

明細書

新規な電池およびその製造方法

技術分野

本発明は、新規な電池およびその製造方法に関する。更に詳細には、電解質を含むケーシング内に、正極活物質層を含む正極、及び負極活物質層を含む負極が多孔性セパレータを介して配設されてなる電池において、該多孔性セパレータが、少なくとも1層の絶縁性物質粒子集合体層からなり、該絶縁性物質粒子集合体層が3次元網目空隙構造を有しており、それにより、該多孔性セパレータに、イオンが通過可能な孔が形成されるように構成されている電池、及びその製造方法に関する。本発明の電池は、安全性を損なうことなく、高い電流密度で優れた放電特性を発揮するだけでなく、従来の電池と比較して電池の単位体積あたりに収容できる活物質の量が多いという優れた特性を有する。

従来技術

近年、電子機器の小型軽量化、多機能化、コードレス化の要求に伴い、高性能電池の開発が積極的に進められている。電池は、一般的に使い切りタイプの一次電池と、充電により繰り返し使用が可能な二次電池に分けることができる。一次電池の例としては、マンガン電池、アルカリマンガン電池等が挙げられる。これ等の一次電池は、様々な改良を加えられ、広範囲に普及している。二次電池の例としては、鉛蓄電池、

ニッケル-カドミウム電池、ニッケル-水素電池等が挙げられるが、最近では特に非水系電解液を用いるリチウムイオン二次電池が、高電圧、高容量でありながら重量が軽く小型になるため、大きな市場を築きつつある。

上記のような電池の高性能化は、電池の単位体積あたりに収容可能な活物質の量や電解質の量を増やすことや、正極・負極間のイオン伝導の効率を良くすること等によって達成することができる。

特に上記のリチウムイオン二次電池等の非水系電解液を用いる電池においては、水系電解液と比べて非水系電解液がイオン伝導性に乏しいため、一般に、正極、負極及びセパレータからなる単位電池層が多数積層または捲回されて正極と負極の対向面積を増やすことにより正極・負極間のイオン伝導の効率を向上させているが、更なる改善が望まれている。

上記の改善を達成する最も有効な手段の1つとしては、厚みが薄く、イオン透過性に優れたセパレータを使用することが挙げられる。

従来、セパレータとしては、一般的にポリエチレンおよびポリプロピレン等のポリオレフィン系樹脂フィルム製微多孔膜が用いられている。その製造は、例えば、日本国特開平3-105851号公報に記載されているように、ポリオレフィン系樹脂組成物を含む熔融物をシート状に押出成形し、ポリオレフィン系樹脂以外の物質を抽出除去した後、そのシー

トを延伸するという方法で行われている。

上記のような樹脂フィルム製のセパレータは、電池の作製時に破断しないよう機械的強度を有することが必要であるため、セパレータをある程度以上薄くすることが難しい。したがって、特に上記のリチウムイオン二次電池のように、単位電池層が多数積層または捲回されてなるタイプの電池においては、セパレータの厚みにより電池の単位体積あたりに収納可能な単位電池層の量が制限されてしまう。また、従来のセパレータの空孔率を増加して、正極・負極間のイオン伝導性を向上させようとしても、理由は明らかではないが満足のいく結果は得られなかった（本明細書比較例 1 参照）。更に、上記のような樹脂フィルム製のセパレータは耐久性に問題があり、二次電池に用いると、充・放電を繰り返す内にセパレータが劣化し、電池のサイクル性が低下するという不利が生じる（本明細書比較例 3 参照）。また、従来のセパレータは上記のような方法で製造されたものを多く用いるため、セパレータは電池構成部材中で比較的価格が高いものとなっている。従って、特に上記のリチウムイオン二次電池のような電池においてはセパレータの使用面積が大きいいため、セパレータの価格が電池製造コストを高くしてしまうという問題があった。

発明の概要

本発明は、上記のような問題点を解決して、安全且つ高性

能で、しかも安価に製造できる電池を開発すべく鋭意研究を重ねた。その結果、電解質を含むケーシング内に、正極活物質層を含む正極、及び負極活物質層を含む負極が多孔性セパレータを介して配設されてなる電池において、該多孔性セパレータが、少なくとも1層の絶縁性物質粒子集合体層からなり、該絶縁性物質粒子集合体層が3次元網目空隙構造を有しており、それにより、該多孔性セパレータに、イオンが通過可能な孔が形成されるように構成されていると、そのような電池は、安全性を損なうことなく、高い電流密度で優れた放電特性を発揮するだけでなく、従来の電池と比較して電池の単位体積あたりに収容できる活物質の量を多くすることができることを意外にも知見した。本発明はこれ等の知見に基づいて完成したものである。

従って、本発明の1つの目的は、安全性を損なうことなく、高い電流密度で優れた放電特性を発揮するだけでなく、従来の電池と比較して電池の単位体積あたりに収容できる活物質の量が多くて、極めて高い性能を発揮することができる電池を提供することにある。

本発明の他の1つの目的は、上記の高性能電池の有利な製造方法を提供することにある。

本発明の上記及びその他の諸目的、諸特徴ならびに諸利益は、添付の図面を参照しながら行う以下の詳細な説明及び請求の範囲の記載から明らかになる。

図面の簡単な説明

添付の図面において、

図 1 (A) は、従来のセパレータを用いた電池の単位電池層の 1 部を示す概略断面図であり；

図 1 (B) は、比較例 1 ～ 7 で用いた、従来のセパレータを有する単位電池層の他の 1 例を示す概略断面図であり；

図 2 は、本発明の電池の 1 つの態様における単位電池層の概略断面図であり；

図 3 は、本発明の電池の他の 1 つの態様における単位電池層の概略断面図であり；

図 4 は、本発明の電池の更に他の 1 つの態様における単位電池層の概略断面図であり；

図 5 は、本発明の電池の更に他の 1 つの態様における単位電池層の概略断面図であり；

図 6 は、本発明の電池の更に他の 1 つの態様における単位電池層の概略断面図であり；

図 7 (a) ～図 7 (c) は、実施例 1 ～ 7 で使用した単位電池層の概略断面図である。

尚、図 1 (A) ～図 7 (c) において、同様の部品又は部分は同様の参照番号又は符号で示す。

符号の説明

1 電池層

1 1 正極

- 1 1 a 正極集電体箔
- 1 1 b 正極活物質層
- 1 2 負極
- 1 2 a 負極集電体箔
- 1 2 b 負極活物質層
- 1 3 従来のセパレータ
- 1 3 A 正極活物質層表面に一体化された形で直接形成された本発明で用いるセパレータ
- 1 3 B 負極活物質層表面に一体化された形で直接形成された本発明で用いるセパレータ
- 1 3 C 正極活物質層表面及び負極活物質層表面の両方に一体化された形で形成された本発明で用いるセパレータ

発明の詳細な説明

本発明の 1 つの態様によれば、
ケーシング、

該ケーシング内に含まれる電解質、

正極活物質層を含む正極、

負極活物質層を含む負極、及び

多孔性セパレータを包含し、

該正極、該負極及び該セパレータは、該ケーシング内に、

該電解質と共働可能に収容されており、

該多孔性セパレータは、該正極と該負極の間に、該多孔

性セパレータの両側表面が該正極活物質層及び該負極活物質層にそれぞれ面するように配置構成されてなる電池であって、

該多孔性セパレータは、少なくとも1層の絶縁性物質粒子集合体層からなり、該少なくとも1層の絶縁性物質粒子集合体層が3次元網目空隙構造を有しており、それにより、該多孔性セパレータに、イオンが通過可能な孔が形成されてなる、

ことを特徴とする電池が提供される。

次に、本発明の理解を容易にするために、まず本発明の基本的特徴及び諸態様を列挙する。

1. ケーシング、

該ケーシング内に含まれる電解質、

正極活物質層を含む正極、

負極活物質層を含む負極、及び

多孔性セパレータを包含し、

該正極、該負極及び該セパレータは、該ケーシング内に、該電解質と共働可能に收容されており、

該多孔性セパレータは、該正極と該負極の間に、該多孔性セパレータの両側表面が該正極活物質層及び該負極活物質層にそれぞれ面するように配置構成されてなる電池であって、

該多孔性セパレータは、少なくとも1層の絶縁性物質粒子集合体層からなり、該少なくとも1層の絶縁性物質粒子集合体層が3次元網目空隙構造を有しており、それにより、該

多孔性セパレータに、イオンが通過可能な孔が形成されてなる、

ことを特徴とする電池。

2. 該粒子集合体が、該粒子同士を結合するバインダーを含むことを特徴とする前項1に記載の電池。

3. 該多孔性セパレータが該正極活物質層及び該負極活物質層よりなる群から選ばれる少なくとも1つの活物質層表面に一体化された形で直接形成されていることを特徴とする前項1又は2に記載の電池。

4. 該多孔性セパレータの空孔率が、乾燥状態で10%以上であることを特徴とする前項1～3のいずれかに記載の電池。

5. 該多孔性セパレータが、該粒子集合体の空隙以外の要因に起因するイオン伝導性を有することを特徴とする前項1～4のいずれかに記載の電池。

6. 該絶縁性物質が無機物であることを特徴とする前項1～5のいずれかに記載の電池。

7. 該絶縁性物質が有機物であることを特徴とする前項1～5のいずれかに記載の電池。

8. 該粒子集合体が、少なくとも2種類の異なる絶縁性物質からなることを特徴とする前項1～7のいずれかに記載の電池。

9. 該多孔性セパレータが、異なる粒子集合体からそれぞれ構成される少なくとも2つの層からなることを特徴とする前項1～8のいずれかに記載の電池。

10. 該多孔性セパレータが、少なくとも1層の無機絶縁性物質粒子集合体層よりなる第1セパレータ層及び少なくとも1層の有機絶縁性物質粒子集合体層よりなる第2セパレータ層とからなり、該第1セパレータ層が、該正極活物質層と該負極活物質層のうちの一方の活物質層の表面に一体化された形で直接形成されており、該第2セパレータ層が該正極活物質層と該負極活物質層のうちの他方の活物質層の表面に一体化された形で直接形成されていることを特徴とする前項1～9のいずれかに記載の電池。

11. 該電解質が非水電解質であることを特徴とする前項1～10のいずれかに記載の電池。

12. 該非水電解質がリチウムイオンを含むことを特徴とする前項11に記載の電池。

13. 該正極活物質層がマンガン酸リチウムを含むことを特

徴とする前項 1 1 又は 1 2 に記載の電池。

1 4. (1) 正極活物質層を含む正極及び負極活物質層を含む負極をそれぞれ提供し、

(2) 絶縁性物質粒子と該粒子用のためのバインダーとの混合物を分散媒に分散せしめた分散液を、該正極活物質層および該負極活物質層よりなる群から選ばれる少なくとも 1 つの活物質層の表面に塗布し、

(3) 該少なくとも 1 つの活物質層の表面に塗布した分散液の分散媒を蒸発させることにより除去して、該粒子同士がバインダーによって結合されてなる該粒子の集合体層を形成し、それにより、該少なくとも 1 つの活物質層の表面に一体化され且つその絶縁性物質粒子集合体層中に 3 次元網目空隙構造を有してなる多孔性セパレータを形成し、

(4) このようにして得られた少なくともどちらか一方の活物質層表面に該多孔性セパレータを形成させてなる該正極及び該負極を、ケーシングに収容し、その際、該多孔性セパレータを挟んで該正極活物質層及び該負極活物質層を対向させ、且つケーシング内の電解質と共働可能になるように配設する、

ことを特徴とする電池の製造方法。

本発明の電池においては、多孔性セパレータを形成する絶縁性物質粒子集合体の空隙によって 3 次元網目構造の孔が該

セパレータに形成されており、その孔中に介在する電解質中をイオンが伝導する一方で、絶縁性物質粒子集合体からなるセパレータの介在によって正極活物質層と負極活物質層とは電氣的に短絡されない構造になっている。本発明に用いるセパレータは、従来のポリオレフィン樹脂フィルム製のセパレータ等と比べて、高いイオン透過性を有する。これは、本発明に用いる多孔性セパレータを形成する絶縁性物質粒子集合体の空隙がセパレータ内においては、従来の樹脂フィルム製セパレータ等と比べて、より効果的な三次元網目空隙構造が形成されているためと考えられる。

上記絶縁性物質粒子としては、無機物の粒子であっても有機物の粒子であってもよい。無機物の例としては、酸化物

〔例えば、 Li_2O 、 BeO 、 B_2O_3 、 Na_2O 、 MgO 、 Al_2O_3 、 SiO_2 、 P_2O_5 、 CaO 、 Cr_2O_3 、 Fe_2O_3 、 ZnO 、 ZrO_2 及び TiO_2 等〕、ゼオライト〔 $\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ （式中、 M は Na 、 K 、 Ca 及び Ba 等の金属原子、 n は金属陽イオン M^{n+} の電荷に相当する数、 x 及び y は SiO_2 及び H_2O のモル数であり $2 \leq x \leq 10$ 、 $2 \leq y \leq 7$ ）〕、窒化物〔例えば、 BN 、 AlN 、 Si_3N_4 及び Ba_3N_2 等〕、炭化ケイ素（ SiC ）、ジルコン（ ZrSiO_4 ）、炭酸塩〔例えば、 MgCO_3 及び CaCO_3 等〕、硫酸塩〔例えば、 CaSO_4 及び BaSO_4 等〕及びこれらの複合体〔例えば磁器の一種である、ステアタイト

