

When the positive electrode active material (A) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.005% by mole, more preferably at least 0.008% by mole, particularly preferably at least 0.01% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (A) contains Al and/or Sn, the total content thereof is preferably 0.01% by mole or more, more preferably 0.05% by mole or more, particularly preferably 0.07% by mole or more based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements.

Also, when the content of Mg is too large in the positive electrode active material (A), the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 0.5% by mole, more preferably less than 0.2% by mole, particularly preferably 0.1° by mole.

Also, when the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (A), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.3% by mole, more preferably less than 0.1% by mole, particularly preferably less than 0.05% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 0.5% by mole, more preferably less than 0.2% by mole, particularly preferably less than 0.1% by mole based on the content of M^1.

Furthermore, when the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B) is used, the content of Mg in the other metal oxide is preferably at least 0.01% by mole, more preferably at least 0.05% by mole, particularly preferably at least 0.07% by mole, based on the amount of the metal element M^1, from the viewpoint of more effectively attaining the effects of Mg.

When the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B) contains at least one metal element selected from Ti, Zr, Ge and Nb, the total content thereof is at least 0.005% by mole, more preferably at least 0.008% by mole, particularly preferably at least 0.01% by mole, based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements. When the positive electrode active material (A) contains Al and/or Sn, the total content thereof is preferably 0.01% by mole or more, more preferably 0.05% by mole or more, particularly preferably 0.07% by mole or more based on the content of M^1, from the viewpoint of more effectively attaining the effects of the use of these metal elements.

However, again in the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B), when the content of Mg is too large, the load characteristic of the battery tends to decrease. Therefore, the content of Mg is preferably less than 2% by mole, more preferably less than 1% by mole, particularly preferably 0.5% by mole, most preferably 0.3% by mole, each based on the content of M^1.

Again, in the lithium-containing transition metal oxide other than the positive electrode active materials (A) and (B), when the content of Ti, Zr, Ge, Nb, Al and/or Sn is too large in the positive electrode active material (A), the effect to increase the capacity of the battery may not be sufficient. Thus, when the oxide contains Ti, Zr, Ge and/or Nb, the total content thereof is preferably less than 0.5% by mole, more preferably less than 0.25% by mole, particularly preferably less than 0.15% by mole based on the content of M^1. When the oxide contains Al and/or Sn, the total amount thereof is preferably less than 1% by mole, more preferably less than 0.5% by mole, particularly preferably less than 0.3% by mole based on the content of M^1.

A method for including the metal element M^2 in the positive electrode active material (B) or the other lithium-containing transition metal oxide(s) is not particularly limited. For example, the element M^2 may be present on the particles of the metal oxide, may be evenly present as a solid solution inside the metal oxides, or may be unevenly present inside the metal oxides with having a density distribution. Furthermore, the element M^2 may form a compound which in turn forms a layer on the particle surfaces. Preferably, the element M^2 is evenly present as a solid solution.

In the formulae (1) and (2) representing the positive electrode active material (B) and the other lithium-containing transition metal oxide(s), respectively, the element M^3 is an element other than Li, M^1 and M^2. The positive electrode active material (B) and the other lithium-containing transition metal oxides may each contain the M^3 in an amount such that the advantageous effects of the present invention are not impaired, or they may contain no M^3.

Examples of the element M^3 include alkali metals other than Li (e.g., Na, K and Rb), alkaline earth metals other than Mg (e.g., Be, Ca, Sr and Ba), Group IIIa metals (e.g., Sc, Y, La), Group IVa metals other than Ti and Zr (e.g., Hf), Group Va metals other than Nb (e.g., V and Ta), Group VIa metals (e.g., Cr, Mo and W), Group VIIb metals other than Mn (e.g., Tc and Re), Group VIII metals other than Co and Ni (e.g., Fe, Ru, and Rh), Group Ib metals (e.g., Cu, Ag and Au), Group IIIb metals other than Zn and Al (e.g., B, Ca and In), Group IVb metals other than Sn and Pb (e.g., Si), P and Bi.

The metal element M^2 contributes to an improvement in the stability of the lithium-containing transition metal oxides. However, when the content thereof is too large, a function of storing and releasing Li ions is impaired so that the battery characteristics may be decreased. Since the positive electrode active material (B) having the smallest average particle size has the particularly small particle size and decreased stability, it is preferable that the content of the element M^2, which is a stabilizing element, is somewhat high. In addition, since the positive electrode active material (B) has the small particle size and in turn the large surface area, it exhibits a high activity. Thus, the presence of the element M^2 in the material (B) has less influence on the function of storing and releasing Li ions.

In contrast, the lithium-containing transition metal oxides having relatively large particle sizes, that is, the lithium-containing transition metal oxides other than the positive electrode active material (B), have better stability than the positive electrode active material (B). Therefore, the former metal oxides have less necessity to contain the element M^2 than the positive electrode active material (B). Furthermore, their function of storing and releasing Li ions is easily impaired by the presence of the element M^2 since the materials have the smaller surface area and the lower activity than the positive electrode active material (B).

Accordingly, it is preferable that the content of the metal element M^2 in the positive electrode active material (B) is larger than that in the lithium-containing transition metal oxide(s) other than the positive electrode active material (B).

That is, z in the formula (1) is preferably larger than c in the formula (2) ($z>c$). In particular, z is at least 1.5 times, more preferably at least 2 times, particularly preferably at least 3 times larger than c. When z is much larger than c, the load characteristics of the battery tend to decrease. Thus, z is preferably less than 5 times as large as c^1, more preferably less than 4 times as large as c, particularly preferably less than 3.5 times as large as c.

When the three or more lithium-containing transition metal oxides having the different average particle sizes are contained in the positive electrode, there is no especial limitation on the relationship of the element M^2 content between the positive electrode active material (A) having the largest average particle size and the other lithium-containing transition metal oxides. Thus, the former may contain a larger amount of the element M^2 than the latter, and vise versa, or the element M^2 contents in the former and the latter may be the same. In a more preferable embodiment, a metal oxide having a smaller average particle size contains a larger amount of the element M^2. In particular, when the three lithium-containing transition metal oxides having different average particle sizes are used, the element M^2 content in the positive electrode active material (B) having the smallest average particle size is largest, that in lithium-containing transition metal oxide having the average particle size between those of the active materials (A) and (B) is second largest, and that in the positive electrode active material (A) having the largest average particle size is smallest.

In the lithium-containing transition metal oxides which constitute the positive electrode active material according to the present invention, the oxides having different average particle sizes may have the same composition of elements, or different compositions of elements between them. When the lithium-containing transition metal oxides according to the present invention are the above-mentioned positive electrode active materials (A) and (B), the following combination may be used: a combination of the positive electrode active material (A) consisting of $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$, and the positive electrode active material (B) consisting of $LiCo_{0.334}Ni_{0.33}Mn_{0.33}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$.

The positive electrode active material comprising the lithium-containing transition metal oxides according to the present invention is formed through a certain synthesizing process and a certain battery producing process. For example, for the preparation of lithium-containing transition metal oxides which contain Co as the transition metal element M^1 and have different average particle sizes, firstly, a solution of an alkali such as NaOH is dropwise added to an acidic aqueous solution containing Co to precipitate $Co(OH)_2$. In order to homogeneously precipitate $Co(OH)_2$, Co may be coprecipitated with a different element, and then the coprecipitated material is calcined to obtain Co_3O_4. The particle size of the precipitates can be adjusted by controlling the period for forming the precipitates. The particle size of Co_3O_4 after calcination is also controlled by the particle size of the precipitate at this time.

When the positive electrode active material is synthesized, conditions such as a mixing condition, calcination temperature, calcination atmosphere, calcination time, starting materials, and also battery fabrication conditions are suitably selected. With regard to the mixing condition in the synthesis of the positive electrode active material, preferably, for example, ethanol or water is added to the powdery starting materials, and then mixed in a planetary ball mill for 0.5 hour or longer. More preferably, ethanol and water are mixed at a volume ratio of 50:50, and the mixture is agitated in a planetary ball mill for 20 hours or longer. Through this mixing step, the powdery starting materials are sufficiently comminuted and mixed to prepare a homogeneous dispersion. The dispersion is dried with a spray drier or the like while keeping homogeneity. The calcination temperature is preferably from

750 to 1,050° C., more preferably from 950 to 1,030° C. The calcination atmosphere is preferably an air. The calcination time is preferably from 10 to 60 hours, more preferably from 20 to 40 hours.

In the preparation of the positive electrode active material, Li_2CO_3 is preferably used as a lithium source. As the sources of other metal such as Mg, Ti, Ge, Zr, Nb, Al and Sn, preferred are nitrates or hydroxides of these metals, or oxides thereof having a particle size of 1 μm or less. It is preferable to use the coprecipitate of the hydroxides since the different elements are uniformly distributed in the active material.

The contents of the metal elements in the positive electrode active materials are measured by the ICP atomic emission spectroscopy or the like. The content of lithium can be measured by an atomic absorption analysis. In the state of a positive electrode, it is difficult to separately measure the contents of the metal elements in each of the positive electrode active material having a larger particle size and one having a smaller particle size. Therefore, the contents or content ratios of the metal elements of the positive electrode active material having different particle sizes may be measured with an electron prove microanalyzer using a mixture of positive electrode active materials having a known mixing ratio as a standard sample. Alternatively, the positive electrode is treated with a suitable solvent such as N-methyl-2-pyrrolidone (NMP) to separate the active material particles from the positive electrode and settled out in the solvent, followed by washing and drying. Then, the particle size distribution of the recovered particles is measured and the peak-separation of the particle size distribution curve is carried out. When the inclusion of two or more particles having different particle sized is confirmed, the particles are classified into a larger one and a smaller one, and the contents of the metal elements in each particle group are measured by the ICP atomic emission spectroscopy.

Herein, the contents of the metal elements in the positive electrode active material may be measured by the ICP atomic emission spectroscopy as follows: about 5 g of the active material is precisely weighed and charged in a 200 ml beaker. Then, 100 ml of aqua regia is added, and the mixture is concentrated by heating to a liquid volume of about 20 to 25 ml. After cooling, the mixture is filtrated through a quantitative filter paper (No. SB available from Advantec MFS, Inc.) to separate the solids. The filtrate and washing liquid are charged in a 100 ml measuring flask and diluted to a specific volume. Then, the contents of the metal elements in the solution are measured with a sequential type ICP analyzer (IPIS 1000 manufactured by Nippon Jarrel-Ash Co., Ltd.).

When the content (I) of at least one metal element selected from the group consisting of Mg, Ti, Zr, Ge, Nb, Al and Sn in the transition metal oxide having the smallest average particle size and a content (II) of the same metal element as one with which the content (I) in the lithium-containing transition metal oxide other than one having the smallest average particle size are measured by the ICP atomic emission spectroscopy described above, the ratio of the content (I) to the content (II) corresponds to the relationship between z in the formula (1) and c in the formula (2). The ratio of the content (I) to the content (II) is preferably at least 1.5, more preferably at least 2, particularly preferably at least 3. Since the load characteristics of the battery tend to decrease when z is much larger than c, the ratio of the content (I) to the content (II) is preferably less than 5, more preferably less than 4, particularly preferably less than 3.5.

The positive electrode used in the present invention is formed by, for example, a method described below. Firstly, the two or more lithium-containing transition metal oxides having different average particle sizes, for example, the positive electrode active materials (A) and (B), are mixed with each other at a predetermined weight ratio. If necessary, an electric conductive aid (e.g., graphite, carbon black, acetylene black, etc.) is added to the mixture. Furthermore, to the mixture, a binder (e.g., polyvinylidene fluoride, poly tetrafluoroethylene, etc.) is added to prepare a positive electrode mixture. A solvent is used to formulate this positive electrode mixture in the form of a paste. The binder may be mixed with the positive electrode active material and the like after the binder is dissolved in a solvent. In this way, the paste containing the positive electrode mixture is prepared. The resultant paste is applied to a positive electrode current collector made of an aluminum foil or the like, and then dried to form a positive electrode mixture layer. If necessary, the layer is pressed to obtain a positive electrode. However, the method for producing the positive electrode is not limited to the above-mentioned method, and may be any other method.

The positive electrode mixture layer according to the present invention may have a density of 3.5 g/cm^3 or more, more preferably 3.6 g/cm^3 or more, particularly preferably 3.8 g/cm^3 or more. With such a density, the capacity of the battery can be increased. However, when the density of the positive electrode mixture layer is too high, the wettability with the nonaqueous electrolyte, which will be explained later, decreases. Thus, the density is preferably 4.6 g/cm^3 or less, more preferably 4.4 g/cm^3 or less, particularly preferably 4.2 g/cm^3 or less.

Herein, the density of the positive electrode mixture layer may be obtained by the following measuring method: The positive electrode is cut to form a sample piece having a predetermined area, the sample piece is weighed with an electronic balance having a minimum scale of 1 mg, and then the weight of the current collector is subtracted from the weight of the sample piece to calculate the weight of the positive electrode mixture layer. The total thickness of the positive electrode is measured at ten points with a micrometer having a minimum scale of 1 μm. Then, the thickness of the current collector is subtracted from the resultant individual thicknesses, and the thicknesses of the positive electrode mixture layer measured at ten points are averaged. From the averaged thicknesses of the positive electrode mixture layer and the surface area, the volume of the positive electrode mixture layer is calculated. Finally, the weight of the positive electrode mixture layer is divided by the volume thereof to obtain the density of the positive electrode mixture layer.

The thickness of the positive electrode mixture layer is preferably from 30 to 200 μm, and the thickness of the current collector used in the positive electrode is preferably from 8 to 20 μm.

In the positive electrode mixture layer, the content of the lithium-containing transition metal oxides as the active materials is preferably 96% by weight or more, more preferably 97% by weight or more, particularly preferably 97.5% by weight or more, while it is preferably 99% by weight or less, more preferably 98% by weight or less. The content of the binder in the positive electrode mixture layer is preferably 1% by weight or more, more preferably 1.3% by weight or more, particularly preferably 1.5% by weight or more, while it is preferably 4% by weight or less, more preferably 3% by weight or less, particularly preferably 2% by weight or less. The content of the electric conductive aid in the positive electrode mixture layer is preferably 1% by weight or more, more preferably 1.1% by weight or more, particularly preferably 1.2% by weight or more, while it is preferably 3% by weight or less, more preferably 2% by weight or less, particularly preferably 1.5% by weight or less.

When the content of the active material in the positive electrode mixture layer is too small, the capacity cannot be increased and also the density of the positive electrode mixture layer cannot be increased. When this content is too large, the resistance may increase or the formability of the positive electrode may be impaired. When the binder content in the positive electrode mixture layer is too large, the capacity may hardly be increased. When this content is too small, the adhesion of the layer to the current collector decreases so that the powder may drop off from the electrode. Thus, the above-mentioned preferable ranges are desirable. Furthermore, when the content of the electric conductive aid in the positive electrode mixture layer is too large, the density of the positive electrode mixture layer may not be made sufficiently high so that the capacity may hardly be increased. When this content is too small, the sufficient electric conduction through the positive electrode mixture layer is not attained so that the charge-discharge cycle characteristic or the load characteristic of the battery may deteriorated.

It is essential for the nonaqueous secondary battery of the present invention to have the positive electrode explained above, and thus there is no specific limitation on other elements or structure of the battery. The battery of the present invention may adopt various elements and structures, which are commonly adopted in the conventional nonaqueous secondary batteries in the state of art.

The negative electrode active material in the negative electrode may be any material that can be doped and de-doped with Li ions. Examples thereof are carbonaceous materials such as graphite, pyrolytic carbons, cokes, glassy carbons, burned bodies of organic polymers, mesocarbon microbeads, carbon fibers and activated carbon. In addition, the following materials can also be used as the negative electrode active material: alloys of Si, Sn, In or the like, oxides of Si, Sn or the like that can be charged and discharged at a low voltage near a voltage at which Li can be charged and discharged, and nitrides of Li and Co such as $Li_{2.6}Co_{0.4}N$. Graphite can be partially substituted with a metal, a metal oxide or the like that can be alloyed with Li. When graphite is used as the negative electrode active material, the voltage when the battery is fully charged can be regarded as about 0.1 V with reference to the potential of lithium, and therefore the voltage of the positive electrode can be conveniently calculated as a voltage obtained by adding 0.1 V to the battery voltage. Consequently, the charge voltage of the positive electrode is easily controlled.

Preferably, graphite has such a form in that a lattice spacing d_{002} of the (002) planes is 0.338 nm or less, since the negative electrode or a negative electrode mixture layer, which will be explained later, has a higher density as the crystallinity is higher. However, when the lattice spacing d_{002} is too large, the high density negative electrode may decrease the discharge characteristic or the load characteristic of the battery. Thus, the lattice spacing d_{002} is preferably 0.335 nm or more, more preferably 0.3355 nm or more.

The crystal size of the graphite in the c axis direction (Lc) is preferably 70 nm or more, more preferably 80 nm or more, particularly preferably 90 nm or more. As the Lc is larger, the charging curve becomes flat so that the voltage of the positive electrode is easily controlled and also the capacity can be made large. When the Lc is too large, the battery capacity tends to decrease with the high-density negative electrode. Thus, the Lc is preferably less than 200 nm.