($\text{MgO} \cdot \text{SiO}_2$)、フォルステライト ($2\text{MgO} \cdot \text{SiO}_2$) 及び、コージェライト ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$)] が挙げられる。有機物の例としては、ポリエチレン、ポリプロピレン、ポリスチレン、ポリ塩化ビニル、ポリ塩化ビニリデン、ポリアクリロニトリル、ポリメタクリル酸メチル、ポリアクリル酸エステル、フッ素樹脂（例えば、ポリテトラフルオロエチレン及びポリフッ化ビニリデン等）、ポリアミド樹脂、ポリイミド樹脂、ポリエステル樹脂、ポリカーボネート樹脂、ポリフェニレンオキシサイド樹脂、ケイ素樹脂、フェノール樹脂、尿素樹脂、メラミン樹脂、ポリウレタン樹脂、ポリエーテル樹脂（例えば、ポリエチレンオキシサイド及びポリプロピレンオキシサイド等）、エポキシ樹脂、アセタール樹脂、AS樹脂及びABS樹脂等の樹脂が挙げられる。

一般に、絶縁性物質粒子としては硬度の高いものを用いるのが好ましい。そのような粒子を用いると活物質層の体積が膨脹するなどしてセパレータに圧力が加わっても粒子が変形しないためセパレータの空隙が潰されるといった不利がない。そのため電解質が存在できる部分が常に確保されるためイオン伝導性が低下することがなく、電池の耐久性が向上する。

また、絶縁性物質粒子としては、融点が 200°C 以上の耐熱性があるもの、例えば $\alpha\text{-Al}_2\text{O}_3$ （融点 2055°C ）や耐熱性樹脂のポリイミド（ $250^\circ\text{C} \sim 400^\circ\text{C}$ で不溶・不融

で分解もしない)などを用いると、従来のポリエチレン製微多孔膜(融点約 140°C)やポリプロピレン製微多孔膜(融点約 180°C)からなるセパレータと比較して耐熱性に優れたセパレータを得ることができる。

上記絶縁性物質粒子の粒径としては、平均粒径が 5 nm ～ $100\text{ }\mu\text{ m}$ であることが好ましく、 5 nm ～ $10\text{ }\mu\text{ m}$ であることがより好ましく、 5 nm ～ $1\text{ }\mu\text{ m}$ であることが更に好ましい。

セパレータの厚みは、特に限定されないが、 100 nm ～ $100\text{ }\mu\text{ m}$ であることが好ましく、 100 nm ～ $10\text{ }\mu\text{ m}$ であることがより好ましい。

本発明においては、上記の粒子集合体が粒子同士を結合するバインダーを含むことが好ましい。

バインダーの例としては、ラテックス(例えば、スチレン-ブタジエン共重合体ラテックス及びアクリロニトリル-ブタジエン共重合体ラテックス)、セルロース誘導体(例えば、カルボキシメチルセルロースのナトリウム塩)、フッ素ゴム(例えば、フッ化ビニリデンとヘキサフルオロプロピレンとテトラフルオロエチレンとの共重合体)やフッ素樹脂(例えば、ポリフッ化ビニリデン及びポリテトラフルオロエチレン)が挙げられる。

またバインダーの量に関しては、バインダーの絶縁性物質粒子に対する体積比が、 $1/500$ ～ $5/3$ になる量を用い

ることが好ましく、 $1/500 \sim 1/2$ になる量を用いることがより好ましく、 $1/500 \sim 1/5$ になる量を用いることが更に好ましい。

また、本発明において、多孔性セパレータは正極活物質層および負極活物質層よりなる群から選ばれる少なくとも1つの活物質層表面に一体化された形で直接形成されていることが好ましい。

従来の電池でセパレータとして使用されている樹脂フィルム製の微多孔膜は、単体で取り扱う必要性から機械的強度を持たせるために $25\mu\text{m}$ より薄くすることは困難であった。しかし、本発明において、上記の活物質層表面に一体化された形で直接形成されたセパレータを用いる場合には、セパレータを単体で扱う必要がないため極端に薄くすることができ、そのため、電池の単位体積あたりに収容可能な活物質の量を増やすことができるだけでなく、内部抵抗が低減できるため過電圧が減少し、入出力特性を著しく向上させることができる。

上記の多孔性セパレータの空孔率は、乾燥状態で10%以上であることが好ましく、20%以上であることがより好ましく、40%以上であることが更に好ましい。また、前記空孔率が高いほどイオン伝導性が向上するため好ましいが、特にセパレータの厚みが小さい場合には、空孔率が高すぎると、正極と負極との短絡を防ぐことが困難となるため、実用的に

は90%以下であることが好ましい。

前記空孔率の測定は、セパレータを単体に行なうことができるが、セパレータが電極に一体化されて単離することができない場合は、以下の方法で空孔率を求めることができる。即ち、セパレータの孔に樹脂溶液を含浸させて固化させた後、SEM

(scanning electron microscope)を用いてセパレータの断面の写真を得、これを分析して、全断面の面積中の樹脂含浸部分の面積の割合(%)を測定する。セパレータの、上記の断面とは異なる10カ所以上の断面について上記と同様の測定を行い、得られた値の平均値を空孔率とする。

また上記のセパレータは、該粒子集合体の空隙以外の要因に起因するイオン伝導性を有していても良い。

そのようなセパレータを得る方法としては、絶縁性物質粒子として多孔質である材料を使用する方法、絶縁性物質粒子として骨格構造内に分子が出入りできる隙間をもつ材料(例えば、ゼオライト)を使用する方法、絶縁性物質粒子及び/又はこれと混合させる物質として電解液に膨潤する材料(例えば、ポリアクリロニトリル、ポリメタクリル酸メチル及びポリフッ化ビニリデン等)を使用する方法、絶縁性物質粒子及び/又はこれらと混合させる物質として固体に電解液を含浸させた後溶媒のみを蒸発させて得られる材料(例えば、ポリエチレンオキサイド、ポリプロピレンオキサイド、ポリフ

オスファゼン等のアルカリ金属塩との複合体)を使用する方法等が挙げられる。

本発明の前記 8、9 及び 10 項の態様においては、本発明の電池は、それぞれ、異なる絶縁性物質からなる粒子集合体からなるセパレータ、異なる粒子集合体からそれぞれ構成される少なくとも 2 つの層からなるセパレータ、及び無機絶縁性物質粒子集合体層よりなる第 1 セパレータ層及び有機絶縁性物質粒子集合体層よりなる第 2 セパレータ層からなるセパレータが用いられる。ここで、「異なる」とは、化学的組成の異なること、化学的組成が同じでも融点等の性質が異なることを意味する。上記の態様を用いることにより、セパレータにヒューズ機能を持たせることが出来る。例えば、前記 8 項の態様に従って、高い融点（例えば 1000℃以上）をもつ無機酸化物の粒子と低い融点（例えば 200℃以下）をもつ樹脂の粒子とを混合して粒子集合体層を形成した場合、また、例えば、前記 10 項の態様において、正極活物質層表面には高い融点（例えば 1000℃以上）をもつ無機酸化物の粒子集合体層を形成し、負極活物質層表面には低い融点（例えば 200℃以下）をもつ樹脂の粒子集合体層を形成した場合には、電池が高温状態に陥ったとき樹脂粒子のみが熔融して空隙を閉塞し電流を遮断するヒューズ機能を発揮し、安全体を確保することができる。

本発明の電池は、例えば、二酸化マンガンーリチウム電池やフッ化黒鉛ーリチウム電池等の一次電池であつてもよく、また、例えば、鉛蓄電池、ニッケルーカドミウム電池や、ニッケルー水素電池等の水系電解液を使用した二次電池や、リチウムイオン二次電池等の非水系電解液を使用した二次電池であつてもよい。

本発明のケーシングとしては、アルミ、SUS、鉄、ニッケル、鍍金を施した鉄などの缶、又ラミネート、樹脂フィルムで形成されたものを挙げることができる。

本発明の電池が一次電池である場合には、正極、負極及び電解質には公知のものを用いることができる。例えば、本発明の電池が二酸化マンガンーリチウム電池である場合には、正極に二酸化マンガン、負極にリチウム金属、電解質として有機溶媒にリチウム塩を溶解させたものを用いることができる。本発明の電池がフッ化黒鉛ーリチウム電池である場合には、正極にフッ化黒鉛、負極及び電解質としては上記の二酸化マンガンーリチウム電池と同様のものを用いることができる。

本発明の電池が二次電池である場合にも、正極、負極及び電解質には公知のものを用いることができる。例えば、本発明の電池が鉛蓄電池である場合は、正極活物質に PbO_2 、負極活物質に Pb 、電解液には H_2SO_4 水溶液を用いることができる。本発明の電池がニッケルーカドミウム電池である

場合は、正極活物質に Ni(OH)_2 、負極活物質に Cd 、電解液には KOH を主体として LiOH や NaOH を添加した水溶液を用いることができる。また、本発明の電池がニッケル-水素電池である場合は、負極活物質に水素（水素吸蔵合金）を用いることができ、正極活物質および電解液にはニッケル-カドミウム電池と同様なものを用いることができる。

また、本発明の電池がリチウムイオン二次電池である場合の正極活物質、負極活物質及び電解質については下記に詳述する。尚、正極用集電体箔としては、例えば、アルミニウム、チタンおよびステンレススチール等の金属箔を用いることができ、アルミニウム箔を用いることが好ましい。負極用集電体箔としては、例えば、銅、ニッケルおよびステンレススチール等の金属箔を用いることができ、銅箔を用いることが好ましい。

リチウムイオン二次電池の場合の正極活物質としては、 Li と Co 、 Ni 、 Mn 、 Fe 等の遷移金属との複合金属酸化物、又は Li と遷移金属と非遷移金属との複合金属酸化物を用いることができる。例えば、層状構造を有し電気化学的にリチウムイオンがインターカレート (intercalate)、ディインターカレート (deintercalate) し得るリチウム複合金属酸化物等を挙げることができる。リチウム複合金属酸化物の具体例としては、日本国特開昭55-136131号公報（米国特許第4357215号に対応）に開示されている Li

$i\text{CoO}_2$ 、日本国特開平3-49155号公報に開示されている $\text{Li}_x\text{Ni}_y\text{Co}_{(1-y)}\text{O}_2$ （但し、 $0 \leq x \leq 1$ 、 $0 \leq y \leq 1$ ）、及び $\text{Li}_x\text{Mn}_2\text{O}_4$ （但し、 $0 \leq x \leq 1$ ）等が挙げられる。

かかる化合物を得るには、水酸化リチウム、酸化リチウム、炭酸リチウム、硝酸リチウム等のリチウム化合物と金属酸化物、金属水酸化物、金属炭酸塩、金属硝酸塩等と、更に、もし望まれるならば、他の金属化合物との焼成反応により容易に得ることができる。

また、リチウムイオン二次電池の負極活物質としては、コークス、グラファイト、非晶質カーボン等の炭素質材料を用いることができ、その形状としては破碎状、鱗片状、球状いずれの形状であっても良い。上記の炭素質材料は、特に限定されるものではないが、例えば、日本国特開昭58-35881号公報（米国特許第4617243号に対応）に記載の高表面積炭素材料、グラファイト、特開昭58-209864号公報に記載のフェノール系樹脂等の焼成炭化物、又日本国特開昭61-111907号公報（米国特許第4725422号に対応）に記載の縮合多環炭化水素系化合物の焼成炭化物等が挙げられる。

また、リチウムイオン二次電池の非水系電解液としては特に限定されないが、例えば LiClO_4 、 LiBF_4 、 LiAsF_6 、 $\text{CF}_3\text{SO}_3\text{Li}$ 、 $(\text{CF}_3\text{SO}_2)_2\text{N} \cdot \text{Li}$ 、

LiPF_6 、 LiI 、 LiAlCl_4 、 NaClO_4 、
 NaBF_4 、 NaI 、 $(n\text{-Bu})_4\text{NClO}_4$ 、 $(n\text{-Bu})_4\text{NBF}_4$ 、 KPF_6 等の電解質を有機溶媒に溶解して有機電解液として使用することができる。有機電解液中の電解質濃度は約 $0.1 \sim 2.5 \text{ mol/l}$ であることが好ましい。