Furthermore, the specific surface area of the graphite is preferably 0.5 m^2/g or more, more preferably 1 m^2/g or more, particularly preferably 2 m^2/g or more, while it is preferably 6 m^2/g or less, more preferably 5 m^2/g or less. Unless the specific surface area of the graphite is somewhat large, the characteristics tend to decrease. When the specific surface area is too large, the graphite easily reacts with the electrolyte and such a reaction may have influences on the properties of the battery.

The graphite used in the negative electrode is preferably made of natural graphite. More preferred is a mixture of two or more graphite materials having different surface crystallinity to achieve the high density of the negative electrode. Since natural graphite is inexpensive and achieves a high capacity, the negative electrode with a high cost performance can be produced. Usually, when natural graphite is used, the battery capacity is easily decreased as the density of the negative electrode is increased. However, the decrease in the battery capacity can be suppressed by mixing the natural graphite with a graphite having a reduced surface crystallinity by a surface treatment.

The surface crystallinity of specific graphite can be determined by the Raman spectrum analysis. When the R value of the Raman spectrum ($R=I_{1350}/I_{1580}$, that is, the ratio of the Raman intensity around 1350 cm^{-1} to that around 1580 cm^{-1}) is 0.01 or more, where the Raman spectrum is measured with graphite which has been excited with an argon laser having a wavelength of 514.5 nm, the surface crystallinity of the specific graphite is slightly lower than that of natural graphite. Thus, with the graphite having a surface crystallinity decreased by the surface treatment, the R value is preferably 0.01 or more, more preferably 0.1 or more, while it is preferably 0.5 or less, more preferably 0.3 or less. The content of the graphite having a surface crystallinity decreased by surface treatment is preferably 100% by weight of the whole graphite in order to increase the density of the negative electrode. However, in order to prevent the decrease of the battery capacity, the content of such graphite is preferably 50% by weight or more, more preferably 70% by weight or more, particularly preferably 85% by weight or more of the whole graphite.

When the average particle size of the graphite is too small, an irreversible capacity increases. Thus, the average particle size of the graphite is preferably 5 μm or more, more preferably 12 μm or more, particularly preferably 18 μm or more. From the viewpoint of the increase of the capacity of the negative electrode, the average particle size of the graphite is 30 μm or less, more preferably 25 μm or less, particularly preferably 20 μm or less.

The negative electrode may be produced by the following method, for example: The negative electrode active material and an optional a binder and/or other additives are mixed to prepare a negative electrode mixture, and the mixture is dispersed in a solvent to prepare a paste. Preferably, the binder is dissolved in a solvent prior to mixing with the negative electrode active material, and then mixed with the negative electrode active material and so on. The paste containing the negative electrode mixture is applied to a negative electrode current collector made of a copper foil or the like, and then dried to form a negative electrode mixture layer. The layer is pressed to obtain a negative electrode. However, the method for producing the negative electrode is not limited to the above-mentioned method, and may be any other method.

The density of the negative electrode mixture layer after pressing is preferably 1.70 g/cm^3 or more, more preferably 1.75 g/cm^3 or more. Based on the theoretical density of graphite, the upper limit of the density of the negative electrode mixture layer formed using graphite is 2.1 to 2.2 g/cm^3. The density of the negative electrode mixture layer is preferably 2.0 g/cm^3 or less, more preferably 1.9 g/cm^3 or less from the viewpoint of the affinity with the nonaqueous electrolyte. It is preferable to press the negative electrode plural times since the negative electrode can be uniformly pressed.

The binder used in the negative electrode is not particularly limited. For the increase of the content of the active material to increase the capacity, the amount of the binder is preferably made as small as possible. To this end, the binder is preferably a mixture of an aqueous resin which can be dissolved or dispersed, and a rubbery polymer, since the use of only a small amount of the aqueous resin can contribute to the dispersion of the graphite and thus prevents the delamination of the negative electrode mixture layer from the current collector caused by the expansion and contraction of the electrode in the charge-discharge cycles.

Examples of the aqueous resins include cellulose resins such as carboxymethylcellulose, and hydroxypropylcellulose, and polyvinylpyrrolidone, polyepichlorohydrin, polyvinylpyridine, polyvinyl alcohol, polyether resins such as polyethylene oxide and polyethylene glycol, etc. Examples of the rubbery polymers include latex, butyl rubber, fluororubber, styrene-butadiene rubber, nitrile-butadiene copolymer rubber, ethylene-propylene-diene copolymer (EPDM), polybutadiene, etc. From the viewpoint of the dispersibility of the graphite particles and the prevention of delamination of the layer, it is preferable to use a cellulose ether compound such as carboxymethylcellulose together with a butadiene copolymer rubber such as a styrene-butadiene rubber. It is particularly preferable to use carboxymethylcellulose together with a butadiene copolymer rubber such as a styrene-butadiene copolymer rubber or a nitrile-butadiene-copolymer rubber. The cellulose ether compound such as carboxymethylcellulose mainly has a thickening effect on the paste containing the negative electrode mixture, while the rubbery polymer such as the styrene-butadiene copolymer rubber has a binding effect on the negative electrode mixture. When the cellulose ether compound such as carboxymethylcellulose and the rubbery polymer such as the styrene-butadiene copolymer rubber are used in combination, the weight of the former to the latter is preferably from 1:1 to 1:15.

The thickness of the negative electrode mixture layer is preferably from 40 to 200 μm. The thickness of the current collector used in the negative electrode is preferably from 5 to 30 μm.

In the negative electrode mixture layer, the content of the binder or binders is preferably 1.5% by weight or more, more preferably 1.8% by weight or more, particularly preferably 2.0% by weight or more of the layer, while it is preferably less than 5% by weight, less than 3% by weight, less than 2.5% by weight. When the amount of the binder in the negative electrode mixture layer is too large, the discharge capacity of the battery may decrease. When the amount is too small, the adhesion between the particles decreases. The content of the negative electrode active material in the negative electrode mixture layer is preferably more than 95% by weight and 98.5% by weight or less.

In the nonaqueous secondary battery of the present invention, the nonaqueous electrolyte is preferably a nonaqueous solvent-base electrolytic solution comprising an electrolyte salt such as a lithium salt dissolved in a nonaqueous solvent such as an organic solvent, from the viewpoint of electric characteristics or handling easiness. A polymer electrolyte or a gel electrolyte may be used without any problem.

The solvent in the nonaqueous electrolytic solution is not particularly limited, and examples thereof include acyclic esters such as dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, and methyl propyl carbonate; cyclic esters having a high dielectric constant, such as ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate; and mixed solvents comprising an acyclic ester and a cyclic ester. Mixed solvents each comprising an acyclic ester as a main solvent and a cyclic ester are particularly suitable.

Apart form the esters exemplified above, the following solvents may also be used: acyclic phosphoric acid triesters such as trimethyl phosphate; ethers such as 1,2-dimethoxyethane, 1,3-dioxolane, tetrahydrofuran, 2-methyl-tetrahydrofuran and diethyl ether; nitrites and dinitriles; isocyanates; and halogen-containing solvents. Furthermore, amine or imide organic solvents may be used.

Furthermore, the nonaqueous electrolytic solution may contain a fluorine-containing organic solvent, which can improve the stability of the battery since it forms a surface protective film on the positive electrode active materials during charging. More preferably, a fluorine-containing organic solvent having a carbon-carbon double bond may be used in combination with other usual fluorine-containing organic solvent. Specific examples of the fluorine-containing organic solvent include HFE7100 ($C_4F_9OCH_3$), F-DPC [$C_2F_5CH_2O(C{=}O)OCH_2C_2F_5$], F-DEC [$CF_3CH_2O(C{=}O)OCH_2CF_3$], fluorobenzene, fluoroethylene carbonate [$(\text{—}OCH_2\text{—}CHFO\text{—}(C{=}O)$, $(\text{—}OCHF\text{—}CHFO\text{—})C{=}O$, etc.], and the like. The amount of such a solvent added is preferably at least 0.1% by weight, more preferably at least 2% by weight, particularly preferably at least 5% by weight, while it is preferably 30% by weight or less, more preferably 20% by weight or less, particularly preferably 15% by weight or less, based on the whole weight of the electrolyte. When the amount of such a solvent is too large, the electric characteristics of the battery tend to decrease. When it is too small, any good protective film may not be formed.

The nonaqueous electrolyte may contain a sulfur-containing organic solvent, which can improve the stability of the battery since it forms a surface protective film on the positive electrode active materials during charging. The sulfur-containing organic solvent is preferably an organic compound having $\text{—}O\text{—}SO_2\text{—}$ bond, more preferably one having a $\text{—}O\text{—}SO_2\text{—}O\text{—}$ bond. Specific examples of such a solvent include sulfone, methylsulfolane, methylethylene sulfate, 1,3-propanesulfone, diethyl sulfate, butyl sulfate, butylsulfone, diphenyldisulfide, etc. The amount of such a solvent is preferably at least 0.1% by weight, more preferably at least 1% by weight, particularly preferably at least 2% by weight, while it is preferably 10% by weight or less, more preferably 5% by weight or less, particularly preferably 3% by weight or less, based on the whole weight of the electrolyte. When the amount of such a solvent is too large, the electric characteristics of the battery tend to decrease. When it is too small, any good protective film may not be formed.

Furthermore, the nonaqueous electrolytic solution may preferably contain a nonionic aromatic compound. Specific examples thereof include aromatic compounds having an alkyl group bonded to an aromatic ring (e.g., cyclohexylbenzene, isopropylbenzene, tert-butylbenzene, tert-amylbenzene, octylbenzene, toluene and xylene); aromatic compounds having a halogen group bonded to an aromatic ring (e.g., fluorobenzene, difluorobenzene, trifluorobenzene and chlorobenzene); aromatic compounds having an alkoxy group bonded to an aromatic ring (e.g., anisole, fluoroanisole, dimethoxybenzene and diethoxybenzene); aromatic carboxylic acid esters such as phthalic acid esters (e.g., dibutyl phthalate and di-2-ethylhexyl phthalate) and benzoic acid esters; carbonic acid esters having a phenyl group (e.g., methylphenyl carbonate, butylphenyl carbonate and diphenyl carbonate); phenyl propionate; and biphenyl. Among them, the compounds having an alkyl group bonded to an aromatic ring (alkaryl compounds) are preferred, and cyclohexylbenzene is particularly preferred.

The aromatic compounds exemplified above can form a film on the surface of the active material in the positive electrode or the negative electrode in the battery. These aromatic compounds may be used alone, while more advantageous effects can be attained by the use of two or more of the aromatic compounds together. Particularly advantageous effects can be attained on the improvement of the safety of the battery by the use of the alkaryl compound together with an aromatic compound, which can be oxidized at a lower voltage than the alkaryl compound, such as biphenyl.

The method for adding the aromatic compound in the nonaqueous electrolytic solution is not particularly limited. In general, the aromatic compound is added to the nonaqueous electrolytic solution prior to the fabrication of the battery.

The content of the aromatic compound in the nonaqueous electrolytic solution is preferably 4% by weight or more from the viewpoint of the safety, and it is preferably 10% by weight or less from the viewpoint of the load characteristic. When two or more aromatic compounds are used together, the total amount thereof is within the above-mentioned range. When the alkaryl(alkylaryl) compound and the aromatic compound which can be oxidized at a lower voltage that the alkaryl compound are used in combination, the content of the alkaryl compound in the nonaqueous electrolytic solution is preferably 0.5% by weight or more, more preferably 2% by weight or more, while it is preferably 8% by weight or less, more preferably 5% by weight or less. The content of the aromatic compound that can be oxidized at a lower voltage than the alkaryl compound in the nonaqueous electrolytic solution is preferably 0.1% by weight or more, more preferably 0.2% by weight or more, while it is preferably 1% by weight or less, more preferably 0.5% by weight or less.

Furthermore, a surface protecting coating can be formed on the surface of the positive electrode active material in the step of initial charging of the battery, when the nonaqueous electrolytic solution contains at least one compound selected from the group consisting of halogen-containing organic solvents (e.g., halogen-containing carbonates), fluorine-containing organic lithium salts, phosphorus-containing organic solvents, silicon-containing organic solvents, nitrogen-containing organic solvents, etc. Specific examples thereof include F-DPC [$C_2F_5CH_2O(C{=}O)OCH_2C_2F_5$], F-DEC [$CF_3CH_2O(C{=}O)OCH_2CF_3$], HFE7100 ($C_4F_9OCH_3$), butyl sulfate ($C_4H_9OSO_2OC_4H_9$), methylethylene sulfate [$(\text{—}OCH(CH_3)CH_2O\text{—})SO_2$], butyl sulfate ($C_4H_9SO_2C_4H_9$), a polymer imide salt ([$\text{—}N(Li)SO_2OCH_2(CF_2)_4\text{—}CH_2OSO_2\text{—}]_n$ wherein n is from 2 to 100), $(C_2F_5SO_2)_2NLi$, and $[(CF_3)_2CHOSO_2]_2NLi$.

Such additives may be used alone. It is particularly preferable to use a fluorine-containing organic solvent together with a fluorine-containing organic lithium salt. The amount of such an additive added is preferably 0.1% by weight or more, more preferably 2% by weight or more, particularly preferably 5% by weight or more, while it is preferably 30% by weight or less, more preferably 10% by weight or less, each based on the whole weight of the nonaqueous electrolytic solution. When the amount of the additive is too large, the electric characteristics of the battery may deteriorate. When the amount is too small, a good coating may hardly be formed.

When the battery comprising the nonaqueous electrolytic solution containing the above-mentioned additive(s) is charged, particularly at a high voltage, a surface protecting coating that contains fluorine or sulfur atoms is formed on the positive electrode active material surface. This surface protecting coating may contain either fluorine atoms or sulfur atoms. Preferably, the coating contains both of fluorine atoms and sulfur atoms.

The amount of the sulfur atoms in the surface protecting coating formed on the positive electrode active material surface is preferably 0.5 atomic % or more, more preferably 1 atomic % or more, particularly preferably 3 atomic % or more. However, when the amount of the sulfur atoms in the positive electrode active material surface is too large, the discharge characteristic of the battery tends to decrease. Thus, the amount is preferably 20 atomic % or less, more preferably 10 atomic % or less, particularly preferably 6 atomic % or less.

The amount of the fluorine atoms in the surface protecting coating formed on the positive electrode active material surface is preferably 15 atomic % or more, more preferably 20 atomic % or more, particularly preferably 25 atomic % or more. However, when the amount of the fluorine atoms in the positive electrode active material surface is too large, the discharge characteristic of the battery tends to fall. Thus, the amount of the fluorine atoms is preferably 50 atomic % or less, more preferably 40 atomic % or less, particularly preferably 30 atomic % or less. The surface protecting coating, which contains the fluorine atoms and/or the sulfur atoms, in the positive electrode active material may not be formed by charging the battery as described above, but the positive electrode (battery) may be formed by the use of the positive electrode active material, that is, the lithium-containing transition metal oxides, which has such a surface protecting coating already formed.

In order to improve the charge-discharge cycle characteristic of the battery, preferably, the nonaqueous electrolytic solution contains at least one carbonate compound selected from the group consisting of vinylene carbonates, such as $(\text{—}OCH{=}CHO\text{—})C{=}O$, $(\text{—}OCH{=}C(CH_3)O\text{—})C{=}O$ and $(\text{—}OC(CH_3){=}C(CH_3)O\text{—})C{=}O$, and derivatives thereof; and fluorine-substituted ethylene carbonates, such as $(\text{—}OCH_2\text{—}CHFO\text{—})C{=}O$ and $(\text{—}OCHF\text{—}CHFO\text{—})C{=}O$. The addition amount thereof is preferably 0.1% by weight or more, more preferably 0.5% by weight or more, particularly preferably 2% by weight or more based on the whole weight of the nonaqueous electrolytic solution. When the addition amount thereof is too large, the load characteristic of the battery tends to decrease. Thus, the addition amount is preferably 10% by weight or less, more preferably 5% by weight or less, particularly preferably 3% by weight or less based on the whole weight of the nonaqueous electrolytic solution.

Examples of the electrolyte salt to be dissolved in the solvent during the preparation of the nonaqueous electrolytic solution include $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiSbF_6$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiCF_3CO_2$, $Li_2C_2F_4(SO_3)_2$, $LiN(RfSO_2)(Rf'SO_2)$, $LiC(RfSO_2)_3$, $LiC_nF_{2n+1}SO_3$ wherein $n \geq 2$, and $LiN(RfOSO_2)_2$ wherein Rf and Rf' each represent a fluoroalkyl group. They may be used alone or in combination of two or more thereof. Among these electrolyte salts, particularly preferred are fluorine-containing organic lithium salts having 2 or more carbon atoms, since such lithium salts have a large anionic property and further ion separation easily occurs so that the salts are easily dissolved in the above-mentioned solvents. The concentration of the electrolyte salt in the nonaqueous electrolytic solution is not particularly limited, and it is preferably 0.3 mol/L or more, more preferably 0.4 mol/L or more, while it is preferably 1.7 mol/L or less, more preferably 1.5 mol/L or less.

In the present invention, the nonaqueous electrolyte may be a gel-form polymer electrolyte besides the nonaqueous electrolytic solution described above. The gel-form polymer electrolyte corresponds to a product obtained by the gelation of the nonaqueous electrolytic solution with a gelling agent. For the gelation of the nonaqueous electrolytic solution, the following gelling agents may be used: a linear polymer such as polyvinylidene fluoride, polyethylene oxide or polyacrylonitrile, or a copolymer thereof; or a polyfunctional monomer which can be polymerized by irradiation with actinic rays such as ultraviolet rays or electron beams (e.g., an acrylate having 4 or more functionalities such as pentaerythritol tetraacrylate, ditrimethylolpropane tetraacrylate, ethoxylated pentaerythritol tetraacrylate, dipentaerythritol hydroxypentaacrylate, or dipentaerythritol hexaacrylate; or a methacrylate having 4 or more functionalities, which are analogous to the above acrylates. In the case of the monomer, the monomer itself does not cause the gelling of the electrolytic solution, but the polymer formed from the monomer acts as a gelling agent.

When a polyfunctional monomer is used to gel the electrolytic solution as described above, a polymerization initiator may optionally be used. Examples of the polymerization initiator include benzoyls, benzoin alkyl ethers, benzophenones, benzoylphenylphosphine oxides, acetophenones, thioxanthones and anthraquinones. As a sensitizer for the polymerization initiator, an alkylamine or an aminoester may be used.

In the present invention, the nonaqueous electrolyte may be a solid electrolyte besides the nonaqueous electrolytic solution or the gel-form polymer electrolyte. The solid electrolyte may be an inorganic solid electrolyte or an organic solid electrolyte.

In the present invention, a separator used in the present invention preferably has a thickness of 5 μm or more, more preferably 10 μm or more, particularly preferably 12 μm or more, while it is preferably less than 25 μm, more preferably less than 20 μm, particularly preferably less than 18 μm, from the viewpoint of imparting the directionality of the tensile strength to the separator, keeping good insulating properties and reducing the thermal shrinkage of the separator. The gas permeability of the separator is preferably 500 second/100-mL or less, more preferably 300 second/100-mL or less, particularly preferably 120 second/100-mL or less. As the gas permeability of the separator is smaller, the load characteristic is made better but an inside short-circuit is more easily caused. Thus, the gas permeability is preferably 50 second/100-mL or more. Here, a gas permeability is measured according to JIS P8117. As the thermal shrinkage factor of the separator in the transverse direction (TD) is smaller, an inside short-circuit is less easily caused when the temperature of the battery rises. Thus, the thermal shrinkage factor in TD of the separator is as small as possible. The thermal shrinkage factor in TD is preferably 10% or less, more preferably 5% or less. In order to restrain the thermal shrinkage of the separator, it is preferable to thermally treat the separator in advance at a temperature of about 100 to 125° C. The separator having such a thermal shrinkage factor is preferably combined with the positive electrode materials according to the present invention to fabricate a battery, since the behaviors of the battery at high temperature become stable.

The thermal shrinkage factor in TD of the separator means the shrinkage factor of a portion thereof that most largely shrinks in TD when the separator having a size of 30 mm square is allowed to stand at 105° C. for 8 hours.

With regard to the strength of the separator, a tensile strength in the machine direction (MD) is preferably 6.8×10^7 N/m^2 or more, more preferably 9.8×10^7 N/m or more. The tensile strength in TD is preferably smaller than that in MD.

The ratio of the tensile strength in TD to that in MD (tensile strength in TD/tensile strength in MD) is preferably 0.95 or less, more preferably 0.9 or less, while it is preferably 0.1 or more. The transverse direction means a direction perpendicular to the direction in which the film resin for the production of the separator is wound up, that is, the machine direction.

The puncture strength of the separator is preferably 2.0 N or more, more preferably 2.5 N or more. As this value is higher, the battery is less easily short-circuited. Usually, however, the upper limit thereof is substantially determined by the material of the separator. In the case of a separator made of polyethylene, the upper limit of the puncture strength is about 10 N. Here, a puncture strength is measured by cutting a sample piece of 50 mm×50 mm from a separator, clamping the sample piece with jigs at the edges of 5 mm, puncturing the sample piece with a needle having a tip end with a radius of 0.5 mm at a rate of 2 mm/sec., and measuring a maximum load before the puncture of the sample piece as a puncture strength.

When a conventional nonaqueous secondary battery is charged at a high positive electrode voltage of 4.35 V or higher with reference to the potential of lithium and is discharged to a final voltage higher than 3.2 V, the crystalline structure of the positive electrode active material decays to decrease the capacity or to induce heating of the battery due to the deterioration of the thermal stability. Thus, the battery may not be practically used. When a positive electrode active material to which a different element such as Mg or Ti is added is used, the decrease of the safety or of the capacity over charge-discharge cycles can be suppressed, but the degree of suppression is not sufficient. Moreover, the filling of the positive electrode is insufficient so that the battery easily expands.

In contrast, the battery of the present invention having the structure explained above is a nonaqueous secondary battery which improves the capacity, the charge-discharge cycle characteristic, the safety and the suppression of expansion of the battery. These advantageous effects can be attained at a usual charging volt (a battery voltage of 4.2 V). Furthermore, when the positive electrode is charged up to a high voltage of 4.35 V with reference to the potential of lithium (i.e., a battery voltage of 4.25 V) and then the discharge of the battery is terminated at a high voltage, that is, a battery voltage of 3.2 V or higher, the crystalline structures of the positive electrode active materials are very stable so that the decrease of the capacity or thermal stability is prevented.

Moreover, the positive electrode active material of any conventional nonaqueous secondary battery generates a low average voltage. Therefore, when a charge-discharge cycle test is repeated under a condition that the discharge final voltage of a unit cell is 4.35 V or higher with reference to the potential of lithium, the positive electrode is doped or dedoped with a large amount of Li ions. This situation is analogous to a case where the battery is subjected to a charge-discharge cycle test under an overcharge condition. Under such a severe condition, any conventional positive electrode active material cannot maintain its crystalline structure so as to cause disadvantages such that the thermal stability declines or the charge-discharge cycle life is shortened. To the contrary, the use of the positive electrode active materials according to the battery of the present invention can overcome such disadvantages of the conventional positive electrode active material. Thus, the present invention provides a nonaqueous secondary battery which can be reversibly charged and discharged even at a high voltage, such as a voltage of 4.35 to 4.6 V with reference to the potential of lithium.

The nonaqueous secondary battery of the present invention has characteristics including a high voltage, a high capacity and a high safety. By making use of such characteristics, the nonaqueous secondary battery of the present invention can be used as a power source of a notebook personal computer, a stylus-operated personal computer, a pocket personal computer, a notebook word processor, a pocket word processor, an electronic book player, a cellular phone, a codeless handset, a pager, a portable terminal, a portable copier, an electrical notebook, an electronic Calculator, a liquid crystal television set, an electric shaver, an electric power tool, an electronic translating machine, an automobile telephone, a transceiver, a voice input device, a memory card, a backup power source, a tape recorder, a radio, a headphone stereo, a handy printer, a handy cleaner, a portable CD player, a video movie, a navigation system, a refrigerator, an air conditioner, a television, a stereo, a water heater, a microwave oven, a dishwasher, a washing machine, a drying machine, a game equipment, a lighting equipment, a toy, a sensor equipment, a load conditioner, a medical machine, an automobile, an electric vehicle, a golf cart, an electrically-powered cart, a security system, a power storing system, or the like. The battery can be used not only for the consumer applications but also for aerospace applications. The capacity-increasing effect of the present invention is enhanced, in particular, in small-sized portable devices. Thus, the battery of the present invention is used in a portable device desirably having a weight of 3 kg or less, more desirably 1 kg or less. The lower limit of the weight of the portable device is not particularly limited. However, the lower limit is desirably a value equal to the weight of the battery, for example, 10 g or more in order to attain the advantageous effects to some degree.

EXAMPLES

The present invention will be described in detail with reference to the following Examples; however, the Examples do not limit the scope of the present invention. Thus, modifications of the examples are encompassed by the scope of the present invention as long as the modifications do not depart from the subject matter of the present invention, which has been described above or will be described hereinafter.

Example 1

Production of Positive Electrode

The lithium-containing positive electrode materials, $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm) as a positive electrode active material (A), and $LiCo_{0.994}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm) as a positive electrode active material (B) at a weight ratio of 65:35 were mixed. Then, 97.3 parts by weight of the mixture and 1.5 parts by weight of a carbonaceous material as an electric conductive aid were charged in a volumetric feeder as a device for supplying powder. An amount of a 10 wt. % solution of polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) to be supplied to the feeder was adjusted to control a solid content in the mixture constantly at 94% by weight during kneading. While the amount of the mixed materials supplied in a unit time was controlled to a predetermined amount, the materials were supplied in a biaxial kneading extruder and then kneaded. In this way, a paste containing the positive electrode mixture was prepared.

Separately, the positive electrode active materials (A) and (B) were dissolved in aqua regia and the ratio of the elements contained in the materials (A) and (B) was measured by the ICP atomic emission spectroscopy, the results of which confirmed that they had the above elementary compositions.

The resultant paste was charged in a planetary mixer, and then a 10 wt. % solution of PVDF in NMP, and NMP were added to dilute the paste, thereby adjusting the viscosity of the paste at a level sufficient for application. This diluted paste containing the positive electrode active material mixture was passed through a 70-mesh net to remove large substances. Thereafter, the paste was uniformly applied to both surfaces of a positive electrode current collector made of an aluminum foil with a thickness of 15 μm, and then dried to form film-form positive electrode mixture layers. In the dried positive electrode mixture layers, the weight ratio of the positive electrode active material/the electric conduction aiding agent/PVDF was 97.3:1.5:1.2. Thereafter, the resultant sheet was pressed and cut out in a predetermined size. To the cut piece, a lead member made of aluminum was welded to form a sheet-form positive electrode. The density of the pressed positive electrode mixture layers (the density of the positive electrode) was 3.8 g/cm^3. The thickness of the positive electrode mixture layers (the total thickness of the layers on both the surfaces, i.e., the thickness obtained by subtracting the thickness of the aluminum foil layer of the positive electrode current collector from the total thickness of the positive electrode) was 135 μm.

The particle size distribution of the mixture of the positive electrode active materials (A) and (B) was measured by a MICROTRAC particle size analyzer (HRA 9320 available from NIKKISO Co., Ltd.). The result is shown in the graph of FIG. **1**, which confirm that the mixture contained two kinds of the particles having an average particle size of about 5 μm and 12 μm, respectively.

In the positive electrode active material (A), the amount of Mg was 0.08% by mole, that of Ti was 0.04% by mole, and that of Al was 0.08% by mole, each based on the amount of Co. An electron prove X-ray microanalyzer (EMPA 1600 manufactured by Shimadzu Corporation) was used to measure the concentration of the metal element M^2 in cross sections of the particles. As a result, no difference in the concentration of each of Mg, Ti and Al was observed between the surface portion and the core portion.

In the positive electrode active material (B), the amount of Mg was 0.24% by mole, that of Ti was 0.12% by mole, and that of Al was 0.24% by mole, each based on the amount of Co. The concentration of the metal element M^2 in the cross sections of the particles was measured in the same manner as in the case of the positive electrode active material (A). As a result, no difference in the concentration of each of Mg, Ti and Al was observed between the surface portion and the core portion.

With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Production of Negative Electrode

As negative electrode active materials, 70 parts by weight of a graphite type carbonaceous materiel (a) (purity: 99.9% or more, average particle size: 18 μm, d_{002}: 0.3356 nm, size of the crystallite in the c axis direction (Lc): 100 nm, R value of the Raman spectrum: 0.18) and 30 parts by weight of a graphite type carbonaceous material (b) (purity: 99.9% or more, average particle size: 21 μm, d_{002}: 0.3363 nm, size of the crystallite in the c axis direction (Lc): 60 nm, R value of the Raman spectrum: 0.11) were mixed. Then, 98 parts by weight of the graphite mixture, 1 part by weight of carboxymethylcellulose and 1 part by weight of a styrene-butadiene rubber were mixed in the presence of water to prepare a paste containing negative electrode mixture. This paste was uniformly applied to both surfaces of a negative electrode current collector made of a strip-form copper foil having a thickness of 10 μm, and then dried to form negative electrode mixture layers. The resultant sheet was pressed with a roller until the density of the negative electrode mixture layers became 1.75 g/cm^3. The resultant sheet was then cut out in a predetermined size. Thereafter, a lead member made of nickel was welded to the cut piece to form a sheet-form negative electrode.

Preparation of Nonaqueous Electrolytic Solution

An amount of $LiPF_6$ was dissolved in a mixed solvent of methylethyl carbonate, diethyl carbonate and ethylene carbonate mixed at a volume ratio of 1.5:0.5:1 to attain a concentration of 1.2 mol/L. To this solution, 3% by weight of fluorobenzene, 0.2% by weight of biphenyl, 0.5%; by weight of propanesulfone, 10% by weight of $C_4F_9OCH_3$, and 3% by weight of vinylene carbonate were added to prepare a nonaqueous electrolytic solution.

Production of Nonaqueous Secondary Battery

The positive electrode and the negative electrode were spirally wound with interposing, therebetween, a separator made of a microporous polyethylene film (porosity: 53%, tensile strength in MD: 2.1×10^8 N/m^2, tensile strength in TD: 0.28×10^8N/m^2, thickness: 16 μm, gas permeability: 80 seconds/100-mL, thermal shrinkage factor after being kept at 105 CC for 8 hours: 3%, puncture strength: 3.5 N (360 g)), to form an electrode body having a spiral structure. Thereafter, the electrode body was pressed to form a flat-shaped electrode body and inserted into a box-shaped battery case made of an aluminum alloy. The positive and negative lead members were welded and a cover plate was laser welded to the edge portion of an opening of the battery case. Then, the nonaqueous electrolytic solution prepared in the above was poured into the battery case through an inlet made in the cover plate. The nonaqueous electrolytic solution was sufficiently infiltrated into the separator and the like. Thereafter, the battery was partially charged, and gas generated during the partial charging was discharged. Then, the inlet was sealed up to make the battery airtight. Thereafter, the battery was charged and aged to yield a rectangular nonaqueous secondary battery having a structure as shown in FIGS. **2**A and **2**B and an external appearance as shown in FIG. **3**, and a width of 34.0 mm, a thickness of 4.0 mm, and a height of 50.0 mm.

Here, the battery shown in FIGS. **2**A, **2**B and **3** will be explained. The positive electrode **1** and the negative electrode **2** are spirally wound with interposing the separator **3** therebetween, as described above, and the spirally wound electrode body is pressed in a flat form to form the electrode laminate **6** having a flat spiral structure. The laminate **6** together with a nonaqueous electrolytic solution is contained in the box-shaped battery case **4**. For simplicity, in FIG. **2**, metal foils as current collectors used to form the positive electrode **1** and the negative electrode **2**, and the electrolytic solution are not depicted.

The battery case **4** is made of an aluminum alloy, and constitutes a main part of the exterior package of the battery. This battery case **4** also functions as a positive electrode terminal. The insulator **5** made of a polytetrafluoroethylene sheet is arranged on the inside bottom of the battery case **4**. The positive electrode lead member **7** and the negative electrode lead member **8** connected to one end of the positive electrode **1** and that of the negative electrode **2**, respectively, are taken out from the electrode laminate **6** having the flat spiral structure. The terminal **11** made of stainless steel is attached to the cover plate **9** made of aluminum for closing the opening of the battery case **4** with interposing the insulation packing **10** made of polypropylene therebetween. The lead plate **13** made of stainless steel is attached to this terminal **11** with interposing the insulator **12** therebetween.

The cover plate **9** is inserted into the opening of the battery case **4**, and their joining portions are welded to each other, thereby closing the opening of the battery case **4** to make the interior of the battery airtight. In the battery shown in FIGS. **2**A and **2**B, the inlet **14** for pouring the electrolytic solution is made in the cover plate **9**, and the inlet **14** is welded and sealed up by, for example, laser welding, with inserting a sealing member (not shown). In this way, the air-tightness of the battery is kept. Accordingly, in the case of the battery shown in FIGS. **2**A, **2**B and **3**, the electrolytic solution pouring inlet **14** is actually composed of the inlet **14** and the sealing member, but the inlet **14** is illustrated as such without a sealing member in order to make the figure simple. The explosion-proof vent **15** is made in the cover plate **9**.

In the battery **1** of Example 1, the positive electrode lead member **7** is directly welded to the cover plate **9**, whereby the combination of the battery case **4** and the cover plate **9** functions as a positive electrode terminal. The negative electrode lead member **9** is welded to the lead plate **13**, and the negative electrode lead member **8** and the terminal **11** are made electrically conductive through the lead plate **13**, whereby the terminal **11** functions as a negative electrode terminal. However, the functions of the positive and negative electrodes may be reversed in accordance with the material of the battery case **4**, etc.

FIG. **3** is a perspective view schematically illustrating the external appearance of the battery shown in FIGS. **2**A and **2**B. FIG. **3** shows that the above-mentioned battery is a rectangular battery. Thus, FIG. **3** schematically shows the battery, and depicts the specific elements out of the constituting elements of the battery.

Example 2

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that fluorobenzene and $C_4F_9OCH_3$ were not used.

Example 3

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that propanesulfone was not used.

Example 4

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.9988}Mg_{0.0008}Ti_{0.0004}O_2$ (average particle size: 12 μm), and the positive electrode active material (B) was changed to $LiCo_{0.9964}Mg_{0.0024}Ti_{0.0012}O_2$ (average particle size: 5 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.79 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg and Ti in the positive electrode active material (B) were 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 5

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the weight ratio of the positive electrode active material (A) to the positive electrode active material (B) was changed to 90:10. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.75 g/cm^3.