用いられる有機溶媒としては、例えば、エーテル類、ケトン類、ラクトン類、ニトリル類、アミン類、アミド類、硫黄化合物、塩素化炭化水素類、エステル類、カーボネート類、ニトロ化合物、リン酸エステル系化合物、スルホラン系化合物等を用いることができるが、これらのうちでもエーテル類、ケトン類、ニトリル類、塩素化炭化水素類、カーボネート類、スルホラン系化合物が好ましい。更に好ましくは環状カーボネート類である。これらの代表例としては、テトラヒドロフラン、2-メチルテトラヒドロフラン、1,4-ジオキサン、アニソール、モノグライム、アセトニトリル、プロピオニトリル、4-メチル-2-ペンタノン、ブチロニトリル、バレロニトリル、ベンゾニトリル、1,2-ジクロロエタン、γ-ブチロラクトン、ジメトキシエタン、メチルフォルメイト、プロピレンカーボネート、エチレンカーボネート、ジエチルカーボネート、ジメチルカーボネート、メチルエチルカーボネート、ビニレンカーボネート、ジメチルホルムアミド、ジメチルスルホキシド、ジメチルチオホルムアミド、スルホラン、3-メチルスルホラン、リン酸トリメチル、リン酸ト

リエチルおよびこれらの混合溶媒等をあげることができるが、必ずしもこれらに限定されるものではない。

上記のリチウムイオン二次電池のような非水系電解質を用いる電池は、非水系電解質がイオン伝導性に乏しいため、正極・負極間のイオン伝導性の効率を向上させるため、従来は、一般に、図1(A)に示すような、正極集電体箔11aの両面に正極活物質が正極活物質層11bとして塗布されてなる正極11と、負極集電体箔12aの両面に負極活物質が負極活物質層12bとして塗布されてなる負極12と、正極活物質層11bと負極活物質層12bとの間に間置された樹脂フィルム製セパレータ13からなる単位電池層が多数積層又は捲回されてなる構造を有する。上記の樹脂フィルム製セパレータ13は単体で取り扱う必要性から機械的強度を持たせるために25 μ mより薄くすることは困難であり、そのため、電池の単位体積あたりに収容可能な活物質の量が制限されてしまう欠点があった。上記のような構造を有する電池に、樹脂フィルム製セパレータ13のかわりに、本発明で用いる上記の多孔性セパレータを用いると電池の単位体積あたりに収容可能な活物質の量及び正極・負極間のイオン伝導性の効率が飛躍的に向上した高性能の電池を得ることができる。更に、従来、上記のような構造を有する電池においては、電池構成部材のうちで比較的高価な樹脂フィルム製セパレータを大量に使用するため、電池製造コストが高くなるという問題があ

った。しかし、本発明で用いるセパレータは非常に安価で得られるため、上記のような高性能の電池を安価で製造することができる。

本発明で用いるセパレータの製造方法は特に限定されないが、例えば図2に参照して説明する以下の方法で製造することができる。集電体箔11a上に正極活物質層11bを従来より公知の方法で形成して正極11を得、正極活物質層11bの表面に絶縁性物質粒子集合体層を形成することによってセパレータ13Aを得ることができる。具体的には、絶縁性物質粒子で正極活物質層11b表面を均一に覆ったのちロールプレスで圧着させたり、絶縁性物質粒子とバインダーとの混合物とを分散媒に分散せしめた分散液を正極活物質層11b表面に所定の厚さで均一に塗布した後、加熱して分散媒を蒸発させて除去することにより、絶縁性物質粒子集合体層を正極活物質上に形成することによりセパレータ13Aを得ることができる。上記の分散液を用いる方法の場合、用いる分散媒は絶縁性物質粒子を溶解せず、バインダーを溶解し、適度な温度で加熱することにより溶解するものであれば特に限定されず、例えば、酢酸エチル、エチレングリコールモノエチルエーテル（2-エトキシエタノール）、1-メチル-2-ピロリドン（NMP）、N,N-ジメチルホルムアミド（DMF）、ジメチルスルホキシド（DMSO）、テトラヒドロフラン（THF）及び水等を用いることができる。また、

加熱による分散媒の除去は、絶縁性物質粒子が変形、又は融解しない程度の温度、時間で行えば良く、一般には、50～200℃で5～30分行う。また、分散液中の固形分（絶縁性物質粒子）濃度は特に限定されないが、40～60重量%の範囲であることが好ましい。

このような方法を用いることにより、各絶縁性物質粒子はセパレータ形成前後で形状等変化することではなく、例えば粒子に熱をかけて粒子同士を融着させる（焼結）するような方法とは基本的に異なっており、本発明においては、粒子集合体中の粒子は粒子同士が融着したり、化学結合を形成しておらず、各粒子はあくまで原形を保っている。

図2に示すような単位電池層を用いて本発明の電池を作成する際には、例えば、この単位電池層をその負極側が外側になるよう捲回するか、複数の単位電池層をセパレータ13Aを介して正極11と負極12とが対向するように積層することにより、セパレータ13Aが正極11と負極12の間に、セパレータ13Aの両側表面が正極活物質層11b及び負極活物質層12bにそれぞれ面するように配置することが出来る。

図2に示すセパレータ13Aのように、電極活物質層表面に一体化した形で直接形成されたセパレータは、既に述べたように、単体で取り扱う必要がないため、絶縁性物質粒子の粒径に応じ、所定の空孔率が確保でき且つ正極と負極の活物

質間に短絡が生じない範囲で薄くすることができる。例えば、絶縁性物質粒子として平均粒径 $1\ \mu\text{m}$ 以下のものを使用すれば、セパレータ 13A の厚さを $5\sim 10\ \mu\text{m}$ とし、空孔率を 60% 程度とすることができる。

さらに、このようなセパレータ 13A は粒子とバインダーによって結合された粒子からなるため、フレキシビリティが高いので、電極活物質表面に一体化した形で直接形成されていることから、セパレータが電極上でずれることはなく、電池生産工程において非常に有利である。このように高いフレキシビリティは、例えば粒子を焼結してセパレータを形成したような場合には得にくいものである。

次に、本発明の電池の具体的構成を説明するために、図 2 ～ 図 6 に参照して、種々の実施態様を説明する。

上記した図 2 では、正極集電体箔 11a の両側の 2 つの正極活物質層 11b、11b の両表面にセパレータ 13A を一体化させて形成したが、図 3 に示すように、負極集電体箔 12a の両側の 2 つの負極活物質層 12b、12b の両表面にセパレータ 13B を一体化させて形成してもよい。

また、図 4 に示すように、正極 11 の片側の活物質層 11b 表面に一体化させてセパレータ 13A を形成し、負極 12 の片側の活物質層 12b 表面に一体化させてセパレータ 13B を形成させ、セパレータ 13A を介して正極活物質層 11b と負極活物質層 12b を対向させて単位電池層 1 を形成し

てもよい。

さらに、図5に示すように、正極11の両側の2つの活物質層11b、11bの両表面に一体化させてセパレータ13A、13Aをそれぞれ形成し、又、負極12の両側の2つの活物質層12b、12bの両表面に一体化させてセパレータ13B、13Bをそれぞれ形成して、これらのセパレータ13A及び13Bの両者を介して正極活物質層11bと負極活物質層12bを対向させて電池層1を形成してもよい。この際、正極11の両側の活物質層11b、11bの両表面にそれぞれ形成されたセパレータ13A、13Aは同じであっても異なってもよく、負極12の両側の活物質層12b、12bの両表面にそれぞれ形成されたセパレータ13B、13Bは同じであっても異なってもよい。また、この図5に示すような構造を持つ単位電池層を用いた電池では、セパレータ13A、13Bのいずれかにピンホール（セパレータの略厚み方向に貫通する孔）が生じた場合でも、2つのセパレータ13A、13Bが重ね合わさっていることによりピンホール同士が重なる確率がほとんどなくなるため、相対向する正極活物質層11aと負極活物質層11bとの短絡を防ぐことができる。

また、本発明においては、セパレータが図6に示すセパレータ13Cのように、正極活物質層11bの表面及び負極活物質層12bの表面の両方に一体化された形で形成されてい

てもよい。このセパレータ13Cの製法としては、絶縁性物質粒子とバインダーとの混合物とを分散媒に分散せしめた分散液を一方の電極の活物質層表面に塗布した後、その表面上に直ちに他方の電極を両電極活物質層が上記の分散液を介して対向するように重ねあわせた後、加熱して分散媒を蒸発させることにより両電極を貼り合わせるという方法、また、少なくとも一方の電極の活物質層表面に上記の分散液塗布後、乾燥させてセパレータ層を形成した後、他方の電極を両電極の活物質層が、このセパレータ層を介して対向するように重ね合わせた後、バインダーが熔融する程度の温度でホットプレスして貼り合わせるという方法、或いは、少なくとも一方の電極の活物質層表面に上記の分散液を塗布後、乾燥させてセパレータ層を形成した後、セパレータ層上にバインダーを溶解する溶媒を塗布し、他方の電極を両極の活物質層がこのセパレータ層を介して対向するよう重ね合わせた後、プレスおよび乾燥して貼り合わせるという方法等が挙げられる。

また本発明の電池においては、正極、負極及びセパレータからなる単位電池層は、図2～図6に示すように複数の正極活物質層及び複数の負極活物質層からなる構造の単位電池層であってもよく、また、実施例において参照する図7(a)～7(c)に示すような1つの正極活物質層と負極活物質層からなる構造の単位電池層であってもよく、またそれらが積層されたり、捲回された構造であってもよい。

尚、本発明の電池の製造方法に関しては特に限定はないが、その好ましい1つの方法として、次の方法を挙げることができる。

(1) 正極活物質層を含む正極及び負極活物質層を含む負極をそれぞれ提供し、

(2) 絶縁性物質粒子と該粒子のためのバインダーとの混合物を分散媒に分散せしめた分散液を、該正極活物質層および該負極活物質層よりなる群から選ばれる少なくとも1つの活物質層の表面に塗布し、

(3) 該少なくとも1つの活物質層の表面に塗布した分散液の分散媒を蒸発させることにより除去して、該粒子同士がバインダーによって結合されてなる該粒子の集合体層を形成し、それにより、該少なくとも1つの活物質層の表面に一体化され且つその絶縁性物質粒子集合体層中に3次元網目空隙構造を有してなる多孔性セパレータを形成し、

(4) このようにして得られた少なくともどちらか一方の活物質層表面に該多孔性セパレータを形成させてなる該正極及び該負極を、ケーシングに収容し、その際、該多孔性セパレータを挟んで該正極活物質層及び該負極活物質層を対向させ、且つケーシング内の電解質と共働可能になるように配設する、

ことを特徴とする電池の製造方法。

発明を実施するための最良の形態

以下、次の実施例を参照し、本発明を更に詳細に説明するが、本発明はこれらによって何ら限定されるものではない。

実施例 1

図 7 (a) に示すような構造を有する実験用小スケールセルにより、本発明の電池の充放電特性を調べた。

シート状の電極を以下のようにして製造した。

正極：正極活物質として LiCoO_2 、フィラーとして

リン片状グラファイトおよびアセチレンブラック及びバインダーとしてフッ素ゴム〔フッ化ビニリデンとヘキサフルオロプロピレンとテトラフルオロエチレンとの共重合体；商品名ミラフロン、日本国旭化成工業（株）製〕

を、 LiCoO_2 ：リン片状グラファイト：アセチレンブラック：フッ素ゴム＝100：2.5：2.5：1.96の重量比で酢酸エチルとエチルセロソルブの体積比1：3の混合溶媒中で混合してスラリーを得、これを厚さ15 μm のアルミニウム箔11a（集電体箔）の片面に塗布後乾燥して、カレンダーロールにてプレスを施して厚さ88 μm の正極活物質層を形成することにより作製した。

負極：負極活物質としてニードルコークス、分散剤としてカルボキシメチルセルロース、バインダーとしてラテックス（スチレンーブタジエン共重合体ラテックス）を、ニードルコークス：カルボキシメチルセルロース：ラテックス＝100：0.8：2.0の重量比で精製水中で混合してスラリーを得、これを厚さ18 μ mの銅箔12a（集電体箔）の片面に塗布後乾燥し、カレンダーロールにてプレスを施して厚さ124 μ mの負極活物質層を形成することにより製造した。

次に、絶縁体粒子の集合体の使用材料およびその作製方法は以下に示すとおりである。

〔使用材料〕

絶縁性物質粒子：平均粒径0.5 μ mの α -Al₂O₃

バインダー：フッ素ゴム〔商品名ミラフロン、

旭化成工業（株）製〕

溶媒：酢酸エチルとエチルセロソルブの体積比1：3の

混合溶媒

上記のミラフロンを酢酸エチルとエチルセロソルブの混合溶媒に溶解させて4.3wt%のミラフロン溶液を調整し、このミラフロン溶液に α -Al₂O₃粉体を混合して固形分率45.3wt%のスラリーを得た。

このスラリーをドクターブレードを用いて上記正極の活物質上に所定の厚みで均一に塗布後、120℃のオーブン中で15分間乾燥することにより固定された α - Al_2O_3 粒子集合体からなるセパレータ13Aを得た。このセパレータ13Aの空孔率は52%であった。この空孔率は、上記と同様のセパレータをアルミニウム箔製の皿上に形成させた後、アルミニウム箔製の皿から剥がして（株）日本国島津製作所製の水銀ポロシメーターにより測定した。

上記のセパレータ13Aが固定された正極11を、1.5 cm×1.0 cmのサイズに加工した。負極12については1.55 cm×1.05 cmのサイズになるように加工した。

次に、上記の正極と負極をセパレータ13Aを介して対向させて配置し、図7(a)に示す構造を有するサンプルを作製した（実施例1-A）。このときのセパレータの厚みは25 μm であった。

更に、負極活物質上にもセパレータ13Aを施した以外は上記（実施例1-A）と同様にして図7(b)に示す構造を有するサンプルを作製した（実施例1-B）。このときのセパレータ13Aの厚みは正極側と負極側をあわせて50 μm であった。これらを、プロピレンカーボネート（PC）、エチレンカーボネート（EC）および γ -ブチロラクトン（ γ -BL）の体積比1:1:2の混合溶媒にLiBF₄を1.