Example 6

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that a mixture of the positive electrode active material (A) consisting of $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm), and the positive electrode active material (B) consisting of $LiCo_{0.994}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm) in a weight ratio of 50:50 was used as a positive electrode active material. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.76 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 7

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Sn_{0.0008}O_2$ (average particle size: 14 μm) and the positive electrode active material (B) was changed to $LiCo_{0.994}Mg_{0.0024}Ti_{0.0012}Sn_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.76 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Sn in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 8

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.998}Mg_{0.0008}Zr_{0.0004}Al_{0.0008}O_2$ (average particle size: 13 μm), and the positive electrode active material (B) was changed to $LiCo_{0.994}Mg_{0.0024}Zr_{0.0012}Al_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.8 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Zr and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 9

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.998}Mg_{0.0008}Ge_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm) and the positive electrode active material (B) was changed to $LiCo_{0.994}Mg_{0.0024}Ge_{0.0012}Al_{0.0024}O_2$ (average particle size: 6 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.79 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ge and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 10

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCo_{0.334}Ni_{0.33}Mn_{0.33}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.72 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg, Ti and Al in the positive electrode active material (B) were 3 times larger, 3 times larger and 3 times larger, respectively, than those in the positive electrode active material (A).

Example 11

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that this positive electrode active material (A) was changed to $LiCo_{0.9988}Mg_{0.0008}Ti_{0.0004}O_2$ (average particle size: 12 μm), and the positive electrode active material (B) was changed to $LiCo_{0.9988}Mg_{0.0008}Ti_{0.0004}O_2$ (average particle size: 5 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.79 g/cm^3. With regard to the contents of the metal elements M^2, the molar contents of Mg and Ti were the same in the positive electrode active materials (A) and (B).

Example 12

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that fluorobenzene was not used.

Example 13

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that methylethylenesulfate was used in place of propanesulfone.

Comparative Example 1

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that only $LiCo_{0.998}Mg_{0.0008}Ti_{0.0004}Al_{0.0008}O_2$ (average particle size: 12 μm) was used as a positive electrode active material. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.7 g/cm^3. This is a comparative example using only a positive electrode active material having a large particle size, that is, the positive electrode active material (A), among the positive electrode active materials used in Example 1.

Comparative Example 2

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that only

$LiCo_{0.994}Mg_{0.0024}Ti_{0.0012}Al_{0.0024}O_2$ (average particle size: 5 μm) was used as a positive electrode active material. The density of the positive electrode mixture layers (positive electrode) after pressing was 3.6 g/cm^3. This is a comparative example using only a positive electrode active material having a small particle size, that is, the positive electrode active material (B), among the positive electrode active materials used in Example 1.

Comparative Example 3

A nonaqueous secondary battery was fabricated in the same manner as in Example 1 except that the positive electrode active material (A) was changed to $LiCoO_2$ (average particle size: 12 μm), and the positive electrode active material (B) was changed to $LiCoO_2$ (average particle size: 5 μm). The density of the positive electrode mixture layers (positive electrode) after pressing was 3.8 g/cm^3.

Comparative Example 4

A nonaqueous secondary battery was fabricated in the same manner as in Comparative Example 1 except that $C_4F_9OCH_3$ was not used. This is a comparative example using only a positive electrode active material having a large particle size, that is, the positive electrode active material (A) used in Example 1, and no fluorine-containing organic solvent.

Comparative Example 5

A nonaqueous secondary battery was fabricated in the same manner as in Comparative Example 1 except that propanesulfone was not used. This is a comparative example using only a positive electrode active material having a large particle size, that is, the positive electrode active material (A) used in Example 1, and no sulfur-containing organic solvent.

With the nonaqueous secondary batteries fabricated in Examples 1-13 and Comparative Examples 1-5, the following properties were evaluated:

Discharge Capacity after Charge-Discharge Cycles

Each of the batteries fabricated in Examples and Comparative Examples was charged at a constant current of 0.2 C up to a voltage of 4.2 V or 4.4 (corresponding to 4.3 V and 4.5 V with reference to the potential of lithium), and then charged at a constant voltage until the total charge time reached 8 hours. Subsequently, the battery was discharged at a constant current of 0.2 C down to a voltage of 3.3 V. Thereby, a discharge capacity of the battery was measured. Then, the above charge-discharge cycle was repeated five times, and the discharge capacity after the fifth cycle was used to evaluate the discharge capacity after the charge-discharge cycles. The results are shown in Table 1. In Table 1, the discharge capacity after the charge-discharge cycles obtained with each battery is shown as a relative value in relation to the discharge capacity of the battery of Comparative Example 1 after the charge-discharge cycles, which is “100”.

TABLE 1

Discharge Capacity after Charge-Discharge Cycles

Example	Charge voltage	
No.	4.2 V	4.4 V
1	103	140
2	102	137
3	102	137
4	103	139
5	103	134
6	103	135
7	103	138
8	103	136
9	103	138
10	103	138
11	102	122
12	102	138
13	102	146
C. 1	100	100
C. 2	99	104
C. 3	102	73
C. 4	100	93
C. 5	102	90

The battery of Example 1 was disassembled after it was charged up to 4.4 V, and the surface of the positive electrode was analyzed by X-ray photoelectron spectroscopy (XPS). The contents of the fluorine atom and sulfur atom were 25 atomic % and 5 atomic %, respectively. In the batteries of Examples 2 and 12, the content of the fluorine atom was 11 atomic % and 20 atomic %, respectively.

The content of the sulfur atoms on the surface of the positive electrode of the battery of Example 3 was less than the detection limit, while it was 4% in the battery of Example 13.

Herein, the XPS analysis of elements was carried out with PHI ESCA 5500MC (manufactured by ULVAC-PHI, Inc.) using the Al—Kα ray at 400 W. Then, an obtained curve was subjected to peak separation, and an atomic percentage of each atom is a ratio of the peak area for each atom to the total peak area for all the atoms.

Safety Evaluation

Each of the batteries fabricated in Examples and Comparative Examples was charged at a constant current of 0.2 C up to 4.4 V, and then charged at a constant voltage until the total charge time reached 8 hours. Subsequently, in a temperature-controlled bath, the battery was heated at a heating rate of 5° C./min. up to 150° C. and maintained at 150° C. for 10 minutes. During this 10 minute period, the change of the surface temperature of the battery was monitored. The lower surface temperature during heating means better safety at high temperature. The results are shown in Table 2.

TABLE 2

Safety Evaluation

Example No.	Charge voltage 4.4 V
1	155
2	158
3	156
4	160
5	155
6	162
7	159
8	156
9	156
10	154
11	167
12	157
13	156

TABLE 2-continued

Safety Evaluation	
Example No.	Charge voltage 4.4 V
C. 1	>170
C. 2	168
C. 3	>170
C. 4	>170
C. 5	>170

As can be seen from the results in Tables 1 and 2, the nonaqueous secondary batteries of Examples 1-13 according to the present invention had larger discharge capacities and better charge-discharge cycle characteristics than those of Comparative Examples 1-5, and further, they suffered from less temperature rising in the full-charged or overcharged state, and had excellent safety.

The invention claimed is:

1. A nonaqueous secondary battery comprising:

a positive electrode having a positive electrode mixture layer, a negative electrode, and a nonaqueous electrolyte,

wherein the positive electrode comprises, as active materials, at least two lithium-containing transition metal oxides having different average particle sizes, and the lithium-containing transition metal oxide having the smallest average particle size is a lithium-containing transition metal oxide represented by the formula (1):

$$Li_xM^1_yM^2_zM^3_vO_2 \quad (1)$$

wherein M^1 represents at least one transition metal element selected from Co, Ni and Mn, M^2 represents Mg and at least one metal element selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn, M^3 represents at least one element selected from the group consisting of Na, K, Rb, Be, Ca, Sr, Ba, Sc, Y, La, Hf, V, Ta, Cr, Mo, W, Tc, Re, Fe, Ru, Rh, Cu, Ag, Au, B, Ca, In, Si, P and Bi, and x, y, z and v are numbers satisfying the equations respectively: $0.97 \le x < 1.02$, $0.8 \le y < 1.02$, $0.002 \le z \le 0.05$, and $0 \le v \le 0.05$, and has an average particle size from 2 μm to 10 μm, and the lithium-containing transition metal oxide having the largest average particle size is a lithium-containing transition metal oxide represented by the formula (2):

$$Li_aM^1_bM^2_cM^3_dO_2 \quad (2)$$

wherein M^1, M^2 and M^3 are the same as defined in the formula (1), and a, b, c and d are numbers satisfying the equations respectively: $0.97 \le a < 1.02$, $0.8 \le b < 1.02$, $0.0002 \le c \le 0.02$, and $0 \le d \le 0.02$, and has an average particle size from 5 μm to 25 μm,

wherein said electrolyte contains a fluorine-containing organic solvent,

wherein the content of Co in the transition metal M^1 of the formulae (1) and (2) is from 30% by mole to 100% by mole,

wherein the content of said lithium-containing transition metal oxide having the smallest average particle size in the lithium-containing transition metal oxides is from 5% by weight to 60% by weight,

wherein the content of said lithium-containing transition metal oxide having the largest average particle size in the lithium-containing transition metal oxides is from 40% by weight to 95% by weight, and

wherein an amount of said fluorine-containing organic solvent is 0.1% by weight to 30% by weight based on the whole weight of the electrolyte.

2. The nonaqueous secondary battery according to claim **1**, wherein the lithium-containing transition metal oxide having the largest average particle size is a lithium-containing transition metal oxide represented by the formula (2) wherein c and d satisfy the following equation, respectively: $0.0002 \le c < 0.005$ and $0 \le d < 0.005$.

3. The nonaqueous secondary battery according to claim **2**, wherein z in the formula (1) is larger than c in the formula (2).

4. The nonaqueous secondary battery according to claim **1**, wherein z in the formula (1) is larger than c in the formula (2).

5. The nonaqueous secondary battery according to claim **1**, wherein, in the formula (1), the metal elements M^2 are Mg and at least one metal element selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn; a content of Mg is from 0.1% by mole to less than 2% by mole based on the amount of the transition metal M^1; when Ti, Zr, Ge or Nb is contained, a total content thereof is from 0.05% by mole to less than 0.5% by mole based on the amount of the transition metal M^1; and when Al or Sn is contained, a total content thereof is from 0.1% by mole to less than 1% by mole based on the amount of the transition metal M^1.

6. The nonaqueous secondary battery according to claim **1**, wherein, in the formula (2), the metal elements M^2 are Mg and at least one metal element selected from the group consisting of Ti, Zr, Ge, Nb, Al and Sn; a content of Mg is from 0.01% by mole to less than 0.5% by mole based on the amount of the transition metal M^1; when Ti, Zr, Ge or Nb is contained, a total content thereof is from 0.005% by mole to less than 0.3% by mole based on the amount of the transition metal M^1; and when Al or Sn is contained, a total content thereof is from 0.01% by mole to less than 0.5% by mole based on the amount of the transition metal M^1.

7. The nonaqueous secondary battery according to claim **1**, wherein said positive electrode mixture layer has a density of 3.5 to 4.6 g/cm^3.

8. The nonaqueous secondary battery according to claim **1**, wherein said electrolyte further contains a fluorine-containing aromatic compound other than said fluorine-containing organic solvent.

9. The nonaqueous secondary battery according to claim **1**, wherein the fluorine-containing organic solvent is fluoroethylene carbonate.

10. The nonaqueous secondary battery according to claim **1**, wherein M^1 represents Co.

11. A method of using a nonaqueous secondary battery according to claim **1** comprising the step of:

charging the battery so that a positive electrode voltage is in a range of 4.35 to 4.6 V with reference to the potential of lithium when the battery is fully charged.

* * * * *

Exhibit 4

US009166251B2

(12) **United States Patent**
Katayama et al.

(10) **Patent No.: US 9,166,251 B2**
(45) **Date of Patent: Oct. 20, 2015**

---

(54) **BATTERY SEPARATOR AND NONAQUEOUS ELECTROLYTE BATTERY**

(75) Inventors: **Hideaki Katayama**, Ibaraki (JP); **Mitsuhiro Kishimi**, Ibaraki (JP); **Yoshinori Sato**, Ibaraki (JP); **Yasutaka Kuroki**, Ibaraki (JP); **Toshiyuki Edamoto**, Ibaraki (JP)

(73) Assignee: **HITACHI MAXELL, LTD.**, Ibaraki-Shi (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 846 days.

(21) Appl. No.: **12/673,961**

(22) PCT Filed: **Sep. 30, 2008**

(86) PCT No.: **PCT/JP2008/067757**

§ 371 (c)(1), (2), (4) Date: **Feb. 17, 2010**

(87) PCT Pub. No.: **WO2009/044741**

PCT Pub. Date: **Apr. 9, 2009**

(65) **Prior Publication Data**

US 2011/0052987 A1 Mar. 3, 2011

(30) **Foreign Application Priority Data**

Oct. 3, 2007	(JP)	2007-259575
Feb. 21, 2008	(JP)	2008-039527

(51) **Int. Cl.**
H01M 2/14 (2006.01)
H01M 10/0525 (2010.01)
(Continued)

(52) **U.S. Cl.**
CPC ***H01M 10/0525*** (2013.01); ***H01M 2/166*** (2013.01); ***H01M 2/1646*** (2013.01); ***H01M 2/1653*** (2013.01); ***H01M 10/4235*** (2013.01); *Y02E 60/122* (2013.01)

(58) **Field of Classification Search**
CPC H01M 2/1686; H01M 2/1673; H01M 2/14
USPC 429/144, 145
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,447,958	B1	9/2002	Shinohara et al.
2001/0005560	A1	6/2001	Yoshida et al.

(Continued)

FOREIGN PATENT DOCUMENTS

CN	101019266	A	8/2007
EP	1 115 166	A1	7/2001

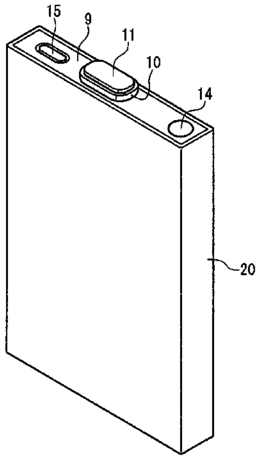
(Continued)

Primary Examiner — Stewart Fraser
Assistant Examiner — Olatunji Godo
(74) *Attorney, Agent, or Firm* — Birch, Stewart, Kolasch & Birch, LLP

(57) **ABSTRACT**

A nonaqueous electrolyte battery of the present invention includes a positive electrode having a positive active material capable of intercalating and deintercalating a lithium ion, a negative electrode having a negative active material capable of intercalating and deintercalating a lithium ion, a separator interposed between the positive electrode and the negative electrode, and a nonaqueous electrolyte. The heat generation starting temperature of the positive electrode is 180° C. or higher. The separator includes heat-resistant fine particles and a thermoplastic resin. The proportion of particles with a particle size of 0.2 μm or less in the heat-resistant fine particles is 10 vol % or less and the proportion of particles with a particle size of 2 μm or more in the heat-resistant fine particles is 10 vol % or less. The separator effects a shutdown in the range of 100° C. to 150° C.

37 Claims, 2 Drawing Sheets



(51) **Int. Cl.**

H01M 2/16	(2006.01)
H01M 10/42	(2006.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

2004/0191611	A1	9/2004	Imachi et al.	
2006/0141352	A1 *	6/2006	Kato et al.	429/144
2007/0231700	A1	10/2007	Watanabe	
2007/0264577	A1	11/2007	Katayama et al.	
2008/0038631	A1	2/2008	Nakura et al.	
2010/0221965	A1	9/2010	Katayama et al.	

FOREIGN PATENT DOCUMENTS

JP	2000-30686	A	1/2000
JP	2004-296325	A	10/2004
JP	2004-303474	A	10/2004
JP	2006-139978	A	6/2006
JP	2006-269359	A	10/2006
JP	2006-351386	A	12/2006
JP	2007-157723	A	6/2007
JP	2007-273123	A	10/2007
JP	2007-273443	A	10/2007
JP	2007-280911	A	10/2007
JP	2007-335294	A	12/2007
JP	2008-27634	A	2/2008
JP	2008-123996	A	5/2008
JP	2008-210541	A	9/2008
KR	10-2007-0083975	A	8/2007
WO	WO-00/79618	A1	12/2000
WO	WO 2006/062153	A1	6/2006
WO	WO-2007/066768	A1	6/2007
WO	WO 2009/096451	A1	8/2009

* cited by examiner

FIG. 1A

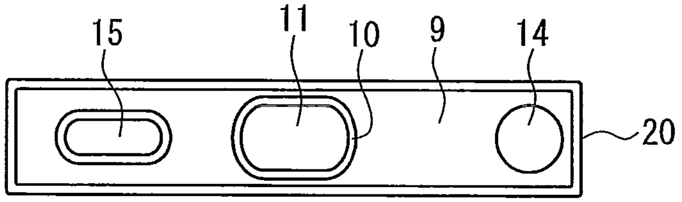
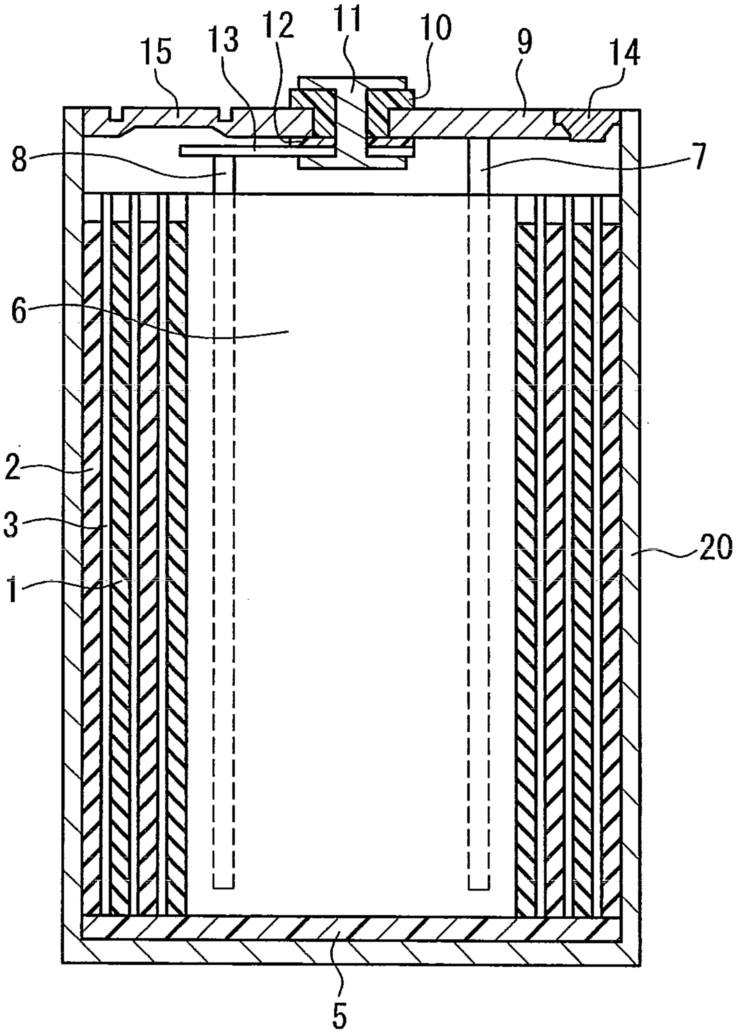


FIG. 1B



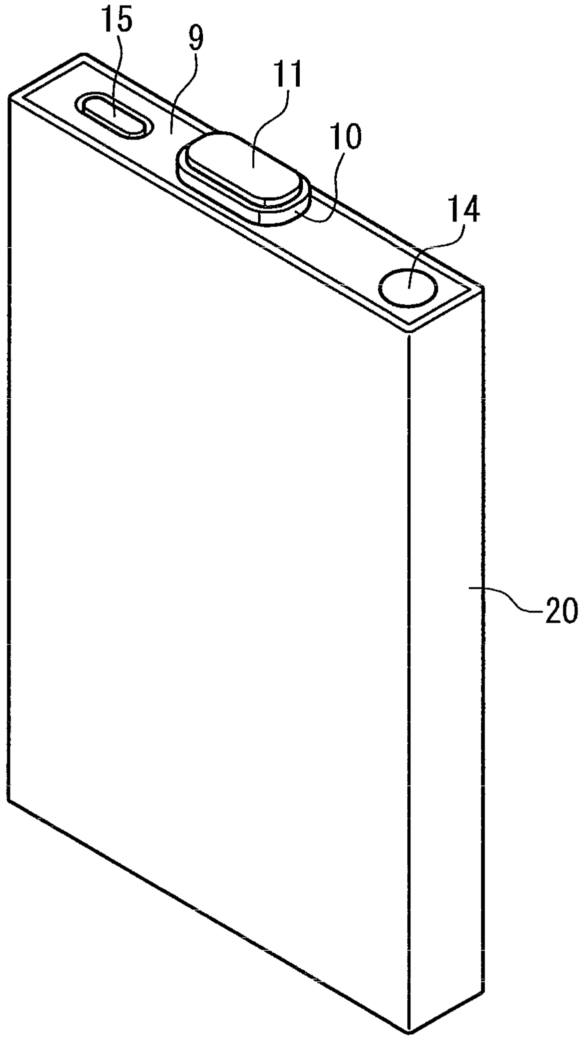


FIG. 2

BATTERY SEPARATOR AND NONAQUEOUS ELECTROLYTE BATTERY

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a National Phase application of PCT/JP2008/067757 filed on Sep. 30, 2008, which claims the benefit under 35 U.S.C. §119(a) to Japanese Patent Application Nos. 2007-259575 (filed on Oct. 3, 2007), and 2008-039527 (filed on Feb. 21, 2008). The entire contents of all of the above applications are hereby incorporated by reference.

TECHNICAL FIELD

The present invention relates to a nonaqueous electrolyte battery that is safe from being allowed to stand at high temperatures.

BACKGROUND ART

A nonaqueous electrolyte battery such as a lithium ion battery is characterized by a high energy density and thus has been widely used as a power source for portable equipment such as a portable telephone and a notebook personal computer. In recent years, the capacity of the nonaqueous electrolyte battery is likely to increase further as the performance of the portable equipment becomes higher. In parallel with this, it is also important to ensure safety.

In the current nonaqueous electrolyte battery, e.g., a polyolefin microporous film with a thickness of about 20 to 30 μm is used as a separator that is interposed between a positive electrode and a negative electrode. However, the commonly used separator easily shrinks when the temperature in the battery becomes extremely high, and can cause a short circuit. Therefore, as a means of improving the safety of the nonaqueous electrolyte battery, the heat resistance of the separator may be improved.

On the other hand, e.g., when the nonaqueous electrolyte battery in a charged state is placed in a high-temperature environment, heat can be generated from the positive electrode to raise the temperature in the battery further. Therefore, as a means of improving the safety of the nonaqueous electrolyte battery, a positive active material having high thermal stability also may be used.

For example, Patent Documents 1 and 2 propose a nonaqueous electrolyte battery that uses a positive active material having high thermal stability along with a separator having good heat resistance. However, in the technology as disclosed in Patent Document 1, there is a limit to the reduction in thickness of the separator because a nonwoven fabric or paper is used for the separator. For example, if the separator has a thickness of 30 μm or less and an active material such as graphite is used for the negative electrode, a short circuit may be likely to occur. Moreover, the technology as disclosed in Patent Document 2 focuses only on thermal shrinkage of the separator at 120° C. Thus, it is difficult to ensure the safety of the battery at temperatures higher than this.

Patent Documents 3 to 7 propose a multilayer separator that includes a high heat-resistant layer as a technology for preventing a short circuit due to thermal shrinkage of the separator. However, the separator needs to be further improved to achieve the safety of the battery at even higher temperatures.

For example, in the case of an electrode body obtained by winding the positive electrode and the negative electrode with the separator interposed between them, a short circuit can occur due to thermal shrinkage of the separator in the width direction. Thus, it is necessary to suppress the thermal shrinkage in the width direction.

Patent Document 1: JP 2004-296325 A
Patent Document 2: JP 2004-303474 A
Patent Document 3: JP 2006-351386 A
Patent Document 4: WO 2007/66768
Patent Document 5: JP 2007-273123 A
Patent Document 6: JP 2007-273443 A
Patent Document 7: JP 2007-280911 A

DISCLOSURE OF INVENTION

Therefore, with the foregoing in mind, it is an object of the present invention to provide a battery separator that can constitute a nonaqueous electrolyte battery having excellent safety in a high-temperature environment, and a nonaqueous electrolyte battery using the battery separator.

A battery separator of the present invention includes heat-resistant fine particles and a thermoplastic resin. The proportion of particles with a particle size of 0.2 μm or less in the heat-resistant fine particles is 10 vol % or less and the proportion of particles with a particle size of 2 μm or more in the heat-resistant fine particles is 10 vol % or less. A shutdown is effected in the range of 100° C. to 150° C.

A nonaqueous electrolyte battery of the present invention includes the following: a positive electrode having a positive active material capable of intercalating and deintercalating a lithium ion; a negative electrode having a negative active material capable of intercalating and deintercalating a lithium ion; a separator interposed between the positive electrode and the negative electrode; and a nonaqueous electrolyte. A heat generation starting temperature of the positive electrode is 180° C. or higher. The separator includes heat-resistant fine particles and a thermoplastic resin. The proportion of particles with a particle size of 0.2 μm or less in the heat-resistant fine particles is 10 vol % or less and the proportion of particles with a particle size of 2 μm or more in the heat-resistant fine particles is 10 vol % or less. The separator effects a shutdown in the range of 100° C. to 150° C.

In the nonaqueous electrolyte battery of the present invention, the heat generation starting temperature of the positive electrode is as high as 180° C. or higher. This can suppress heat to be generated from the positive electrode when the battery is placed in a high-temperature environment. Moreover, the nonaqueous electrolyte battery uses the battery separator that includes a thermoplastic resin and heat-resistant fine particles containing particles with a particle size of 0.2 μm or less in a proportion of 10 vol % or less and particles with a particle size of 2 μm or more in a proportion of 10 vol % or less, and that effects a shutdown in the range of 100° C. to 150° C. This can reliably prevent a short circuit due to contact between the positive electrode and the negative electrode at high temperatures. As a result of these effects, it is possible to provide a nonaqueous electrolyte battery having excellent safety in a high-temperature environment.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1**A is a schematic plan view of a nonaqueous electrolyte battery of the present invention. FIG. **1**B is a schematic cross-sectional view of a nonaqueous electrolyte battery of the present invention.

FIG. **2** is schematic diagram showing the appearance of a nonaqueous electrolyte battery of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

The heat generation starting temperature of the positive electrode of the nonaqueous electrolyte battery of the present invention is 180° C. or higher, and preferably 200° C. or higher.

In the present specification, the heat generation starting temperature of the positive electrode is determined as follows. First, a DSC curve is obtained by measuring the positive electrode in a charged state with a differential scanning calorimeter (DSC) from 30° C. at a rate of temperature rise of 10° C./min in the presence of a nonaqueous electrolyte used for the battery (as will be described later). In this DSC curve, the heat generation starting temperature indicates a temperature at an intersection point of two lines: one is an extension line of the base line on the high temperature side; and the other is a tangent to the curve of the exothermic peak on the low temperature side at a point where the curve has the maximum slope. The "charged state" of the positive electrode indicates a full-charge state according to the battery design. Specifically, assuming that the rated charging voltage of the battery is V_{max}, a constant-current and constant-voltage charge is performed in such a manner that the battery is charged at a constant current until the battery voltage reaches the V_{max}, and subsequently charged at a constant voltage of V_{max}. The battery is considered in the full-charge state when the current value during the constant-voltage charge is reduced to 1/10 of a current value (1 C) based on the rated capacity of the battery.

The positive electrode of the present invention includes a current collector and a positive electrode mixture layer formed on one side or both sides of the current collector. The positive electrode mixture layer is composed of a positive electrode mixture that is obtained by mixing a positive active material, a conductive assistant, a binder, etc.

To set the heat generation starting temperature of the positive electrode at 180° C. or higher, it is preferable to use the positive active material having good thermal stability and a high heat generation starting temperature. Specifically, it is preferable to use at least one compound selected from the following: a spinel-type lithium-containing complex oxide expressed as a general formula $Li_{1+t}Mn_{(2-x)}M^1_xO_4$ (where M^1 is at least one element selected from the group consisting of Fe, Ni, Mg, Zn, Co, Cr, Al, B, V, Si, Sn, Nb, Ta, Cu, Mo, Ti, and W, $-0.1 \leq t \leq 0.1$, and $0 \leq x \leq 0.6$); an olivine-type lithium-containing complex oxide expressed as a general formula LiM^2PO_4 (where M^2 is Co, Ni, Mn, or Fe); a lithium-containing complex oxide having a layered crystal structure expressed as a general formula $Li_{(1+a)}M^3_{2b}Mn_{(0.5-b)}Ni_{(0.5-b)}O_2$ (where M^3 is at least one element selected from the group consisting of Fe, Mg, Zn, Co, Cr, Al, B, V, Si, Sn, Nb, Ta, Cu, Mo, Ti, and W, $-0.1 < a < 0.1$, and $0 \leq b \leq 0.05$); and a lithium-containing complex oxide expressed as a general formula $Li_{(1+y+\alpha)}Ni_{(1-y-z-\delta)/2}Mn_{(1-y-z-\delta)/2}M^4_zO_2$ (where M^4 is at least one element selected from the group consisting of Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, Sn, Mg, and Zr, $-0.1 \leq y \leq 0.1$, $-0.05 \leq \alpha \leq 0.05$, $0 \leq z < 0.45$, and $-0.24 \leq \delta \leq 0.6$). In particular, the lithium-containing complex oxide expressed as the general formula $Li_{(1+y+\alpha)}Ni_{(1-y-z+\delta)/2}Mn_{(1-y-z-\delta)/2}M^4_zO_2$ is preferred, in which $0 \leq y \leq 0.05$ is more preferred, $0 \leq z \leq 0.4$ is more preferred, $-0.1 \leq \delta$ is more preferred, and $\delta \leq 0.24$ is more preferred.

Although only the above compounds can be used as the positive active material, another compound such as $LiCoO_2$ having a low heat generation starting temperature may be used with the above compounds unless the heat generation starting temperature of the positive electrode is below 180° C. The particle size of the positive active material is preferably 0.01 to 30 μm.

The conductive assistant of the positive electrode may be a carbon material such as carbon black. The binder of the positive electrode may be a fluorocarbon resin such as polyvinylidene fluoride (PVDF).

The current collector of the positive electrode may be, e.g., a foil, a punched metal, a mesh, or an expanded metal, which are made of aluminum or the like. In general, an aluminum foil with a thickness of 10 to 30 μm can be suitably used.

A lead portion of the positive electrode is generally provided in the following manner. A part of the current collector remains exposed without forming the positive electrode mixture layer when the positive electrode is produced, and this exposed portion can serve as the lead portion. However, the lead portion does not necessarily need to be integrated with the current collector from the beginning and may be provided by connecting an aluminum foil or the like to the current collector afterward.

The composition of the positive electrode mixture layer of the positive electrode is preferably 80 to 98 mass % of the positive active material, 1 to 18 mass % of the conductive assistant, and 1 to 10 mass % of the binder. The thickness of the positive electrode mixture layer (per one side of the current collector) is preferably 20 to 100 μm.

To suppress thermal shrinkage and provide a shutdown property, it is preferable that the separator of the nonaqueous electrolyte battery of the present invention has a multilayer structure. Specifically, the multilayer structure includes a heat-resistant layer for suppressing the thermal shrinkage and isolating the positive electrode from the negative electrode at high temperatures and a shutdown layer for ensuring the shutdown property.

In the present specification, a shutdown is effected in such a manner that the resin constituting the separator is melted at a temperature not more than the thermal runaway (abnormal heat generation) temperature of the battery and the pores of the separator are filled with the molten resin, thereby increasing the internal resistance of the battery to interrupt the current.

A temperature at which the separator effects a shutdown (i.e., a shutdown temperature) is preferably 100° C. or higher, since if the shutdown temperature is too low, a shutdown is effected during the normal operation of the battery, and thus can increase the internal resistance of the battery. On the other hand, if the shutdown temperature of the separator is too high, the current interruption does not succeed by a shutdown when heat is rapidly generated due to, e.g., an internal short circuit of the battery. Therefore, the temperature in the battery is raised to a temperature close to or higher than the exothermic peak temperature of the positive active material, which may result in thermal runaway. Thus, the shutdown temperature is preferably at least 20° C. lower than the exothermic peak temperature of the positive electrode (i.e., the temperature at an apex of the exothermic peak of the DSC curve that is obtained to determine the heat generation starting temperature, as described above), and more preferably 150° C. or lower.

The separator has a structure in which the heat-resistant layer may be either integrated with the shutdown layer (i.e., a single film separator) or not integrated with the shutdown layer. In both cases, the shutdown temperature in the present specification is defined as a temperature at which a Gurley value obtained by a method according to the Japanese Industrial Standards (JIS) P 8117 and expressed as the length of time (seconds) it takes for 100 ml air to pass through a membrane at a pressure of 0.879 g/mm^2 is at least ten times as large as the Gurley value at room temperature before heating.

The heat-resistant layer of the separator is preferably a porous layer including heat-resistant fine particles and a binder as components. In the present specification, the "heat-resistant fine particles" are fine particles with a heat-resistant temperature of 200° C. or higher, and the "heat-resistant temperature" is a temperature at which a substantial physical change such as a thermal deformation does not occur.

The heat-resistant fine particles are not particularly limited as long as they are electrochemically stable and have electrical insulation, but are preferably inorganic fine particles. Specific examples of the inorganic fine particles include the following: fine particles of inorganic oxides such as an iron oxide, silica (SiO_2), alumina (Al_2O_3), TiO_2, and $BaTiO_3$; fine particles of inorganic nitrides such as an aluminum nitride and a silicon nitride; fine particles of hardly-soluble ionic crystals such as a calcium fluoride, a barium fluoride, and a barium sulfate; and fine particles of covalent crystals such as silicon and diamond. The inorganic oxide fine particles may be fine particles of materials derived from the mineral resources such as boehmite, zeolite, apatite, kaoline, mullite, spinel, olivine, and mica or artificial products of these materials. Moreover, the inorganic fine particles may be electrically insulating particles obtained by covering the surface of a conductive material with a material having electrical insulation (e.g., any of the above inorganic oxides). Examples of the conductive material include conductive oxides such as a metal, SnO_2, and an indium tin oxide (ITO) and carbonaceous materials such as carbon black and graphite.