0 m o l / l 溶解させた電解液中で下記の条件により充放電させた。

[充放電条件]

温度：25℃

第1サイクル

充電：1.0 mA / cm²で8時間充電し、電圧を4.2 Vとする。

放電：1.0 mA / cm² (1 / 3 C相当) で電圧が2.7 Vとなるまで放電を行う。

第2～15サイクル

充電：1.0 mA / cm²で6時間充電し、電圧を4.2 Vとする。

放電：1.0 mA / cm² (1 / 3 C相当) で電圧が2.7 Vとなるまで放電を行う。

第16、17サイクル

充電：第2～15サイクルに同じ

放電：3.0 mA / cm² (1.0 C相当) で電圧が2.7 Vとなるまで放電を行う。

第18サイクル

充電：第2～15サイクルに同じ

放電：第2～15サイクルに同じ

第19サイクル

充電：第2～15サイクルに同じ

放電：6.0 mA/cm² (2.0 C相当) で電圧が2.7 Vとなるまで放電を行う。

それぞれのサンプルに関して、15サイクル目と16サイクル目の放電容量変化率、及び18サイクル目と19サイクル目の放電容量変化率を求めた。結果を表1に示す。

比較例 1

実施例1と実質的に同様な方法で作成した正極と負極をそれぞれ1.5 cm×1.0 cm、1.55 cm×1.05 cmのなるように加工し、厚さ25 μm及び空孔率48%のポリエチレン (PE) 微多孔膜からなるセパレータを用いて作成した図1 (B) に示す構造を有するサンプルを作成 (比較例1-A)、更に厚さ34 μm及び空孔率63%のポリエチレン微多孔膜からなるセパレータを用いた以外は上記サンプルと同様にしてサンプルを作成した [(比較例 (1-B))]。

なお、PE微多孔膜の空孔率は、空孔容積/多孔膜容積×100 (ただし、空孔容積=含水重量-絶乾重量) より求めた。

実施例1と同電解液中かつ同充放電条件により充放電させた。15サイクル目と16サイクル目の放電容量変化率、及び18サイクル目と19サイクル目の放電容量変化率を求めた。結果を表1に示す。

表 1

	15サイクル目 1/3C放電 容量 E_{15} mAh	16サイクル目 1.0C放電 容量 E_{16} mAh	15→16サイ クル 容量変化率 %	18サイクル目 1/3C放電 容量 E_{18} mAh	19サイクル目 2.0C放電 容量 E_{19} mAh	18→19サイ クル 容量変化率 %
実施例 1-A	4.326	4.017	-7.1	4.311	2.354	-45.4
実施例 1-B	4.342	4.076	-6.1	4.303	1.553	-63.9
比較例 1-A	4.350	3.959	-9.0	4.337	1.341	-69.1
比較例 1-B	4.383	4.058	-7.4	4.364	1.502	-65.6

$$n \text{ サイクル目} \rightarrow (n-1) \text{ サイクル目の容量変化率} \% : [E_n - E_{(n-1)}] / E_{(n-1)} \times 100$$

この表に示すように、セパレータの膜厚が同等である実施例 1-A と比較例 1-A を比較した場合、放電の電流密度を $1/3\text{ C}$ から 2.0 C に変化させた $18 \rightarrow 19$ サイクルの放電容量変化率は実施例 1 が著しく小さくなった。これは、本発明における絶縁性物質粒子の集合体からなるセパレータと、従来のポリエチレン製微多孔膜からなるセパレータとにおける、セパレータ中の空孔の大きさや分布状態が異なることに起因して、本発明のセパレータ中のイオン伝導性が向上して、高い電流密度での放電特性が向上したものと推定される。このことは、比較例 1-A および 1-B よりもセパレータの膜厚がはるかに厚い実施例 1-B が前者 2 例と同等以上の放電特性を示していることから裏付けられる。

また、実施例 1-A と比較例 1-B を比較した場合、放電の電流密度を $1/3\text{ C}$ から 2.0 C に変化させた $18 \rightarrow 19$ サイクルの放電容量変化率は、セパレータの空孔率は低いが、膜厚の薄い実施例 1-A が著しく小さくなった。これは、本発明のセパレータにおいて空孔率は低くても膜厚が薄くなっていることにより、セパレータ中のイオン伝導性が向上して、高い電流密度での放電特性が向上したものと推定される。

実施例 2

実施例 1 と同様に、実験用の小スケールセルにより本発明の電池の充放電特性を調べた。

まず、電極はシート状で以下のものを用意した。

〔電極〕

正極： LiCoO_2 を正極活物質、リン片状グラファイトおよびアセチレンブラックをフィラー、フッ素ゴムをバインダーとし、 LiCoO_2 ：リン片状グラファイト：アセチレンブラック：フッ素ゴム＝100：2.5：2.5：1.96の重量比で酢酸エチルとエチルセロソルブの体積比1：3の混合溶媒中で混合してペーストとし、厚さ15 μm のアルミニウム箔（集電体箔）上に塗布後乾燥して、プレスをして厚さ87 μm の正極活物質層を形成したもの

負極：メソフェーズピッチカーボンファイバーグラファイトおよびリン片状グラファイトを負極活物質、カルボキシメチルセルロースを分散剤、ラテックスをバインダーとし、メソフェーズカーボンファイバーグラファイト：リン片状グラファイト：カルボキシメチルセルロース：ラテックス＝90：10：1.4：1.8の重量比で精製水中で混合してペーストとし、厚さ12 μm の銅箔（集電体箔）上に塗布後乾燥し、プレスをして厚さ81 μm の負極活物質層を形成したもの

次に、絶縁性物質粒子の集合体の使用材料およびその作製方法は以下に示すとおりである。

〔使用材料〕

絶縁性物質粒子：平均粒径 $1.0 \mu\text{m}$ の $\alpha\text{-Al}_2\text{O}_3$

バインダー：ポリフッ化ビニリデン (PVDF)

KF # 1100〔呉羽化学工業 (株) 製〕

溶媒：1-メチル-2-ピロリドン (NMP)

上記の $\alpha\text{-Al}_2\text{O}_3$ 粉体と PVDF 粉体を重量比 100 : 5 で粉体状態のまま混合し、それに NMP を加えてさらに混合し、固形分率 56.8 wt % のスラリーを得た。

このスラリーをドクターブレードを用いて前記電極シート上に所定の厚みで均一に塗布後、 120°C のオープン中で15分間乾燥して、電極上に $\alpha\text{-Al}_2\text{O}_3$ 粒子集合体を固定しセパレータとした。このセパレータの空孔率は52%であった。この空孔率は、前記セパレータを単独で形成させ、(株)島津製作所製の水銀ポロシメーターにより測定した。

上記のシートを、 $\alpha\text{-Al}_2\text{O}_3$ 粒子集合体塗布部分が、正極については $1.5 \text{ cm} \times 1.0 \text{ cm}$ の面積、負極については $1.55 \text{ cm} \times 1.05 \text{ cm}$ の面積になるように加工し、塗布部分を対向させて、図7(b)のようなサンプルを作製した。このときのセパレータの厚みは正極側と負極側をあわせて $25 \mu\text{m}$ のもの (実施例2-A) と $10 \mu\text{m}$ (実施例2-B) のものを用意した。

また、上記スラリーを正極上に塗布した後、直ちに負極活物質層が対向するように重ねあわせた後、加熱して溶媒を蒸

発させて貼り合わせた。これを $1.5 \text{ cm} \times 1.0 \text{ cm}$ の面積になるように加工し図 7 (c) のようなサンプルを作製した (実施例 2-C)。このときのセパレータの厚みは $25 \mu\text{m}$ であった。

これらを、エチレンカーボネート (EC) とジエチルカーボネート (DEC) の体積比 1 : 1 の混合溶媒に LiPF_6 を 1.0 mol/l 溶解させた電解液中で下記の条件により充放電させた。

比較例 2 として、 $\alpha\text{-Al}_2\text{O}_3$ 粒子集合体を形成させていない実施例 2-A および 2-B と同じ正極と負極をそれぞれ $1.5 \text{ cm} \times 1.0 \text{ cm}$ 、 $1.55 \text{ cm} \times 1.05 \text{ cm}$ の面積となるように加工し、ポリエチレン (PE) 微多孔膜からなる厚さ $25 \mu\text{m}$ のセパレータ (空孔率 36%) を挟んで両極を対向させて、図 1 (B) のようなサンプルを作製し、実施例 2 と同電解液中かつ同充放電条件により充放電させた。

なお、PE 微多孔膜の空孔率は、空孔容積 / 多孔膜容積 $\times 100$ (ただし、空孔容積 = 含水重量 - 絶乾重量) より求めた。

〔充放電条件〕

温度 : 25°C

1 ~ 10 サイクル

充電 : 1.0 mA/cm^2 で 6 時間充電し、電圧を 4 .

2 Vとする。

放電：1.0 mA / cm² (1 / 3 C相当) で電圧が2.7 Vとなるまで放電を行う。

1 1 サイクル

充電：1 ~ 10 サイクルに同じ

放電：3.0 mA / cm² (1.0 C相当) で電圧が2.7 Vとなるまで放電を行う。

1 2 サイクル

充電：1 ~ 10 サイクルに同じ

放電：1 ~ 10 サイクルに同じ

1 3 サイクル

充電：1 ~ 10 サイクルに同じ

放電：6.0 mA / cm² (2.0 C相当) で電圧が2.7 Vとなるまで放電を行う。

実施例 2 - A、2 - B、2 - C および比較例 2 における 10 サイクル目と 1 1 サイクル目の放電容量変化率、及び 1 2 サイクル目と 1 3 サイクル目の放電容量変化率は下記の表 2 に示す結果となった。

表 2

	10サイクル目 1/3C放電 容量 E_{10} mAh	11サイクル目 1.0C放電 容量 E_{11} mAh	10→11サイク ル 容量変化率 %	12サイクル目 1/3C放電 容量 E_{12} mAh	1サイクル目 2.0C放電 容量 E_{13} mAh	12→13サイク ル 容量変化率 %
実施例 2-A	5.027	4.944	-1.7	5.002	4.695	-6.1
実施例 2-B	5.031	4.977	-1.1	5.005	4.821	-3.7
実施例 2-C	5.011	4.933	-1.6	4.998	4.655	-6.9
比較例 2	5.025	4.925	-2.0	5.000	4.425	-11.5

nサイクル目 → (n-1) サイクル目の容量変化率% : $[E_n - E_{(n-1)}] / E_{(n-1)} \times 100$

この表に示すように、セパレータの膜厚が同等である実施例 2-A と比較例 2 を比較した場合、放電の電流密度を 1 / 3 C から 2 . 0 C に変化させた 1 2 → 1 3 サイクルの放電容量変化率は実施例 2 が著しく小さくなった。これは、本発明における絶縁性物質粒子の集合体からなるセパレータと、従来のポリエチレン製微多孔膜からなるセパレータとにおける、セパレータ中の空孔の大きさや分布状態が異なることに起因して、本発明のセパレータ中のイオン伝導性が向上して、高い電流密度での放電特性が向上したものと推定される。

また、実施例 2-B では、セパレータの膜厚がさらに薄くなっていることにより、さらに放電特性が向上したものと推定される。

さらに、実施例 2-C では、セパレータが正極と負極の両方に固定されていても同様な性能向上を示すことが証明された。

実施例 3

実施例 3 として実施例 2-A と同様な実験用小スケールセルを作製し、また比較例 3 として比較例 2 と同様な実験用小スケールセルを作製し、以下の充放電条件でサイクル特性評価を行った。この実施例は本発明のセパレータが従来よりもイオン伝導性が優れていることだけでなく、耐久性も向上していることを証明するために行った。

〔充放電条件〕

1 サイクル

充電：1.0 mA / cm² で6時間充電し、電圧を4.2 Vとする。

放電：1.0 mA / cm² (1 / 3 C相当) で電圧が2.7 Vとなるまで放電を行う。

2 ~ 200 サイクル

充電：3.0 mA / cm² で3時間充電し、電圧を4.2 Vとする。

放電：3.0 mA / cm² で電圧が2.7 Vとなるまで放電を行う。

2 サイクル目の放電容量に対する200サイクル目の放電容量維持率は、実施例3では88.8%、比較例3では83.8%であった。この結果が示すように、セパレータの膜厚が同等である実施例3と比較例3を比較した場合、放電容量維持率は実施例3が上回っている。これは、本発明における絶縁性物質粒子の集合体からなるセパレータは、従来のポリエチレン製微多孔膜からなるセパレータと比較して、耐久性が向上したことを証明している。