Organic fine particles also can be used as the heat-resistant fine particles. Specific examples of the organic fine particles include the following: fine particles of cross-linked polymers such as polyimide, a melamine resin, a phenol resin, cross-linked polymethyl methacrylate (cross-linked PMMA), cross-linked polystyrene (cross-linked PS), polydivinylbenzene (PDVB), and a benzoguanamine-formaldehyde condensation product; and fine particles of heat-resistant polymers such as thermoplastic polyimide. The organic resin constituting these organic fine particles may be a mixture, a modified product, a derivative, a copolymer (a random copolymer, an alternating copolymer, a block copolymer, or a graft copolymer), or a cross-linked product (in the case of the heat-resistant polymer) of the above polymeric materials.

The above examples of the heat-resistant fine particles may be used individually or in combination of two or more. Among the above heat-resistant fine particles, the inorganic oxide fine particles are more suitable, and alumina, silica, and boehmite are even more suitable. This is because these materials have a high heat-resistant temperature as well as high electrochemical stability.

The heat-resistant fine particles contain particles with a particle size of 0.2 μm or less in a proportion of 10 vol % or less and particles with a particle size of 2 μm or more in a proportion of 10 vol % or less, and also have a narrow particle size distribution and a uniform particle size. This configuration can suppress thermal shrinkage of the separator at a temperature T (° C.) that is close to, e.g., 10° C. lower than the heat generation starting temperature of the positive electrode (in this case, the upper limit of T is 200° C., and T does not exceed 200° C. even if the heat generation starting temperature of the positive electrode is higher than 210° C.). Thus, it is possible to prevent the electrode body from being short-circuited due to the thermal shrinkage of the separator in the width direction.

To make the proportions of particles with a particle size of 0.2 μm or less and particles with a particle size of 2 μm or more in the heat-resistant fine particles not more than 10 vol %, respectively, the particle size of the material particles may be controlled in the range of 0.2 to 2 μm. If the particle size of the material particles is too large, the material particles can be pulverized with a grinder such as a ball mill, a sand mill, a jet mill, or a cyclone mill to reduce the particle size. If the particle size of the material particles is too small, the particles size can be increased with a granulator such as mechanofusion or a spray drier. Moreover, the particles with a particle size of 0.2 μm or less and the particles with a particle size of 2 μm or more may be filtered out with various types of classifiers such as a sieve, a classification cyclone, and a filter, so that the remaining particles are used.

The thermal shrinkage ratio of the separator of the present invention is preferably 10% or less, and more preferably 5% or less at the temperature T. Specifically, the thermal shrinkage ratio of the separator in the width direction is preferably 10% or less at 200° C. By controlling the particle size of the heat-resistant fine particles, the separator with such a small thermal shrinkage ratio can be achieved even if the separator has a structure in which the heat-resistant layer is integrated with the shutdown layer. Thus, it is possible to sufficiently suppress the occurrence of a short circuit due to shrinkage of the separator when the temperature in the battery becomes high. The thermal shrinkage ratio is preferably as small as possible, and particularly preferably 0%.

When the separator has a structure in which the heat-resistant layer and the shutdown layer are not integrated, but separated from each other, the thermal shrinkage ratio of the heat-resistant layer is preferably 10% or less, and more preferably 5% or less at the temperature T. Specifically, the thermal shrinkage ratio of the heat-resistant layer in the width direction is preferably 10% or less at 200° C. In this case, the above thermal shrinkage ratio also can be ensured by controlling the particle size of the heat-resistant fine particles. Thus, it is possible to sufficiently suppress the occurrence of a short circuit due to shrinkage of the shutdown layer when the temperature in the battery becomes high. Needless to say, the thermal shrinkage ratio is preferably as small as possible, and particularly preferably 0%.

By ensuring the above thermal shrinkage ratio, the separator can be maintained to have a width larger than, e.g., the width of the negative electrode at the temperature T when actually incorporated into the battery. Therefore, the occurrence of a short circuit can be sufficiently suppressed.

The average particle size of the heat-resistant fine particles is in the range of preferably 0.3 μm, more preferably 0.4 μm, most preferably 0.5 μm to preferably 1.5 μm, more preferably 1.2 μm, most preferably 1 μm. The average particle size of the heat-resistant fine particles can be defined as a number average particle size that is measured with a laser diffraction particle size analyzer (e.g., LA-920 manufactured by Horiba, Ltd.) by dispersing the heat-resistant fine particles in a medium, in which the particles are insoluble.

The heat-resistant fine particles can have any shape such as a sphere (true sphere or substantial sphere), a rugby ball, a polyhedron, or a plate-like particle. However, it is more preferable that the heat-resistant fine particles are in the form of plate-like particles. The use of plate-like particles as the heat-resistant fine particles makes it easier to form a heat-resistant layer that is less susceptible to thermal shrinkage. Therefore, even if the separator has a structure in which the heat-resistant layer is integrated with the shutdown layer that is a porous film made of a thermoplastic resin, thermal shrinkage of the whole separator caused by thermal shrinkage of the shutdown layer can be effectively suppressed. For example, the thermal shrinkage ratio of the separator can be 5% or less at 165° C., which is measured by a method as will be described later. Although the reason the thermal shrinkage of the separator or the heat-resistant layer is easily suppressed by using the heat-resistant fine particles in the form of plate-like particles is not clear, it is considered that the plane surfaces of the individual particles are likely to be oriented in the direction parallel to the plane direction of the separator, and the particles are more closely packed because of such orientation, thereby resisting the shrinkage.

In the present specification, the thermal shrinkage ratios of the separator and the heat-resistant layer are determined in the following manner. The separator or the heat-resistant layer is cut into 3 cm×3 cm, and then interposed between two glass plates, each of which has a thickness of 5 mm. This sample is allowed to stand in a thermostatic bath at a predetermined temperature for 1 hour and heated. Subsequently, dimensional changes of the sample are measured. That is, the thermal shrinkage ratio is defined as a ratio of decrease in the width of the separator after heating to that of the separator at room temperature before heating. When the thermal shrinkage ratio involves directivity, it is defined as a ratio of decrease in the width of the separator in the direction in which the separator shrinks the most.

In the present invention, it is preferable that the heat-resistant layer includes a binder to integrate the heat-resistant layer with the shutdown layer or the electrode, or to bind the heat-resistant fine particles constituting the heat-resistant layer. Examples of the binder include the following: an ethylene-vinyl acetate copolymer (EVA having 20 to 35 mol % of a structural unit derived from vinyl acetate); an ethylene-acrylic acid copolymer such as an ethylene-ethyl acrylate copolymer (EEA); fluoro-rubber; styrene-butadiene rubber (SBR); carboxymethyl cellulose (CMC); hydroxyethyl cellulose (HEC); polyvinyl alcohol (PVA); polyvinyl butyral (PVB); polyvinyl pyrrolidone (PVP); poly-N-vinylacetamide; a cross-linked acrylic resin; polyurethane; and an epoxy resin. The above examples of the binder may be used individually or in combinations of two or more.

Among the above binders, the heat-resistant resins having heat resistance at 150° C. or higher are suitable. In particular, highly flexible materials such as the ethylene-acrylic acid copolymer, the fluoro-rubber, and the SBR are more suitable. Specific examples of the highly flexible materials include the following: EVA, "EVAFLEX series (trade mane)" manufactured by DU PONT-MITSUI POLYCHEMICALS CO., LTD.; EVA manufactured by NIPPON UNICAR CO., LTD.; an ethylene-acrylic acid copolymer, "EVAFLEX-EEA series (trade name)" manufactured by DU PONT-MITSUI POLYCHEMICALS CO., LTD.; EEA manufactured by NIPPON UNICAR CO., LTD.; fluoro-rubber, "DAI-EL LATEX series (trade name)" manufactured by DAIKIN INDUSTRIES, Ltd.; SBR, "TRD-2001 (trade name)" manufactured by JSR Corporation; and SBR, "EM-400B (trade name)" manufactured by ZEON CORPORATION. Moreover, the cross-linked acrylic resin (self-cross-linking acrylic resin) that has a low glass transition temperature is also suitable, and includes butyl acrylate as the main component and has cross-linking of the butyl acrylate.

When the binder is used, it may be dissolved or emulsified in a medium (solvent) of a composition (slurry etc.) for forming the heat-resistant layer, as will be described later.

The heat-resistant layer may further include a porous base material as long as the heat resistance is not impaired. The porous base material may be, e.g., a porous film made of a heat-resistant resin, or a woven or nonwoven fabric made of heat-resistant fibers. Examples of the constituents of the porous base material includes the following: cellulose and a modified product of the cellulose such as carboxymethyl cellulose; polypropylene (PP); polyesters such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and polybutylene terephthalate (PBT); resins such as polyacrylonitrile (PAN), aramid, amide-imide, and polyimide; and inorganic materials (inorganic oxides) such as glass, alumina, and silica. The porous base material may include either one type or more than one type of these constituents. The porous base material also may include various types of additives (e.g., an antioxidant when the resin is used) as needed in addition to the above constituents.

The content of the heat-resistant fine particles in the heat-resistant layer is preferably 20 vol % or more, more preferably 50 vol % or more, and further preferably 80 vol % or more of the total volume of components in the heat-resistant layer. By increasing the content of the heat-resistant fine particles in the heat-resistant layer, thermal shrinkage of the heat-resistant layer or the whole separator can be favorably suppressed. As described above, the heat-resistant layer preferably includes a binder. In view of this, the preferred upper limit of the content of the heat-resistant fine particles in the heat-resistant layer is, e.g., 99 vol % of the total volume of components in the heat-resistant layer. If the content of the heat-resistant fine particles in the heat-resistant layer is too small, e.g., the content of the binder in the heat-resistant layer should be increased. In such a case, however, the pores of the heat-resistant layer are filled with the binder, which may impair, e.g., the function of the separator. On the other hand, if a hole-opening agent or the like is used to provide a porous heat-resistant layer, the space between the heat-resistant fine particles becomes extremely large, so that the effect of suppressing thermal shrinkage may be reduced.

The content of the binder in the heat-resistant layer is preferably 1 to 20 vol % of the total volume of components in the heat-resistant layer.

When the heat-resistant layer includes the porous base material composed of the heat-resistant resin or the heat-resistant fibers, the content of the heat-resistant resin or the heat-resistant fibers of the porous base material in the heat-resistant layer is in the range of preferably 10 vol %, more preferably 30 vol % to preferably 90 vol %, more preferably 70 vol % of the total volume of components in the heat-resistant layer.

The material of the shutdown layer of the separator is not particularly limited as long as it is a thermoplastic resin that is electrochemically stable, also stable to the nonaqueous electrolyte of the battery, and preferably able to ensure the shutdown temperature. In particular, polyolefin (polyethylene, polypropylene, an ethylene-propylene copolymer, etc.) having a softening point (melting point, glass transition point, etc.) of 100 to 150° C. is suitable. Moreover, polyester also can be used.

The shutdown layer may be in any form as long as it has sufficient ionic conductance to obtain necessary battery characteristics. As the shutdown layer, porous films can be used, including a porous film that is formed by aggregating fine particles and an ion-permeable porous film (microporous film) that has many pores and is formed by a conventional solvent extraction method, a dry or wet drawing method, or the like. More specifically, a polyethylene porous film, a polypropylene porous film, a polyester porous film, etc. are suitable for the shutdown layer.

When the shutdown layer is formed, e.g., by aggregating thermoplastic resin fine particles, the shutdown layer may include a binder as needed to bind the fine particles or to integrate the shutdown later with the heat-resistant layer or the electrode. The various types of binders that may be included in the heat-resistant layer also can be used for the shutdown layer. These binders may be used individually or in combinations of two or more. Like the heat-resistant layer, when the binder is used, it may be dissolved or emulsified in a medium (solvent) of a composition (slurry etc.) for forming the shutdown layer, as will be described later.

When the shutdown layer includes the binder, it is preferable that the content of the thermoplastic resin fine particles is 70 to 99 vol % of the total volume of components in the shutdown layer, and the content of the binder is 1 to 30 vol % of the total volume of components in the shutdown layer.

Although the separator can have one heat-resistant layer and one shutdown layer, it may have a plurality of heat-resistant layers that are disposed, e.g., on both sides of the shutdown layer or a plurality of shutdown layers. However, the thickness of the separator increases with the number of layers, which may lead to an increase in the internal resistance or a reduction in the energy density. Therefore, the separator should not include too many layers, and the total number of layers (the heat-resistant layer and the shutdown layer) constituting the separator is preferably five layers or less, and more preferably two layers.

When the separator has a multilayer structure of the heat-resistant layer and the shutdown layer, the heat-resistant layer may be integrated with the shutdown layer. Alternatively, the heat-resistant layer and the shutdown layer are not integrated, but may be provided as independent films, or the heat-resistant layer or the shutdown layer may be individually integrated with the electrode. When the heat-resistant layer and the shutdown layer are not integrated, the separator may be configured by laminating the heat-resistant layer and the shutdown layer together in the nonaqueous electrolyte battery.

In terms of isolating the positive electrode from the negative electrode more reliably, the thickness of the separator is preferably 6 μm or more, and more preferably 10 μm or more. On the other hand, if the separator is too thick, the energy density of the battery may be reduced. Therefore, the thickness of the separator is preferably 50 μm or less, and more preferably 30 μm or less.

When the thicknesses of the shutdown layer and the heat-resistant layer of the separator are represented by A (μm) and B (μm), respectively, the ratio A/B of A to B is in the range of preferably ¼, more preferably ½ to preferably 5, more preferably 4. As described above, in the separator of the present invention, even if the thickness ratio is increased by reducing the thickness of the heat-resistant layer, the occurrence of a short circuit due to thermal shrinkage of the separator can be highly suppressed in the nonaqueous electrolyte battery. When the separator has a plurality of shutdown layers, A represents the total thickness of the plurality of shutdown layers. When the separator has a plurality of heat-resistant layers, B represents the total thickness of the plurality of heat-resistant layers.

Specific values of A and B are as follows. The thickness of the shutdown layer (the total thickness in the case of a plurality of shutdown layers) is preferably 5 μm to 30 μm. The thickness of the heat-resistant layer (the total thickness in the case of a plurality of heat-resistant layers) is in the range of preferably 1 μm, more preferably 2 μm, even more preferably 4 μm to preferably 20 μm, more preferably 10 μm. If the shutdown layer is too thin, the shutdown property may be weakened. If the shutdown layer is too thick, the energy density of the battery may be reduced, and also the effect of suppressing thermal shrinkage of the whole separator may be reduced because the force of the thermal shrinkage is increased when the separator has a structure in which the heat-resistant layer is integrated with the shutdown layer. Moreover, if the heat-resistant layer is too thin, the function of isolating the positive electrode from the negative electrode at high temperatures may be reduced, and also the effect of suppressing thermal shrinkage of the whole separator may be reduced when the separator has a structure in which the heat-resistant layer is integrated with the shutdown layer. If the heat-resistant layer is too thick, the thickness of the whole separator is increased.

The average pore diameter of the separator is in the range of preferably 0.01 μm, more preferably 0.05 μm to preferably 1 μm, more preferably 0.5 μm. The average pore diameter of the shutdown layer is preferably 0.01 to 5 μm. The average pore diameter of the heat-resistant layer is preferably 0.05 to 1 μm. In the case of the battery that includes a wound electrode body obtained by winding the positive electrode and the negative electrode via the separator in a spiral fashion, the separator is bent while the electrode body is wound, and thus can cause a crack or the like in the heat-resistant layer. However, when the separator has the above average pore diameter (particularly, the shutdown layer has the above average pore diameter), even if the heat-resistant layer has a crack or the like, it is possible to prevent lithium dendrites from passing through the crack of the heat-resistant layer. In the case of the battery that includes a so-called laminated electrode body obtained by laminating the positive electrode, the negative electrode, and the separator, instead of the wound electrode body, the average pore diameters of the separator, the shutdown layer, and the heat-resistant layer do not have to meet the above suitable values, but more preferably fall in the respective ranges.

In terms of improving the ion permeability by ensuring the retention of the nonaqueous electrolyte, the porosity of the whole separator is preferably 30% or more in a dry state. On the other hand, in terms of ensuring the strength of the separator and preventing an internal short circuit, the porosity of the whole separator is preferably 70% or less in a dry state. The porosity P (%) of the separator can be calculated from the thickness of the separator, the mass per unit area of the separator, and the densities of the components of the separator by obtaining a summation for each component i with the following formula (1).

$$P=100-(\Sigma a_i/\rho_i)\times(m/t) \quad (1)$$

where a_i represents the ratio of a component i expressed as a mass percentage, ρ_i represents the density (g/cm^3) of the component i, m represents the mass (g/cm^2) per unit area of the separator, and t represents the thickness (cm) of the separator.