実施例 4

実施例1および2と同様に、実験用の小スケールセルにより本発明の電池の充放電特性を調べた。

まず、電極はシート状で実施例2および3と同じものを用意した。

次に、絶縁性物質粒子の集合体の使用材料およびその作製方法は以下に示すとおりである。

〔使用材料〕

絶縁性物質粒子： $\text{SiO}_2/\text{Al}_2\text{O}_3=29$ の分子数比の
ゼオライト

バインダー：ポリフッ化ビニリデン（PVDF）

KF#1100〔呉羽化学工業（株）製〕

溶媒：1-メチル-2-ピロリドン（NMP）

上記のゼオライト粉体とPVDF粉体を重量比100：5で粉体状態のまま混合し、それにNMPを加えてさらに混合し、固形分率55.0wt%のスラリーを得た。

このスラリーをドクターブレードを用いて前記電極シート上に均一に塗布後、120℃のオーブン中で15分間乾燥して、電極上にゼオライト粒子集合体を固定しセパレータとした。このセパレータの空孔率は50%であった。この空孔率は、前記セパレータを単独で形成させ、（株）島津製作所製の水銀ポロシメーターにより測定した。

上記のシートを、ゼオライト粒子集合体塗布部分が、正極については1.5cm×1.0cmの面積、負極については1.55cm×1.05cmの面積になるように加工し、塗布部分を対向させて、図7（b）のようなサンプルを作製した。このセパレータの厚みは正極側と負極側をあわせて25μmであった。これを、エチレンカーボネート（EC）とジ

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エチルカーボネート（DEC）の体積比1：1の混合溶媒にLiPF₆を1.0mol/l溶解させた電解液中で充放電させた（実施例4）。充放電条件は実施例2と同じにした。

比較例4として、実施例2で行った比較例2を引用した。

実施例4および比較例4の10サイクル目と11サイクル目の放電容量変化率、及び12サイクル目と13サイクル目の放電容量変化率は下記の表3に示す結果となった。

表 3

	10サイクル目 1/3C放電 容量 E_{10} mAh	11サイクル目 1.0C放電 容量 E_{11} mAh	10→11サイク ル 容量変化率 %	12サイクル目 1/3C放電 容量 E_{12} mAh	1サイクル目 2.0C放電 容量 E_{13} mAh	12→13サイク ル 容量変化率 %
実施例 4	5.040	4.960	-1.6	5.009	4.771	-4.8
比較例 4	5.025	4.925	-2.0	5.000	4.425	-11.5

この表に示すように、セパレータの膜厚が同等である実施例 4 と比較例 4 を比較した場合、放電の電流密度を $1/3\text{ C}$ から 2.0 C に変化させた $12 \rightarrow 13$ サイクルの放電容量変化率は実施例 4 が著しく小さくなった。これは、本発明のセパレータ中のイオン伝導性が向上して、高い電流密度での放電特性が向上したものと推定される。

実施例 5

実施例 1、2 および 4 と同様に、実験用の小スケールセルにより本発明の電池の充放電特性を調べた。

まず、電極はシート状で実施例 2、3 および 4 と同じものを用意した。

次に、絶縁性物質粒子の集合体の使用材料およびその作製方法は以下に示すとおりである。

[使用材料]

絶縁性物質粒子：ポリパラフェニレンテレフタルアミド
(アラミド)

商品名 T w a r o n [日本アラミド (株) 製]

バインダー：ポリフッ化ビニリデン (P V D F)

K F # 1 1 0 0 [呉羽化学工業 (株) 製]

溶媒：1-メチル-2-ピロリドン (NMP)

上記のアラミド粉体と P V D F 粉体を重量比 $100:5$ で粉体状態のまま混合し、それに NMP を加えてさらに混合し、固形分率 $50.0\text{ wt}\%$ のスラリーを得た。

このスラリーをドクターブレードを用いて前記電極シート上に均一に塗布後、 120°C のオープン中で15分間乾燥して、電極上にアラミド粒子集合体を固定しセパレータとした。このセパレータの空孔率は50%であった。この空孔率は、前記セパレータを単独で形成させ、(株)島津製作所製の水銀ポロシメーターにより測定した。

上記のシートを、アラミド粒子集合体塗布部分が、正極については $1.5\text{ cm} \times 1.0\text{ cm}$ の面積、負極については $1.55\text{ cm} \times 1.05\text{ cm}$ の面積になるように加工し、塗布部分を対向させて、図7(b)のようなサンプルを作製した。このセパレータの厚みは正極側と負極側をあわせて $25\text{ }\mu\text{m}$ であった。これを、エチレンカーボネート(EC)とジエチルカーボネート(DEC)の体積比1:1の混合溶媒にLiPF₆を 1.0 mol/l 溶解させた電解液中で充放電させた(実施例5)。充放電条件は実施例2および4と同じにした。

比較例5として、実施例2で行った比較例2を引用した。

実施例5および比較例5における10サイクル目と11サイクル目の放電容量変化率、及び12サイクル目と13サイクル目の放電容量変化率は下記の表4に示す結果となった。

表 4

	10サイクル目 1/3C放電 容量 E_{10} mAh	11サイクル目 1.0C放電 容量 E_{11} mAh	10→11サイ クル 容量変化率 %	12サイクル目 1/3C放電 容量 E_{12} mAh	1サイクル目 2.0C放電 容量 E_{13} mAh	12→13サイ クル 容量変化率 %
実施例 5	5.027	4.944	-1.7	5.003	4.766	-4.7
比較例 5	5.025	4.925	-2.0	5.000	4.425	-11.5

この表に示すように、セパレータの膜厚が同等である実施例 5 と比較例 5 を比較した場合、放電の電流密度を $1/3\text{ C}$ から 2.0 C に変化させた $12 \rightarrow 13$ サイクルの放電容量変化率は実施例 5 が著しく小さくなった。

実施例 6

実施例 1、2、4 および 5 と同様に、実験用の小スケールセルにより本発明の電池の充放電特性を調べた。

まず、電極はシート状で実施例 2、3、4 および 5 と同じものを用意した。

次に、絶縁性物質粒子の集合体の使用材料およびその作製方法は以下に示すとおりである。

[正極上塗布用の使用材料]

絶縁性物質粒子：平均粒径 $1.0\text{ }\mu\text{m}$ の $\alpha\text{-Al}_2\text{O}_3$

バインダー：ポリフッ化ビニリデン (PVDF)

KF#1100 [呉羽化学工業 (株) 製]

溶媒：1-メチル-2-ピロリドン (NMP)

上記の $\alpha\text{-Al}_2\text{O}_3$ 粉体と PVDF 粉体を重量比 100 : 5 で粉体状態のまま混合し、それに NMP を加えてさらに混合し、固形分率 56.8 wt % のスラリーを得た。

このスラリーをドクターブレードを用いて前記正極シート上に所定の厚みで均一に塗布後、 120°C のオーブン中で 15 分間乾燥して、電極上に $\alpha\text{-Al}_2\text{O}_3$ 粒子集合体を固定しセパレータとした。このセパレータの空孔率は 52 % であっ

た。この空孔率は、前記セパレータを単独で形成させ、(株)島津製作所製の水銀ポロシメーターにより測定した。

上記のシートを、 α - Al_2O_3 粒子集合体塗布部分が1.5 cm $\times$ 1.0 cmの面積になるように加工した。

〔負極上塗布用の使用材料〕

絶縁性物質粒子：ポリエチレン

バインダー：カルボキシメチルセルロース、ラテックス

溶媒：精製水

上記のカルボキシメチルセルロースを精製水に溶解させ2.0 wt %の水溶液とし、これにポリエチレン粉体を混合し、さらに4.2 wt %ラテックス水溶液を加えて混合して、重量比がポリエチレン：カルボキシメチルセルロース：ラテックス=100：1：2、固形分率45.0 wt %のスラリーを得た。

このスラリーをドクターブレードを用いて前記正極シート上に所定の厚みで均一に塗布後、100℃のオーブン中で15分間乾燥して、電極上にポリエチレン粒子集合体を固定しセパレータとした。このセパレータの空孔率は50%であった。この空孔率は、前記セパレータを単独で形成させ、(株)島津製作所製の水銀ポロシメーターにより測定した。

上記のシートを、ポリエチレン粒子集合体塗布部分が1.55 cm $\times$ 1.05 cmの面積になるように加工した。

そして、正極側と負極側の絶縁性物質粒子塗布部分を対向

させて、図7(b)のようなサンプルを作製した。このときのセパレータの厚みは正極側と負極側をあわせて $25\mu\text{m}$ であった。これを、エチレンカーボネート(EC)とジエチルカーボネート(DEC)の体積比1:1の混合溶媒にLiPF₆を 1.0mol/l 溶解させた電解液中で下記の条件により充放電させた(実施例6)。充放電条件は実施例2、4および5と同じにした。

比較例6として、実施例2で行った比較例2を引用した。

実施例6および比較例6における10サイクル目と11サイクル目の放電容量変化率、及び12サイクル目と13サイクル目の放電容量変化率は下記の表5に示す結果となった。

表 5

	10サイクル目 1/3C放電 容量 E_{10} mAh	11サイクル目 1.0C放電 容量 E_{11} mAh	10→11サイク ル 容量変化率 %	12サイクル目 1/3C放電 容量 E_{12} mAh	1サイクル目 2.0C放電 容量 E_{13} mAh	12→13サイク ル 容量変化率 %
実施例 6	5.016	4.923	-1.9	4.998	4.732	-5.3
比較例 6	5.025	4.925	-2.0	5.000	4.425	-11.5

この表に示すように、セパレータの膜厚が同等である実施例6と比較例6を比較した場合、放電の電流密度を1/3Cから2.0Cに変化させた12→13サイクルの放電容量変化率は実施例6が著しく小さくなった。これは、本発明のセパレータを用いることによりセパレータ中のイオン伝導性が向上したために、急速放電特性が向上したものと推定される。

また、実施例6のように、正極上には高い融点（この場合2055℃）をもつ無機酸化物の粒子層、負極上には低い融点（この場合140℃程度）をもつの樹脂の粒子層を形成させたことにより、電池が高温状態に陥ったときに樹脂粒子のみが熔融して空孔を閉塞させて電流を遮断するヒューズ効果をもたせることができる。

実施例7

実施例1、2、4、5および6と同様に、実験用の小スケールセルにより本発明の電池の充放電特性を調べた。

まず、電極はシート状で以下のものを用意した。

〔電極〕

正極：LiMn₂O₄を正極活物質、リン片状グラファイトをフィラー、フッ素ゴムをバインダーとし、LiMn₂O₄：リン片状グラファイト：フッ素ゴム＝100：6：1.96の重量比で酢酸エチルとエチルセロソルブの体積比1：3の混合溶媒中で

混合してペーストとし、厚さ $15\mu\text{m}$ のアルミニウム箔（集電体箔）上に塗布後乾燥して、プレスをして厚さ $112\mu\text{m}$ の正極活物質層を形成したもの

負極：メソフェーズピッチカーボンファイバークラフアイトおよびリン片状グラファイトを負極活物質、カルボキシメチルセルロースを分散剤、ラテックスをバインダーとし、メソフェーズカーボンファイバークラフアイト：リン片状グラファイト：カルボキシメチルセルロース：ラテックス＝ $90:10:1.4:1.8$ の重量比で精製水中で混合してペーストとし、厚さ $12\mu\text{m}$ の銅箔（集電体箔）上に塗布後乾燥し、プレスをして厚さ $8.1\mu\text{m}$ の負極活物質層を形成したもの

次に、絶縁性物質粒子の集合体の使用材料およびその作製方法は以下に示すとおりである。

〔使用材料〕

絶縁性物質粒子：平均粒径 $1.0\mu\text{m}$ の $\alpha\text{-Al}_2\text{O}_3$

バインダー：ポリフッ化ビニリデン（PVDF）

KF#1100〔呉羽化学工業（株）製〕

溶媒：1-メチル-2-ピロリドン（NMP）

上記の $\alpha\text{-Al}_2\text{O}_3$ 粉体とPVDF粉体を重量比 $100:$

5 で粉体状態のまま混合し、それにNMPを加えてさらに混

合し、固形分率 56.8 wt % のスラリーを得た。

このスラリーをドクターブレードを用いて前記電極上に所定の厚みで均一に塗布後、120℃のオーブン中で15分間乾燥して、電極上に α - Al_2O_3 粒子集合体を固定しセパレータとした。このセパレータの空孔率は52%であった。この空孔率は、前記セパレータを単独で形成させ、(株)島津製作所製の水銀ポロシメーターにより測定した。

上記のシートを、 α - Al_2O_3 粒子集合体塗布部分が、正極については1.5 cm×1.0 cmの面積、負極については1.55 cm×1.05 cmの面積になるように加工し、塗布部分を対向させて、図7(b)のようなサンプルを作製した。このときのセパレータの厚みは正極側と負極側をあわせて25 μm のものを用意した。これを、エチレンカーボネート(EC)とジエチルカーボネート(DEC)の体積比1:1の混合溶媒に LiPF_6 を1.0 mol/l溶解させた電解液中で充放電させた(実施例7)。充放電条件は実施例2、4、5および6と同じにした。