In the formula (1), when m represents the mass (g/cm^2) per unit area of the shutdown layer and t represents the thickness (cm) of the shutdown layer, the porosity P (%) of the shutdown layer can be determined. The porosity of the shutdown layer obtained in this manner is preferably 30 to 70%.

In the formula (1), when m represents the mass (g/cm^2) per unit area of the heat-resistant layer and t represents the thickness (cm) of the heat-resistant layer, the porosity P (%) of the heat-resistant layer also can be determined. The porosity of the heat-resistant layer obtained in this manner is preferably 20 to 60%.

It is desirable that the separator of the present invention has an air permeability of 30 to 300 sec, which is indicated by the Gurley value. The Gurley value is obtained by a method according to JIS P 8117 and expressed as the length of time (seconds) it takes for 100 ml air to pass through a membrane at a pressure of 0.879 g/mm^2. If the air permeability is too large, the ion permeability can be reduced. On the other hand, if the air permeability is too small, the strength of the separator can be reduced. It is desirable that the strength of the separator is penetrating strength measured using a 1 mm diameter needle, and that the penetrating strength is 50 g or more. If the penetrating strength is too small, lithium dendrite crystals may penetrate the separator when they are produced, thus leading to a short circuit. The separator having the multilayer structure as described above can ensure the air permeability and the penetrating strength.

The separator of the present invention can be produced in the following manner. For example, the heat-resistant fine particles, the binder, etc. constituting the heat-resistant layer are dispersed in a dispersion medium, namely an organic solvent such as water or N-methyl-2-pyrrolidone (NMP) to prepare a slurry or paste-like composition for forming the heat-resistant layer (the binder may be dissolved in the dispersion medium). This composition is applied to the surface of the shutdown layer and dried.

When the shutdown layer is a microporous film made of a thermoplastic resin, the composition for forming the heat-resistant layer can be applied to the surface of the shutdown layer, e.g., by coating the surface of the microporous film with the composition using a coater or by immersing the microporous film in the composition.

When the shutdown layer is composed of aggregated thermoplastic resin fine particles, the thermoplastic resin fine particles, the binder used as needed, etc. constituting the shutdown layer are dispersed in a dispersion medium such as water or an organic solvent to prepare a slurry or paste-like composition for forming the shutdown layer (the binder may be dissolved in the dispersion medium). This composition is applied to a substrate and dried, so that a shutdown layer is formed beforehand. Subsequently, the composition for forming the heat-resistant layer can be applied to the surface of this shutdown layer in the same manner as the microporous film. The separator also can be produced in a manner contrary to the above. That is, the composition for forming the heat-resistant layer is applied to a substrate and dried, so that a heat-resistant layer is formed beforehand. Subsequently, the composition for forming the shutdown layer is applied to the surface of this heat-resistant layer and dried.

The heat-resistant layer and the shutdown layer can be simultaneously formed by applying one of the compositions for forming the heat-resistant layer and the shutdown layer to a substrate, and then applying the other composition before the previously applied composition is completely dried.

When the heat-resistant layer includes the porous base material, the composition for forming the heat-resistant layer may be applied to the porous base material or the porous base material may be immersed in the composition, and then the composition is dried to form the heat-resistant layer.

As described above, the heat-resistant layer and the shutdown layer are not necessarily integrated, but can be independent of each other and laminated together in the battery. Moreover, one or both of the heat-resistant layer and the shutdown layer may be integrated with the electrode (positive electrode or negative electrode). To integrate the heat-resistant layer or the shutdown layer with the electrode, e.g., the heat-resistant layer or the shutdown layer serving as an independent film can be laminated with the electrode, or the composition for forming the heat-resistant layer or the shutdown layer can be applied to the electrode, thereby forming the heat-resistant layer or the shutdown layer. It is preferable that the heat-resistant layer is integrated with the shutdown layer because a conventional manufacturing process can be used to produce a battery.

The negative electrode of the battery of the present invention is not particularly limited as long as it can be used for the nonaqueous electrolyte battery. Examples of the negative active material include mixtures of two or more carbon materials capable of intercalating and deintercalating lithium such as graphite, pyrolytic carbon, coke, glassy carbon, a calcined organic polymer compound, mesocarbon microbeads, and a carbon fiber. Moreover, examples of the negative active material also include the following: alloys of Si, Sn, Ge, Bi, Sb, and In; compounds that can be charged/discharged at a low voltage close to lithium metal such as a lithium-containing nitride and a lithium-containing oxide; a lithium metal; and a Li/Ai alloy. The negative electrode may be produced in such a manner that a negative electrode mixture is obtained by adding the conductive assistant or the binder (e.g., PVDF) appropriately to the negative active material, and then formed into a compact (a negative electrode mixture layer) while a current collector such as a copper foil is used as a core material. Alternatively, foils of the above alloys or lithium metal can be used individually or in the form of a laminate with the current collector (e.g., a copper foil) as the negative electrode.

When the negative electrode of the present invention includes a current collector, the current collector may be, e.g., a foil, a punched metal, a mesh, or an expanded metal, which are made of copper, nickel, or the like. In general, a cooper foil is used. If the thickness of the whole negative electrode is reduced to achieve a battery with high energy density, the current collector of the negative electrode preferably has a thickness of 5 to 30 μm.

A lead portion of the negative electrode is generally provided in the following manner. A part of the current collector remains exposed without forming the negative electrode mixture layer when the negative electrode is produced, and this exposed portion can serve as the lead portion. However, the lead portion does not necessarily need to be integrated with the current collector from the beginning and may be provided by connecting a copper foil or the like to the current collector afterward.

The nonaqueous electrolyte of the present invention can be a nonaqueous electrolyte (nonaqueous electrolytic solution) produced by dissolving at least one lithium salt selected from the group consisting of $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiSbF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, $Li_2C_2F_4(SO_3)_2$, $LiN(CF_3SO_2)_2$, $LiC(CF_3SO_2)_3$, $LiCriF_{2n+1}SO_3$ ($2 \leq n \leq 5$), and $LiN(RfOSO_2)_2$ (where Rf represents a fluoroalkyl group) in an organic solvent such as a dimethyl carbonate, a diethyl carbonate, a methyl ethyl carbonate, methyl propionate, an ethylene carbonate, a propylene carbonate, a butylene carbonate, γ-butyrolactone, ethylene glycol sulfite, 1,2-dimethoxyethane, 1,3-dioxolane, tetrahydrofuran, 2-methyltetrahydrofuran, or diethyl ether. The concentration of the lithium salt in the electrolyte is preferably 0.5 to 1.5 mol/l, and more preferably 0.9 to 1.25 mol/l.

The nonaqueous electrolyte battery of the present invention may be in the form of a rectangular or circular cylinder and have an outer can made of steel or aluminum. Moreover, the nonaqueous electrolyte battery may be a soft package battery using a metal-deposited laminated film as an outer package.

The electrode used in the nonaqueous electrolyte battery of the present invention may be in the form of a laminated electrode body obtained by laminating the positive electrode and the negative electrode via the separator of the present invention or in the form of a wound electrode body obtained by winding the laminated electrode body. In this case, since the thermal shrinkage of a conventional separator is large in the width direction, the width W_s of the separator needs to be much larger than the width W_a of the negative electrode to prevent a short circuit at high temperatures. On the other hand, the thermal shrinkage of the separator of the present invention in the width direction can be sufficiently suppressed even if the heat-resistant layer is integrated with the shutdown layer to form the separator. Therefore, in the above wound electrode body, a short circuit due to contact between the positive electrode and the negative electrode can be prevented only by making the width W_s of the separator slightly larger than the width W_a of the negative electrode.

When the shutdown layer is made of a material having somewhat inferior resistance to oxidation such as polyolefin, it is desirable to avoid contact between the shutdown layer and the positive active material so as to prevent degradation of the separator caused by oxidation and improve the charge-discharge cycle life and the high-temperature storage characteristics of the battery. In particular, when the charging potential is 4.3 V or more, the oxidation action becomes prominent. Moreover, when the shutdown layer is located on the negative electrode side, particularly is brought into contact with the negative electrode mixture layer, a film of the thermoplastic resin of the shutdown layer is formed on the surface of the negative electrode mixture layer after a shutdown is effected. This can suppress a reaction between the air that flows into the battery, e.g., after a cleavable vent has opened (as will be described later) and the negative active material, and thus can further improve the safety at high temperatures.

Hereinafter, an example of the nonaqueous electrolyte battery of the present invention will be described with reference to the drawings. FIG. **1**A is a schematic plan view of the nonaqueous electrolyte battery of the present invention. FIG. **1**B is a schematic cross-sectional view of the nonaqueous electrolyte battery of the present invention. FIG. **2** is a schematic diagram showing the appearance of the nonaqueous electrolyte battery of the present invention.

In the battery shown in FIGS. **1**A, **1**B, and **2**, a negative electrode **1** and a positive electrode **2** are wound via a separator **3** of the present invention in a spiral fashion, and then pressed into a flat shape, thereby providing a wound electrode body **6**. The wound electrode body **6**, together with a nonaqueous electrolyte, is housed in a rectangular cylindrical outer can **20**. For the sake of simplicity, FIG. **1**B does not illustrate a metal foil that is a current collector of the negative electrode **1** or the positive electrode **2**, a nonaqueous electrolyte, etc. and also does not show hatching that indicates the cross sections of the center of the wound electrode body **6** and the separator **3**.

The outer can **20** is made of an aluminum alloy, serves as an outer package of the battery, and is also used as a positive terminal. An insulator **5** made of a polyethylene sheet is placed at the bottom of the outer can **20**. A negative electrode lead **8** and a positive electrode lead **7** connected to the respective ends of the negative electrode **1** and the positive electrode **2** are drawn from the wound electrode body **6** including the negative electrode **1**, the positive electrode **2**, and the separator **3**. A stainless steel terminal **11** is attached to a cover **9** via a polypropylene insulating packing **10**. The cover **9** is made of an aluminum alloy and used to seal the opening of the outer can **20**. A stainless steel lead plate **13** is connected to the terminal **11** via an insulator **12**.

The cover **9** is inserted in the opening of the outer can **20**, and the joint between them is welded to seal the opening, so that the inside of the battery is hermetically sealed. Moreover, the cover **9** has an inlet **14** through which the nonaqueous electrolyte is injected. The inlet **14** is sealed with a sealing member by laser welding or the like. Thus, the sealing properties of the battery are ensured. For convenience, in FIGS. **1**A, **1**B, and **2**, the inlet **14** includes the sealing member as well as itself. The cover **9** has a cleavable vent **15** as a mechanism for discharging the gas contained in the battery to the outside at the time the internal pressure is raised due to a rise in temperature or the like.

In the nonaqueous electrolyte battery shown in FIGS. **1**A, **1**B, and **2**, the positive electrode lead **7** is directly welded to the cover **9**, so that the outer can **20** and the cover **9** can function as a positive terminal. Moreover, the negative electrode lead **8** is welded to the lead plate **13**, and thus electrically connected to the terminal **11** via the lead plate **13**, so that the terminal **11** can function as a negative terminal. However, the positive and negative electrodes may be reversed depending on the material of the outer can **20** or the like.

The nonaqueous electrolyte battery of the present invention can be used in the same application as that of a conventional nonaqueous electrolyte battery.

Next, the present invention will be described in detail by way of examples. However, the present invention is not limited to the following examples.

Example 1

Production of Positive Electrode

A positive electrode mixture containing paste was prepared by mixing 90 parts by mass of $LiCo_{0.33}Ni_{0.33}Mn_{0.33}O_2$ (positive active material), 7 parts by mass of acetylene black (conductive assistant), and 3 parts by mass of PVDF (binder) uniformly by using NMP as a solvent. This paste was intermittently applied to both surfaces of a current collector (aluminum foil) with a thickness of 15 μm so that the applied length was 280 mm on the upper surface and 210 mm on the lower surface, which then was dried and calendered. Thus, the thicknesses of the positive electrode mixture layers were adjusted so that the total thickness was 150 μm. Subsequently, this current collector having the positive electrode mixture layers was cut into a length of 300 mm and a width of 43 mm, thereby producing a positive electrode. Moreover, a lead portion was formed by welding a tab to the exposed portion of the aluminum foil of the positive electrode.

<Production of Negative Electrode>

A negative electrode mixture containing paste was prepared by mixing 95 parts by mass of graphite (negative active material) and 5 parts by mass of PVDF (binder) uniformly by using NMP as a solvent. This paste was intermittently applied to both surfaces of a current collector (copper foil) with a thickness of 10 μm so that the applied length was 290 mm on the upper surface and 230 mm on the lower surface, which then was dried and calendered. Thus, the thicknesses of the negative electrode mixture layers were adjusted so that the total thickness was 142 μm. Subsequently, this current collector having the negative electrode mixture layers was cut into a length of 300 mm and a width of 45 mm, thereby producing a negative electrode. Moreover, a lead portion was formed by welding a tab to the exposed portion of the copper foil of the negative electrode.

<Production of Separator>

200 g of an emulsion of a self-cross-linking acrylic resin serving as a binder (with a solid content of 40 mass %) and 4000 g of water were put in a container and stirred at room temperature until the binder was uniformly dissolved in water. Then, 4000 g of a plate-like boehmite powder serving as heat-resistant fine particles (an average particle size: 1 μm, a proportion of particles with a particle size of 0.2 μm or less: 0 vol %, a proportion of particles with a particle size of 2 μm or more: 4 vol %, and an aspect ratio: 10) was added to this solution at four different times, and dispersed with a Disper at 2800 rpm for 5 hours, resulting in a uniform slurry. Next, the

slurry was applied to a polyethylene microporous film (with a thickness of 16 μm, a porosity of 40%, an average pore diameter of 0.02 μm, and a melting point of 135° C.) using a micro-gravure coater and dried, so that cross-links were formed by the acrylic resin. Thus, a separator that had a thickness of 20 μm and included a heat-resistant layer containing boehmite and a shutdown layer formed of the polyethylene microporous film (with a melting point of 135° C.) was produced. Then, the separator was cut into a width of 47 mm and used to produce a battery.

<Production of Battery>

The positive electrode and the negative electrode were laminated with the separator interposed between them so that the shutdown layer faced the negative electrode, and then wound in a spiral fashion to form a wound electrode body. Next, the wound electrode body was pressed into a flat shape and placed in an aluminum rectangular outer can with a thickness of 4 mm, a height of 50 mm, and a width of 34 mm. Moreover, a nonaqueous electrolyte (obtained by dissolving $LiPF_6$ at a concentration of 1.2 mol/l in a solvent containing an ethylene carbonate and an ethyl methyl carbonate at a volume ratio of 1:2) was injected, and the outer can was sealed in a vacuum, resulting in a nonaqueous electrolyte battery.

Example 2

A positive electrode was produced in the same manner as Example 1 except that the positive active material was changed to $LiMn_{1.9}Al_{0.1}O_4$.

The same slurry as that in Example 1 was applied to the surface of a PET nonwoven fabric (with a thickness of 15 μm and a weight of 10 g/m^2) using a dip coater and dried, thereby providing a heat-resistant layer with a thickness of 18 μm. Then, a water dispersion of polyethylene fine particles (with an average particle size of 1 μm, a melting point of 125° C., and a solid content of 20 mass %) was applied to the surface of the heat-resistant layer using a die coater and dried, thereby providing a shutdown layer. Thus, a separator was produced. The thickness of the separator was 23 μm.

A nonaqueous electrolyte battery was produced in the same manner as Example 1 except that the positive electrode and the separator of this example were used.

Example 3

A positive electrode was produced in the same manner as Example 1 except that the positive active material was changed to $LiFePO_4$.

Next, 600 g of an NMP solution of PVDF serving as a binder (with a solid content of 15 mass %) and 1000 g of NMP were put in a container and stirred at room temperature until the solution was uniform. Then, 3000 g of an alumina powder serving as heat-resistant fine particles (an average particle size: 0.4 μm, a proportion of particles with a particle size of 0.2 μm or less: 0 vol %, and a proportion of particles with a particle size of 2 μm or more: 0 vol %) was added to this solution at four different times, and dispersed with a Disper at 2800 rpm for 1 hour, resulting in a uniform slurry. Next, the slurry was applied to the surface of the above positive electrode using a die coater and dried, thereby providing a heat-resistant layer with a thickness of 4 μm.

A nonaqueous electrolyte battery was produced in the same manner as Example 1 except that the above positive electrode including the heat-resistant layer, the same negative electrode as that prepared in Example 1, and a polyethylene microporous film with a thickness of 16 μm were used, and a wound electrode body was formed so that the polyethylene microporous film was located between the heat-resistant layer of the positive electrode and the negative electrode. In this example, the heat-resistant layer formed on the surface of the positive electrode and the polyethylene microporous film (shutdown layer) corresponded to the separator.

Example 4

Production of Negative Electrode

A negative electrode with a length of 510 mm and a width of 45 mm was produced in the same manner as Example 1 except that the negative electrode mixture containing paste was intermittently applied so that the applied length was 500 mm on the upper surface and 440 mm on the lower surface.