比較例7として、 α - Al_2O_3 粒子集合体を形成させていない実施例7と同じ正極と負極をそれぞれ1.5 cm×1.0 cm、1.55 cm×1.05 cmの面積となるように加工し、ポリエチレン(PE)微多孔膜からなる厚さ25 μm のセパレータ(空孔率36%)を挟んで両極を対向させて、図1(B)のようなサンプルを作製し、実施例2と同電解液

中かつ同充放電条件により充放電させた。

実施例7および比較例7における10サイクル目と11サイクル目の放電容量変化率、及び12サイクル目と13サイクル目の放電容量変化率は下記の表6に示す結果となった。

表 6

	10サイクル目 1/3C放電 容量E ₁₀ mAh	11サイクル目 1.0C放電 容量E ₁₁ mAh	10→11サイク ル 容量変化率 %	12サイクル目 1/3C放電 容量E ₁₂ mAh	1サイクル目 2.0C放電 容量E ₁₃ mAh	12→13サイク ル 容量変化率 %
実施例 7	4.957	4.755	-4.1	4.925	4.451	-9.6
比較例 7	4.949	4.639	-6.3	4.910	4.009	-18.4

この表に示すように、セパレータの膜厚が同等である実施例 7 と比較例 7 を比較した場合、放電の電流密度を $1/3\text{ C}$ から 2.0 C に変化させた $12 \rightarrow 13$ サイクルの放電容量変化率は実施例 7 が著しく小さくなった。これは、本発明のセパレータを用いることによりセパレータ中のイオン伝導性が向上したために、急速放電特性が向上したものと推定される。

産業上の利用可能性

本発明の電池は、安全性を損なうことなく、高い電流密度で優れた放電特性を発揮するだけでなく、従来の電池と比較して電池の単位体積あたりに収容できる活物質の量が多く、従来の電池と比較して極めて高い性能を発揮することができる。電池の性能を維持しながら小型化軽量化を達成することもできる。

請求の範囲

1. ケーシング、

該ケーシング内に含まれる電解質、

正極活物質層を含む正極、

負極活物質層を含む負極、及び

多孔性セパレータを包含し、

該正極、該負極及び該セパレータは、該ケーシング内に、
該電解質と共に可能に収容されており、

該多孔性セパレータは、該正極と該負極の間に、該多孔
性セパレータの両側表面が該正極活物質層及び該負極活物質
層にそれぞれ面するように配置構成されてなる電池であって、

該多孔性セパレータは、少なくとも1層の絶縁性物質粒
子集合体層からなり、該少なくとも1層の絶縁性物質粒子集
合体層が3次元網目空隙構造を有しており、それにより、該
多孔性セパレータに、イオンが通過可能な孔が形成されてな
る、

ことを特徴とする電池。

2. 該粒子集合体が、該粒子同士を結合するバインダーを含
むことを特徴とする請求項1に記載の電池。

3. 該多孔性セパレータが該正極活物質層及び該負極活物質
層よりなる群から選ばれる少なくとも1つの活物質層表面に



一体化された形で直接形成されていることを特徴とする請求項1又は2に記載の電池。

4. 該多孔性セパレータの空孔率が、乾燥状態で10%以上であることを特徴とする請求項1～3のいずれかに記載の電池。

5. 該多孔性セパレータが、該粒子集合体の空隙以外の要因に起因するイオン伝導性を有することを特徴とする請求項1～4のいずれかに記載の電池。

6. 該絶縁性物質が無機物であることを特徴とする請求項1～5のいずれかに記載の電池。

7. 該絶縁性物質が有機物であることを特徴とする請求項1～5のいずれかに記載の電池。

8. 該粒子集合体が、少なくとも2種類の異なる絶縁性物質からなることを特徴とする請求項1～7のいずれかに記載の電池。

9. 該多孔性セパレータが、異なる粒子集合体からそれぞれ構成される少なくとも2つの層からなることを特徴とする請求項1～8のいずれかに記載の電池。

10. 該多孔性セパレータが、少なくとも1層の無機絶縁性



物質粒子集合体層よりなる第1セパレータ層及び少なくとも1層の有機絶縁性物質粒子集合体層よりなる第2セパレータ層とからなり、該第1セパレータ層が、該正極活物質層と該負極活物質層のうちの一方の活物質層の表面に一体化された形で直接形成されており、該第2セパレータ層が該正極活物質層と該負極活物質層のうちの他方の活物質層の表面に一体化された形で直接形成されていることを特徴とする請求項1～9のいずれかに記載の電池。

11. 該電解質が非水電解質であることを特徴とする請求項1～10のいずれかに記載の電池。

12. 該非水電解質がリチウムイオンを含むことを特徴とする請求項11に記載の電池。

13. 該正極活物質層がマンガン酸リチウムを含むことを特徴とする請求項11又は12に記載の電池。

14. (1) 正極活物質層を含む正極及び負極活物質層を含む負極をそれぞれ提供し、

(2) 絶縁性物質粒子と該粒子のためのバインダーとの混合物を分散媒に分散せしめた分散液を、該正極活物質層および該負極活物質層よりなる群から選ばれる少なくとも1つの活物質層の表面に塗布し、

(3) 該少なくとも1つの活物質層の表面に塗布した



分散液の分散媒を蒸発させることにより除去して、該粒子同士がバインダーによって結合されてなる該粒子の集合体層を形成し、それにより、該少なくとも1つの活物質層の表面に一体化され且つその絶縁性物質粒子集合体層中に3次元網目空隙構造を有してなる多孔性セパレータを形成し、

(4) このようにして得られた少なくともどちらか一方の活物質層表面に該多孔性セパレータを形成させてなる該正極及び該負極を、ケーシングに収容し、その際、該多孔性セパレータを挟んで該正極活物質層及び該負極活物質層を対向させ、且つケーシング内の電解質と共働可能になるように配設する、

ことを特徴とする電池の製造方法。



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FIG. 1 (A) (従来技術)

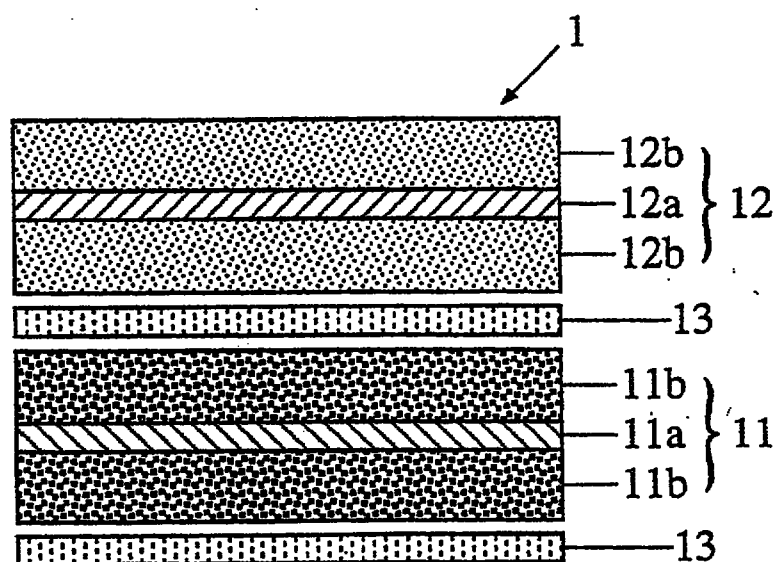
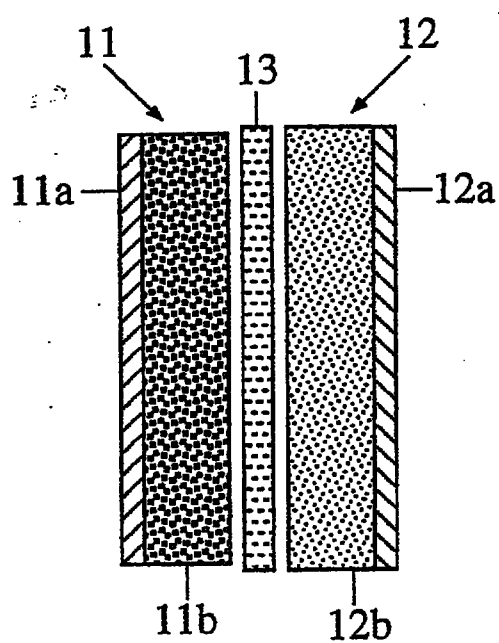


FIG. 1 (B) (従来技術)



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FIG. 2

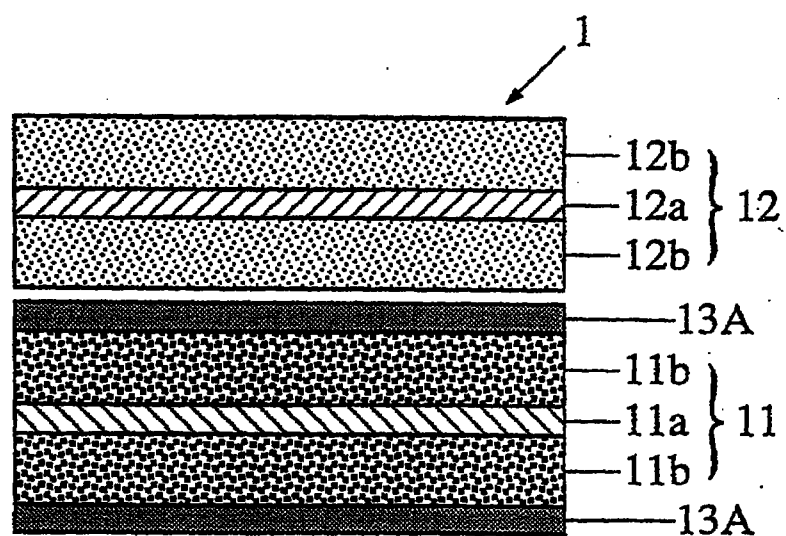
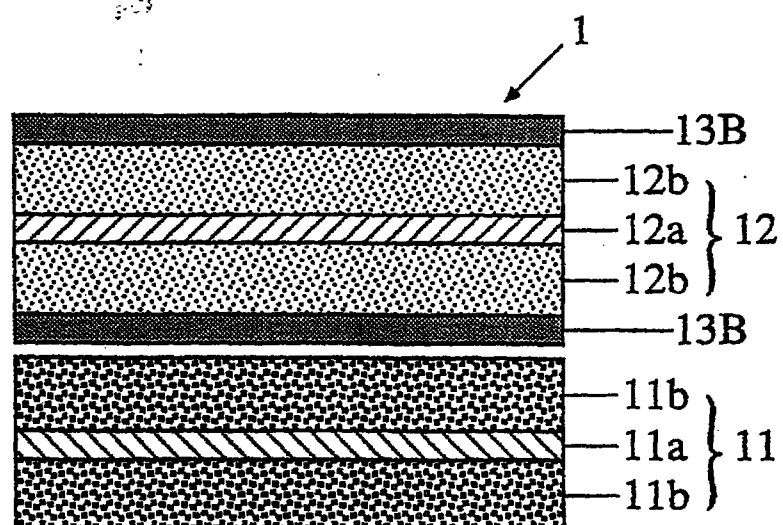


FIG. 3



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FIG. 4

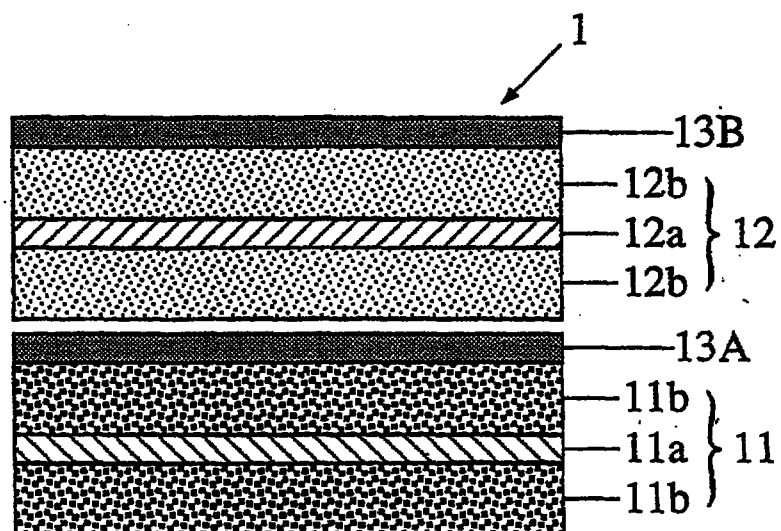
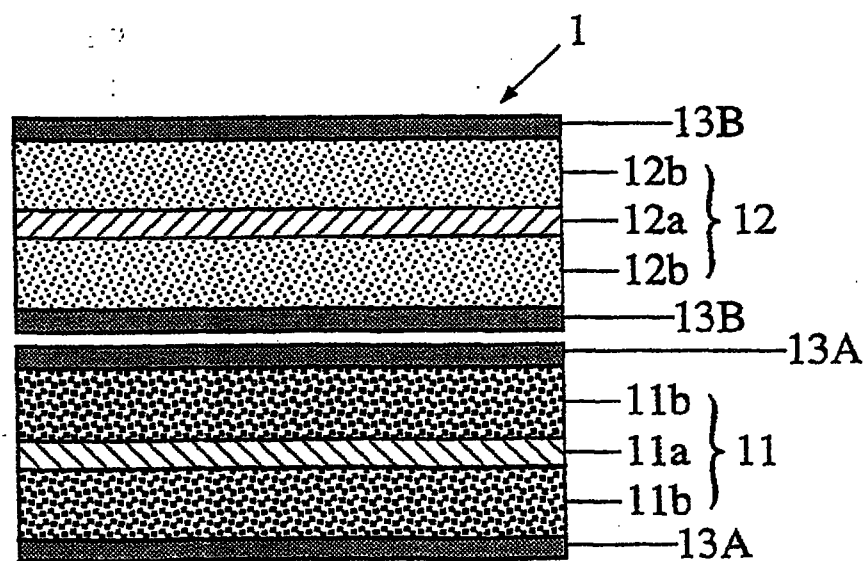


FIG. 5



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FIG. 6

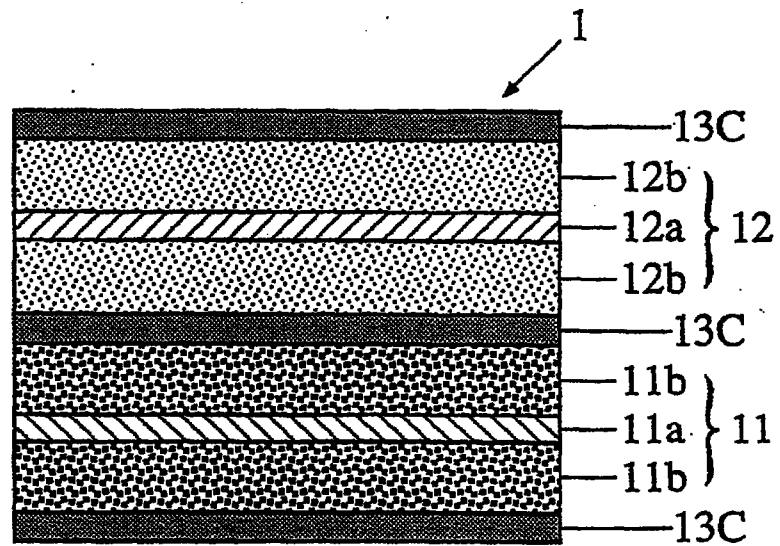
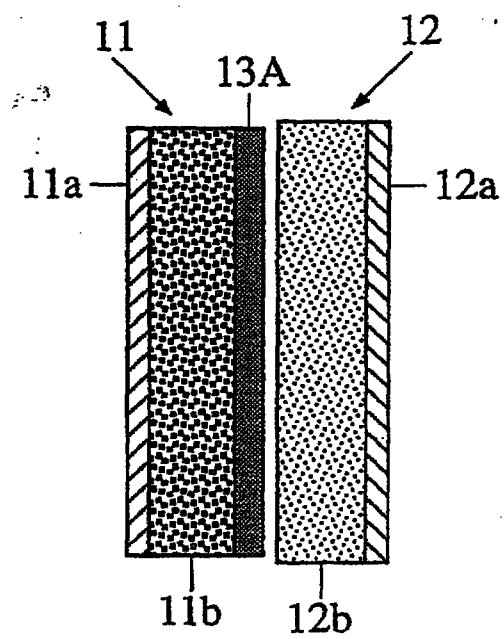


FIG. 7(a)



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FIG. 7(b)

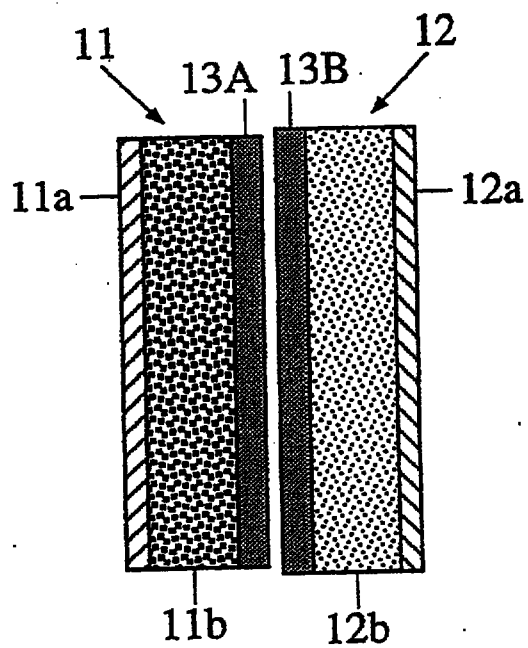
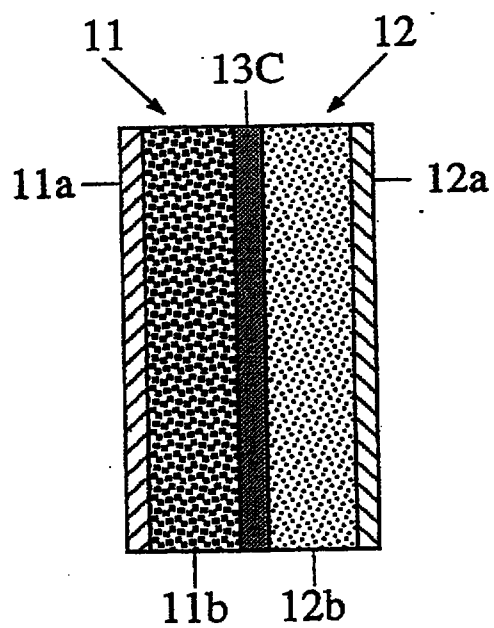


FIG. 7(c)



TITLE OF THE INVENTION

Novel battery and method for producing the same

BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a novel battery
and a method for producing the same. More particular-
ly, the present invention is concerned with a battery
comprising a positive electrode comprising a cathode
active material layer, a negative electrode comprising
10 an anode active material layer, and a porous separator
disposed between the positive electrode and the nega-
tive electrode, wherein the positive electrode, the
negative electrode and the separator are disposed in a
casing containing an electrolyte, and wherein the
15 porous separator comprises at least one layer of an
aggregate form of particles of at least one insulating
substance, the layer of the aggregate form of particles
having a three-dimensional network of voids which
function as pores in the porous separator and which are
20 capable of passing ions therethrough. The present
invention is also concerned with a method for producing
the above-mentioned novel battery. The battery of the
present invention is advantageous not only in that the
battery exhibits excellent discharge characteristics
25 even at a high discharge current density without sacri-

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ficing safety, but also in that the amount of active materials which can be accommodated in the battery per unit volume thereof is large, as compared to the amounts in the case of conventional batteries.

5

Prior Art

In recent years, various demands have been made on electrical appliances, wherein the electrical appliances should be reduced in size and weight, wherein they should have multifunctionality and wherein they should be codeless (portable). For meeting these demands, development of high performance batteries has been vigorously studied. Batteries can be generally classified into a primary battery which is not rechargeable and a secondary battery which is rechargeable so that it can be repeatedly used. Examples of primary batteries include a manganese dioxide battery and an alkaline manganese dioxide dry cell. With respect to these primary batteries, various improvements have been made, and the primary batteries are used in a wide variety of fields. On the other hand, examples of secondary batteries include a lead storage battery, a nickel-cadmium battery and a nickel-hydrogen battery. Recently, a commercial demand for a secondary battery, particularly a lithium ion secondary battery using a non-

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aqueous electrolytic liquid has been increasing, since the lithium ion secondary battery can exhibit high voltage and high capacity even in a compact and light weight form.

5 The performance of the above-mentioned batteries can be improved, for example, by increasing the amount of active materials and/or the amount of electrolyte, which can be accommodated in a battery per unit volume of the battery, or by improving the ion conductive
10 property between the positive electrode and the negative electrode.

 Particularly, in the case of a battery using a non-aqueous electrolytic liquid (such a battery is hereinafter, frequently, referred to simply as a "non-
15 aqueous battery"), such as the above-mentioned lithium ion secondary battery, since the non-aqueous liquid used in such a battery has a poor ion conductive property as compared to an aqueous electrolytic liquid, it is desired to improve the ion conductive property between the positive electrode and the negative electrode.
20 For this purpose, generally, such a battery is designed to have a construction in which a plurality of unit cells (each comprising a positive electrode, a negative electrode and a separator) are laminated, or a construction in which a unit cell is spirally wound into a
25

spirally wound structure, so as to increase the effective area of electrodes, at which the positive electrode and the negative electrode face each other.

However, a satisfactory improvement in the ion conductive property has not yet been achieved.

As an example of the most effective methods for achieving an improvement in the ion conductive property, there can be mentioned a method in which a separator having a small thickness and an excellent ion permeability is used.

As a separator used in a conventional battery, generally, use is made of a microporous film made of a polyolefin resin, such as polyethylene or polypropylene. For example, as described in Unexamined Japanese Patent Laid-Open Specification No. 3-105851, the above-mentioned microporous film can be produced by a method in which a molten mixture comprising a polyolefin resin composition is extrusion-molded into a sheet, substances other than the polyolefin resin are removed from the sheet by extraction, and the resultant sheet is subjected to stretching.

The above-mentioned resin film separator needs to have a mechanical strength such that occurrence of the breakage of the separator can be avoided during the production of a battery. Due to such a required me-

chanical strength, it is difficult to reduce the thickness of the separator to less than a certain thickness. Therefore, in the case of the above-mentioned non-aqueous battery (such as a lithium ion secondary battery) having a construction in which a plurality of unit cells are laminated, or a construction in which a unit cell is spirally wound into a spirally wound structure, the amount of the unit cell which can be accommodated in the battery per unit volume thereof inevitably becomes small due to the restriction in respect of reduction of the thickness of the separator. Further, even when it is attempted to improve the ion conductive property between the positive electrode and the negative electrode by increasing the porosity of the conventional resin film separator, satisfactory results cannot be obtained (see Comparative Example 1 of the present specification) (the reason for this has not yet been elucidated). The above-mentioned separator made of a resin film is also disadvantageous in that the resin film separator has poor durability. Therefore, when such a separator is used in a secondary battery, the separator is deteriorated during the repetition of the charge/discharge operations, so that the cycle characteristics of the battery become poor (see Comparative Example 3 of the present specifica-

tion). Further, in a battery using a conventional separator, use must be made of a large amount of the separator which is produced by the above-mentioned cumbersome, costly method, so that the ratio of the cost for the separator to the total cost for the battery becomes relatively high. Therefore, especially in the case of the above-mentioned non-aqueous battery, such as the lithium ion secondary battery, in which the conventional resin film separator is used, a large area of separator is needed due to the above-mentioned unique construction of such a battery and the cost for the separator becomes disadvantageously high, thereby rendering high the production cost for the battery.

SUMMARY OF THE INVENTION

The present inventors have made extensive and intensive studies with a view toward developing a battery which is free from the above-mentioned problems and which not only has high performance and high safety, but also can be produced at low cost. As a result, it has unexpectedly been found that a specific battery as defined below is advantageous not only in that the battery exhibits excellent discharge characteristics even at a high discharge current density without sacrificing safety, but also in that a large amount of active materials can be accommodated in the battery per

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unit volume thereof, as compared to the amounts in the case of conventional batteries. Such a specific battery comprises a positive electrode comprising a cathode active material layer, a negative electrode comprising an anode active material layer, and a porous separator disposed between the positive electrode and the negative electrode, wherein the positive electrode, the negative electrode and the separator are disposed in a casing containing an electrolyte, and wherein the porous separator comprises at least one layer of an aggregate form of particles of at least one insulating substance, the layer of the aggregate form of particles having a three-dimensional network of voids which function as pores in the porous separator and which are capable of passing ions therethrough. The present invention has been completed, based on the above novel findings.

Accordingly, it is a primary object of the present invention to provide a high performance battery which is advantageous not only in that the battery exhibits excellent discharge characteristics even at a high discharge current density without sacrificing safety, but also in that a large amount of active materials can be accommodated in the battery per unit volume thereof, as compared to the amounts in the case of conventional

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batteries.

It is another object of the present invention to provide an advantageous method for producing the above-mentioned high performance battery.

5 The foregoing and other objects, features and advantages of the present invention will be apparent from the following detailed description taken in connection with the accompanying drawings and the appended claims.

10

Brief Description of the Drawings

In the drawings:

15 Fig. 1(A) is a diagrammatic cross-sectional view showing the structure of a unit cell of a conventional battery in which a conventional separator is used.

 Fig. 1(B) is a diagrammatic cross-sectional view showing the structure of a unit cell of another conventional battery in which a conventional separator is used.

20 Fig. 2 is a diagrammatic cross-sectional view showing the structure of a unit cell of a battery according to one embodiment of the present invention.

25 Fig. 3 is diagrammatic cross-sectional view showing the structure of a unit cell of a battery according to another embodiment of the present invention.