<Production of Positive Electrode>

90 parts by mass of $LiNi_{0.65}Mn_{0.15}Cu_{0.2}O_2$ (with a number average particle size of 17 μm) and 10 parts by mass of $LiCoO_2$ (with a number average particle size of 5 μm) were dry-mixed, to which 20 parts by mass of an NMP solution including 10 mass % of PVDF serving as a binder were added, and then further mixed. Next, 1 part by mass of artificial graphite and 1 part by mass of Ketjenblack were added to this mixture as a conductive assistant and kneaded with a two-axis kneader. Moreover, NMP was added to adjust the viscosity of the mixture, and thus a positive electrode mixture containing paste was prepared. A positive electrode with a length of 520 mm and a width of 43 mm was produced in the same manner as Example 1 except that the positive electrode mixture containing paste was intermittently applied so that the applied length was 500 mm on the upper surface and 425 mm on the lower surface.

<Production of Separator>

A separator with a thickness of 22 μm was produced in the same manner as Example 1 except that 200 g of the emulsion of the self-cross-linking acrylic resin were changed to 100 g of an emulsion of SBR (with a solid content of 40 mass %). The volume ratio of the heat-resistant fine particles to the heat-resistant layer of the separator was 91 vol %, and the porosity of the heat-resistant layer was 48%.

<Production of Battery>

A nonaqueous electrolyte battery was produced in the same manner as Example 1 except that an aluminum rectangular outer can with a thickness of 6 mm, a height of 50 mm, and a width of 34 mm was used.

Comparative Example 1

A nonaqueous electrolyte battery was produced in the same manner as Example 1 except that the separator was changed to a polyethylene microporous film with a thickness of 16 μm.

Comparative Example 2

A nonaqueous electrolyte battery was produced in the same manner as Example 1 except that the positive active material was changed to $LiCoO_2$.

Comparative Example 3

A nonaqueous electrolyte battery was produced in the same manner as Example 1 except that the separator was changed to a PET nonwoven fabric (with a thickness of 15 μm and a weight of 10 g/m^2).

[Measurement of Heat Generation Starting Temperature of Positive Electrode]

The heat generation starting temperature of the positive electrode in each of the nonaqueous electrolyte batteries of Examples 1 to 4 and Comparative Examples 1 to 3 was measured using a DSC "Pyris 1" manufactured by PerkinElmer Co., Ltd. Each of the nonaqueous electrolyte batteries charged to 4.25 V was disassembled in a glove box having an Ar atmosphere, and the positive electrode was taken out and punched into a circular shape with a diameter of 3.5 mm. This positive electrode was weighed and then sealed in a sample pan that had a gold-plated surface and was able to withstand 150 atm. Next, the temperature was raised from 30 to 400° C. at 10° C./min, and a DSC curve was obtained. In the DSC curve, the heat generation starting temperature of the positive electrode indicated a temperature at an intersection point of two lines: one is an extension line of the base line on the high temperature side; and the other is a tangent to the curve of the exothermic peak on the low temperature side at a point where the curve has the maximum slope. Table 1 shows the results.

[Measurement of Thermal Shrinkage Ratio at T° C.]

The separator used in each of the nonaqueous electrolyte batteries of Examples 1 to 4 and Comparative Examples 1 to 3 was allowed to stand in a thermostatic bath at T° C. that was 10° C. lower than the heat generation starting temperature of the positive electrode (where the upper limit of T was 200° C.) for 1 hour. Then, the thermal shrinkage ratio of the separator was measured by the above-described method. Table 1 shows the results along with T° C.

[Measurement of Shutdown Temperature]

The separator used in each of the nonaqueous electrolyte batteries of Examples 1 to 4 and Comparative Examples 1 to 2 was placed in a thermostatic bath and heated by raising the temperature from 100° C. in 5° C. increments for 10 minutes, and subsequently the Gurley value was measured. Next, changes in the Gurley value before and after the heating of the separator in the thermostatic bath were determined, and a temperature at which the Gurley value was at least ten times larger than that before heating was defined as the shutdown temperature. The Gurley value was obtained by a method according to JIS P 8117 and expressed as the length of time (seconds) it took for 100 ml air to pass through a membrane at a pressure of 0.879 g/mm^2.

With respect to the separator of Example 3, the thermal shrinkage ratio and the change of the Gurley value were determined for each of the heat-resistant layer and the polyethylene microporous film used in Example 3. In this case, the heat-resistant layer was prepared in the following manner. The slurry for forming the heat-resistant layer was applied to a PET film, which had been subjected to a peeling treatment, and dried to form a heat-resistant layer. Then, this heat-resistant layer was removed from the PET film. Comparing the heat-resistant layer and the polyethylene microporous film, a smaller value of the thermal shrinkage ratios and a larger value of the changes in the Gurley value were selected as the thermal shrinkage ratio and the shutdown temperature of the separator of Example 3, respectively.

Table 1 also shows the width of each of the separators after the thermal shrinkage at T° C. in Examples 1, 2, and 4 and Comparative Examples 1 to 3, and the width of the heat-resistant layer after the thermal shrinkage at T° C. in Example 3.

TABLE 1

	Heat generation starting temperature of positive electrode (° C.)	Shutdown temperature (° C.)	T ° C.	Thermal shrinkage ratio at T ° C. (%)	Width of separator or heat-resistant layer at T ° C. (mm)
Example 1	229	135	200	2	46.1
Example 2	200	135	190	0	47
Example 3	229	135	200	0	47
Example 4	220	135	200	1	46.5
Comparative Example 1	229	140	200	35	30.6
Comparative Example 2	161	135	151	1	46.5
Comparative Example 3	229	—	200	0	47

As can be seen from Table 1, the heating characteristics of all the batteries of Examples 1 to 4 were satisfactory. On the other hand, the battery of Comparative Example 1 used the separator including no heat-resistant fine particle, and therefore the thermal shrinkage ratio was 35% at T° C., and the width of the separator was smaller than 45 mm, which was the width of the negative electrode. In the battery of Comparative Example 2, the heat generation starting temperature of the positive electrode was below 180° C. Moreover, the battery of Comparative Example 3 used the separator including no thermoplastic resin, and therefore a shutdown was not effected.

[Evaluation of Charge-Discharge Characteristics]

The nonaqueous electrolyte batteries of Examples 1 to 4 and Comparative Examples 1 to 3 were initially charged by performing a constant-current and constant-voltage charge so that a constant-current charge was performed at a current value of 150 mA at 25° C. until the voltage reached 4.2 V, and subsequently a constant-voltage charge was performed at a voltage of 4.2 V. The duration of the initial charge (i.e., the total charge time) was 12 hours. Next, a constant-current discharge was performed on these batteries at a current value of 150 mA and a final voltage of 3.0 V. Moreover, for each of the discharged batteries, a constant-current and constant-voltage charge was performed (for a duration of 2.5 hours) so that a constant-current charge was performed at a current value of 500 mA until the voltage reached 4.2 V, and subsequently a constant-voltage charge was performed at a voltage of 4.2 V. Further, a constant-current discharge was performed on these batteries at a current value of 500 mA and a final voltage of 3.0 V. Then, the charge/discharge characteristics of each of the batteries were evaluated.

As a result of the evaluation of the charge/discharge characteristics, the batteries of Examples 1 to 4 and Comparative Examples 1 to 2 had good charge/discharge characteristics. However, the battery of Comparative Example 3 caused a short circuit during the initial charge and could not be charged. Therefore, the subsequent evaluation of the battery of Comparative Example 3 ceased.

[Heat Test]

For the nonaqueous electrolyte batteries of Examples 1 to 4 and Comparative Examples 1 to 2, a constant-current and constant-voltage charge was performed in such a manner that each of the batteries was charged at a constant current of 0.2 C until the voltage reached 4.25 V, and subsequently charged at a constant voltage of 4.25 V. The duration of this constant-current and constant-voltage charge was 8 hours. Each of the charged batteries was allowed to stand in a thermostatic bath at 165° C. for 3 hours, and the surface temperature of the battery was observed. Table 2 shows the results.

TABLE 2

	Surface temperature of battery after heat test
Example 1	No anomaly
Example 2	No anomaly
Example 3	No anomaly
Example 4	No anomaly
Comparative Example 1	The temperature was raised.
Comparative Example 2	The temperature was raised.

As can be seen from Table 2, no anomaly was observed in the nonaqueous electrolyte batteries of Examples 1 to 4 during the heat test at 165° C. Accordingly, the batteries of Examples 1 to 4 are superior to the batteries of Comparative Examples 1 to 2 in their safety when allowed to stand at high temperatures.

The invention may be embodied in other forms without departing from the spirit or essential characteristics thereof. The embodiments disclosed in this application are to be considered in all respects as illustrative and not limiting. The scope of the invention is indicated by the appended claims rather than by the foregoing description, and all changes that come within the meaning and range of equivalency of the claims are intended to be embraced therein.

INDUSTRIAL APPLICABILITY

As described above, the present invention can provide a battery separator that can constitute a nonaqueous electrolyte battery having excellent safety in a high-temperature environment, and a nonaqueous electrolyte battery using the battery separator.

The invention claimed is:

1. A battery separator comprising:

heat-resistant fine particles; and

a thermoplastic resin,

wherein the heat-resistant fine particles along with a binder constitute a heat-resistant layer,

the thermoplastic resin constitutes a shutdown layer formed of a heat-shrinkable microporous film,

the heat-resistant layer and the shutdown layer are integrated into a multilayer structure,

the shutdown layer has a thickness A (μm) of 5 to 30, the heat-resistant layer has a thickness B (μm) of 1 to 10, a sum of A and B is 6 to 23, and a ratio A/B is 1/2 to 4,

a content of the heat-resistant fine particles in the heat-resistant layer is 50 vol % or more of a total volume of components in the heat-resistant layer,

a proportion of particles with a particle size of 0.2 μm or less in the heat-resistant fine particles is 10 vol % or less and a proportion of particles with a particle size of 2 μm or more in the heat-resistant fine particles is 10 vol % or less, and

a shutdown is effected in a range of 135° C. to 150° C.

2. The battery separator according to claim **1**, wherein a thermal shrinkage ratio in a width direction is 10% or less at 200° C.

3. The battery separator according to claim **1**, wherein the content of the heat-resistant fine particles in the heat-resistant layer is 80 vol % or more of the total volume of components in the heat-resistant layer.

4. The battery separator according to claim **1**, wherein the heat-resistant fine particles are inorganic fine particles.

5. The battery separator according to claim **4**, wherein the inorganic fine particles include fine particles of at least one selected from the group consisting of alumina, silica, $BaTiO_3$, boehmite, zeolite, and kaoline.

6. The battery separator according to claim **1**, wherein the heat-resistant fine particles include plate-like particles.

7. The battery separator according to claim **1**, wherein the heat-resistant layer has a thickness of 2 μm to 6 μm.

8. The battery separator according to claim **1**, wherein the thermoplastic resin includes polyolefin.

9. The battery separator according to claim **1**, wherein the heat-resistant fine particles have an average particle size of 1.5 μm or less.

10. A nonaqueous electrolyte batter comprising:

a positive electrode having a positive active material capable of intercalating and deintercalating a lithium ion;

a negative electrode having a negative active material capable of intercalating and deintercalating a lithium ion;

a separator interposed between the positive electrode and the negative electrode; and

a nonaqueous electrolyte,

wherein a heat generation starting temperature of the positive electrode is 180° C. or higher, and

wherein the separator is the battery separator according to claim **1**.

11. The nonaqueous electrolyte battery according to claim **10**, wherein a thermal shrinkage ratio of the separator is 10% or less at a temperature T (° C.) that is 10° C. lower than the heat generation starting temperature of the positive electrode (where an upper limit of T is 200° C.).

12. The nonaqueous electrolyte battery according to claim **10**, wherein a width of the separator is larger than that of the negative electrode at a temperature T (° C.) that is 10° C. lower than the heat generation starting temperature of the positive electrode (where an upper limit of T is 200° C.).

13. The nonaqueous electrolyte battery according to claim **10**, wherein the positive active material is at least one selected from the group consisting of the following: a spinel-type lithium-containing complex oxide expressed as a general formula $Li_{1+t}Mn_{(2-x)}M^1{}_xO_4$ (where M^1 is at least one element selected from the group consisting of Fe, Ni, Mg, Zn, Co, Cr, Al, B, V, Si, Sn, Nb, Ta, Cu, Mo, Ti, and W, $-0.1 \leq t \leq 0.1$, and $0 \leq x \leq 0.6$); an olivine-type lithium-containing complex oxide expressed as a general formula LiM^2PO_4 (where M^2 is Co, Ni, Mn, or Fe); a lithium-containing complex oxide having a layered crystal structure expressed as a general formula $Li_{(1+a)}M^3{}_{2b}Mn_{(0.5-b)}Ni_{(0.5-b)}O_2$ (where M^3 is at least one element selected from the group consisting of Fe, Mg, Zn, Co, Cr, Al, B, V, Si, Sn, Nb, Ta, Cu, Mo, Ti, and W, $-0.1<<0.1$, and $0 \leq b \leq 0.05$); and a lithium-containing complex oxide expressed as a general formula $Li_{(1+y+\alpha)}Ni_{(1-y-z-\delta)/2}Mn_{(1-y-z-\delta)/2}M^4{}_zO_2$ (where M^4 is at least one element selected from the group consisting of Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, Sn, Mg, and Zr, $-0.1 \leq y \leq 0.1$, $-0.05 \leq \alpha \leq 0.05$, $0 \leq z < 0.45$, and $-0.24 \leq \delta \leq 0.6$).

14. The nonaqueous electrolyte battery according to claim **10**, wherein a content of the heat-resistant fine particles in the heat-resistant layer of the separator is 80 vol % or more of a total volume of components in the heat-resistant layer.

15. The nonaqueous electrolyte battery according to claim **10**, wherein the heat-resistant fine particles of the separator are inorganic fine particles.

16. The nonaqueous electrolyte battery according to claim **15**, wherein the inorganic fine particles include line particles of at least one selected from the group consisting of alumina, silica, $BaTiO_3$, boehmite, zeolite, and kaoline.

17. The nonaqueous electrolyte battery according to claim **10**, wherein the heat-resistant fine particles of the separator include plate-like particles.

18. The nonaqueous electrolyte battery according to claim **10**, wherein the heat-resistant layer of the separator has a thickness of 2 μm to 6 μm.

19. The nonaqueous electrolyte battery according to claim **10**, wherein the thermoplastic resin of the separator includes polyolefin.

20. The nonaqueous electrolyte battery according to claim **10**, wherein the shutdown layer of the separator is located on a negative electrode side.

21. The nonaqueous electrolyte battery according to claim **10**, wherein the shutdown layer of the separator is not in contact with the positive active material.

22. The nonaqueous electrolyte battery according to claim **10**, wherein the heat-resistant fine particles of the separator have an average particle size of 1.5 μm or less.

23. The battery separator according to claim **1**, wherein the shutdown layer has a thickness of 16 μm or less.

24. The battery separator according to claim **1**, wherein a content of the binder in the heat-resistant layer is 1 to 20 vol % of a total volume of components in the heat-resistant layer.

25. The battery separator according to claim **1**, wherein the binder includes at least one selected from the group consisting of an ethylene-vinyl acetate copolymer (having 20 to 35 mol % of a structural unit derived from vinyl acetate); an ethylene-acrylic acid copolymer; fluoro-rubber; styrene-butadiene rubber; carboxymethyl cellulose; hydroxyethyl cellulose; polyvinyl alcohol; polyvinyl butyral; polyvinyl pyrrolidone; poly-N-vinylacetamide; a cross-linked acrylic resin; polyurethane; and an epoxy resin.

26. The battery separator according to claim **1**, wherein the heat-resistant line particles have an average particle size of 0.3 μm or more.

27. The nonaqueous electrolyte battery according to claim **10**, wherein the shutdown layer of the separator has a thickness of 16 μm or less.

28. The nonaqueous electrolyte battery according to claim **10**, wherein a content of the binder in the heat-resistant layer of the separator is 1 to 20 vol % of a total volume of components in the heat-resistant layer.

29. The nonaqueous electrolyte battery according to claim **10**, wherein the binder of the separator includes at least one selected from the group consisting of an ethylene-vinyl acetate copolymer (having 20 to 35 mol % of a structural unit derived from vinyl acetate); an ethylene-acrylic acid copolymer; fluoro-rubber; styrene-butadiene rubber; carboxymethyl cellulose; hydroxyethyl cellulose; polyvinyl alcohol; polyvinyl butyral; polyvinyl pyrrolidone; poly-N-vinylacetamide; a cross-linked acrylic resin; polyurethane; and an epoxy resin.

30. The nonaqueous electrolyte battery according to claim **10**, wherein the heat-resistant fine particles of the separator have an average particle size of 0.3 μm or more.

31. The nonaqueous electrolyte battery according to claim **10**, wherein the shutdown layer of the separator is not in contact with the positive active material, and a charging potential of the positive electrode is 4.3 V or more.

32. The battery separator according to claim **1**, wherein the heat-resistant layer has a porosity of 20% to 60%.

33. The battery separator according to claim **1**, wherein the whole separator has a porosity of 30% to 70%.

34. The nonaqueous electrolyte battery according to claim **10**, wherein the heat-resistant layer has a porosity of 20% to 60%.

35. The nonaqueous electrolyte battery according to claim **10**, wherein the whole separator has a porosity of 30% to 70%.

36. The battery separator according to claim **1**, wherein the microporous film is formed by a solvent extraction method, a dry drawing method, or a wet drawing method.

37. The nonaqueous electrolyte battery according to claim **10**, wherein the microporous film is formed by a solvent extraction method, a dry drawing method, or a wet drawing method.

* * * * *