Fig. 4 is a diagrammatic cross-sectional view showing the structure of a unit cell of a battery according to still another embodiment of the present invention.

5 Fig. 5 is a diagrammatic cross-sectional view showing the structure of a unit cell of a battery according to still another embodiment of the present invention.

10 Fig. 6 is a diagrammatic cross-sectional view showing the structure of a unit cell of a battery according to still another embodiment of the present invention.

15 Figs. 7(a) to 7(c) are diagrammatic cross-sectional views showing the respective structures of unit cells employed in Examples 1 to 7, respectively.

 In Figs. 1(A) to 7(c), like parts and portions are designated by like numerals.

Description of the Reference Numerals

20 1 : Unit cell
 11 : Positive electrode
 11a : Current collector foil for positive electrode
 11b : Cathode active material layer
 12 : Negative electrode
25 12a : Current collector foil for negative electrode

12b : Anode active material layer

13 : Conventional separator

13A : Separator used in the present invention, which is
directly formed, in an immobilized form, on the
surface of a cathode active material layer.

13B : Separator used in the present invention, which is
directly formed, in an immobilized form, on the
surface of an anode active material layer.

13C : Separator used in the present invention, which is
directly formed, in an immobilized form, on each
of the surface of a cathode active material layer
and the surface of an anode active material layer.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

Essentially, according to the present invention,
there is provided a battery comprising:

a casing,

an electrolyte contained in the casing,

a positive electrode comprising a cathode active
material layer,

a negative electrode comprising an anode active
material layer, and

a porous separator disposed between the positive
electrode and the negative electrode, wherein two
opposite surfaces of the porous separator face the

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cathode active material layer and the anode active material layer, respectively,

the positive electrode, the negative electrode and the separator being disposed in the casing, operatively with the electrolyte,

the porous separator comprising at least one layer of an aggregate form of particles of at least one insulating substance, wherein the at least one layer of the aggregate form of particles has a three-dimensional network of voids which function as pores in the porous separator and which are capable of passing ions there-through.

For an easy understanding of the present invention, the essential features and various preferred embodiments of the present invention are enumerated below.

1. A battery comprising:

a casing,

an electrolyte contained in the casing,

a positive electrode comprising a cathode active material layer,

a negative electrode comprising a anode active material layer,

a porous separator disposed between the positive electrode and the negative electrode, wherein two

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opposite surfaces of the porous separator face the cathode active material layer and the anode active material layer, respectively,

5 the positive electrode, the negative electrode and the separator being disposed in the casing, operatively with the electrolyte,

the porous separator comprising at least one layer of an aggregate form of particles of at least one insulating substance, wherein the at least one layer of
10 the aggregate form of particles has a three-dimensional network of voids which function as pores in the porous separator and which are capable of passing ions there-through.

2. The battery according to item 1 above, wherein the
15 porous separator further comprises a binder which is mixed with the particles to thereby bind the particles together.

3. The battery according to item 1 or 2 above, wherein the porous separator is directly formed, in an
20 immobilized form, on at least one active material layer selected from the group consisting of the cathode active material layer and the anode active material layer.

4. The battery according to any one of items 1 to 3
25 above, wherein the porous separator has a porosity of

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10 % or more as measured in the dry state of the porous separator.

5 5. The battery according to any one of items 1 to 4 above, wherein the porous separator has an ion conductive property ascribed to a factor other than the voids of the aggregate form of particles.

6. The battery according to any one of items 1 to 5 above, wherein the insulating substance is an inorganic substance.

10 7. The battery according to any one of items 1 to 5 above, wherein the insulating substance is an organic substance.

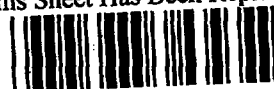
15 8. The battery according to any one of items 1 to 7 above, wherein the aggregate form of particles comprises particles of at least two different insulating substances.

20 9. The battery according to any one of items 1 to 8 above, wherein the porous separator comprises at least two layers respectively comprised of different aggregate forms of particles.

25 10. The battery according to any one of items 1 to 9 above, wherein the separator comprises a first separator layer comprising at least one layer of an aggregate form of particles of at least one inorganic insulating substance and a second separator layer comprising at

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- least one layer of an aggregate form of particles of at least one organic insulating substance, the first separator layer being directly formed, in an immobilized form, on one active material layer selected from the cathode active material layer and the anode active material layer, the second separator layer being directly formed, in an immobilized form, on the other active material layer remaining between the cathode active material layer and the anode active material layer.
11. The battery according to any one of items 1 to 10 above, wherein the electrolyte is a non-aqueous electrolyte.
12. The battery according to item 11 above, wherein the non-aqueous electrolyte contains lithium ions.
13. The battery according to item 11 or 12 above, wherein the cathode active material layer comprises lithium manganate.
14. A method for producing a battery, comprising:
- (1) individually providing a positive electrode comprising a cathode active material layer and a negative electrode comprising an anode active material layer;
- (2) coating a dispersion of a mixture of particles of at least one insulating substance and a binder

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for the particles in a dispersion medium on at least one active material layer selected from the group consisting of the cathode active material layer and the anode active material layer;

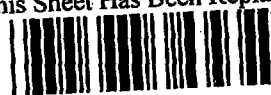
5 (3) removing, by evaporation, the dispersion medium of the dispersion coated on the at least one active material layer to form a layer of an aggregate form of the particles, wherein the particles are bound together by means of the binder, thereby providing a
10 porous separator formed directly, in an immobilized form, on the at least one active material layer, wherein the layer of an aggregate form of particles has a three dimensional network of voids; and

 (4) disposing the positive electrode and the
15 negative electrode, at least one of which has the porous separator formed on the active material layer thereof, in a casing so that the cathode active material layer and the anode active material layer are arranged, operatively with an electrolyte contained in
20 the casing, in a positional relationship opposite to each other through the porous separator formed on the at least one active material layer.

 In the battery of the present invention, the porous separator used therein, which comprises an
25 aggregate form of particles of at least one insulating

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substance, has a unique pore structure formed by a three-dimensional network of voids formed in the aggregate form of the particles, so that the separator allows the ions to be transmitted through the electrolyte contained in the pores of the separator, while preventing occurrence of short-circuiting between the cathode active material layer and the anode active material layer. The separator used in the present invention has high ion permeability as compared to the conventional polyolefin resin film separator. The reason for this is considered to be as follows. In the porous separator used in the present invention, the above-mentioned unique pore structure formed by the three-dimensional network of voids formed in the aggregate form of particles is more effective for achieving high ion permeability than the pore structure of the conventional polyolefin resin film separator or the like.

The above-mentioned insulating substance may be either an inorganic substance or an organic substance. Examples of inorganic substances include oxides, (e.g., Li_2O , BeO , B_2O_3 , Na_2O , MgO , Al_2O_3 , SiO_2 , P_2O_5 , CaO , Cr_2O_3 , Fe_2O_3 , ZnO , ZrO_2 and TiO_2), zeolite (e.g., $\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, wherein M represents a metal atom, such as Na, K, Ca and Ba; n is a number corre-

sponding to the electric charge of a positive ion M^{n+} of the metal atom M; x and y are the molar number of SiO_2 and the molar number of H_2O , respectively, and wherein $2 \leq x \leq 10$, and $2 \leq y \leq 7$), nitrides (e.g., BN, AlN, Si_3N_4 and Ba_3N_2), silicon carbide (SiC), zircon ($ZrSiO_4$), salts of carbonic acids (e.g., $MgCO_3$ and $CaCO_3$), salts of sulfuric acids (e.g., $CaSO_4$ and $BaSO_4$), and composites of the above-mentioned compounds {e.g., porcelains, such as steatite ($MgO \cdot SiO_2$), forsterite ($2MgO \cdot SiO_2$) and cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$)}. Examples of organic substances include polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(vinylidene chloride), polyacrylonitrile, poly(methyl methacrylate), polyacrylate, fluororesins {e.g., polytetrafluoroethylene and poly(vinylidene fluoride)}, polyamide resins, polyimide resins, polyester resins, polycarbonate resins, polyphenylene oxide resins, silicone resins, phenolic resins, urea resins, melamine resins, polyurethane resins, polyether resins {e.g., poly(ethylene oxide) and poly(propylene oxide)}, epoxy resins, acetal resins, acrylonitrile-styrene (AS) resins and acrylonitrile-butadiene-styrene (ABS) resins.

Generally, with respect to the particles of at least one insulating substance, it is preferred that

the particles have high hardness. The use of a porous separator obtained using such particles having high hardness in a battery is advantageous for the following reason. Even when such a porous separator sustains a pressure caused by a volume increase of the active material layers, the porous separator is free from occurrence of a deformation of the pores, so that the porous separator does not suffer from a volume decrease of the pores. Therefore, the amount of the electrolyte contained in each pore of the porous separator can be constantly maintained at the same level, so that the porous separator does not suffer a lowering in the ion conductive property. Therefore, the battery using such a separator exhibits improved durability.

Further, with respect to the particles of at least one insulating substance, it is preferred to use an insulating substance having such a high heat resistance as represented by the melting point of 200 °C or more, for example α -Al₂O₃ (melting point: 2055 °C) and polyimide resins (heat resistant resins which do not undergo dissolution, melting or decomposition at a temperature of from 250 to 400 °C). By the use of particles of such an insulating substance having high heat resistance, it becomes possible to obtain a separator having high heat resistance as compared to conventional sepa-

rator materials, such as a polyethylene microporous film (melting point: about 140 °C) and a polypropylene microporous film (melting point: about 180 °C).

5 With respect to the average particle diameter of the above-mentioned particles of at least one insulating substance, it is preferred that the average particle diameter is from 5 nm to 100 μm , more preferably from 5 nm to 10 μm , most preferably from 5 nm to 1 μm .

10 With respect to the thickness of the above-mentioned porous separator, there is no particular limitation. However, it is preferred that the thickness of the separator is from 100 nm to 100 μm , more preferably from 100 nm to 10 μm .

15 In the present invention, it is preferred that the porous separator further comprises a binder which is mixed with the particles to thereby bind the particles together.

20 Examples of binders include latexes (e.g., a styrene-butadiene copolymer latex and an acrylonitrile-butadiene copolymer latex), cellulose derivatives (e.g., a sodium salt of carboxymethylcellulose), fluororubbers (e.g., a copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene) and fluo-
25 roresins {e.g., poly(vinylidene fluoride) and polytetrafluoroethylene}.

With respect to the amount of the above-mentioned binder, it is preferred that the binder is used in an amount of from $1/500$ to $5/3$, more preferably from $1/500$ to $1/2$, most preferably from $1/500$ to $1/5$, in terms of the volume ratio of the binder to the particles of at least one insulating substance.

In the present invention, it is preferred that the porous separator used in the battery is directly formed, in an immobilized form, on at least one active material layer selected from the group consisting of the cathode active material layer and the anode active material layer.

With respect to the conventional battery, in which a microporous resin film is used as a separator, the separator needs to be handled as an independent film. Therefore, such a separator used in the conventional battery needs to have high mechanical strength so as to avoid breakage of the separator during the handling thereof. For this reason, it has conventionally been difficult to reduce the thickness of a separator to a level less than $25\text{ }\mu\text{m}$. On the other hand, in the case of the battery of the present invention, which has a construction in which the separator is directly formed, in an immobilized form, on the active material layer, the separator need not be handled as an independent

film during the production the battery, so that a separator having an extremely small thickness can be employed. Therefore, by the use of the above-mentioned construction, it becomes possible not only to increase
5 the amount of active materials which can be accommodated in the battery per unit volume thereof, but also to reduce the internal resistance of the battery (the low internal resistance of the battery has a favorable effect of lowering the overvoltage, thereby markedly
10 improving the input/output characteristics of the battery).

It is preferred that the porosity of the above-mentioned porous separator is 10 % or more, more preferably 20 % or more, most preferably 40 % or more, as
15 measured in the dry state of the porous separator. With respect to the porosity of the porous separator, the higher the porosity, the higher the ion conductive property of the porous separator. Therefore, it is preferred that the porous separator has a porosity as
20 high as possible. However, when the porosity of the porous separator is too high (especially, in the case of a porous separator having a small thickness), it is difficult to prevent occurrence of the short-circuiting between the positive electrode and the negative elec-
25 trode. Therefore, from a practical point of view, it

is preferred that the porosity of the porous separator is not higher than 90 %.

The above-mentioned porosity of the porous separator can be measured as follows. In the case of a separator which is formed in an independent form, the porosity of the separator can be measured by means of a mercury porosimeter. On the other hand, in the case of a separator which is formed, in an immobilized form, on at least one active material layer and which cannot be separated from the active material layer(s), the porosity of such a separator can be determined by the following method. The separator is impregnated with a resin solution so as to fill the pores of the separator with the resin solution, followed by curing the resin. The resultant separator having pores thereof filled with the cured resin is cut to obtain a cross section of the separator in which the cross sections of the cured resin-filled pores are exposed. A photograph of the cross section thereof is taken by means of a scanning electron microscope (SEM). The obtained photograph of the cross section of the separator is examined to obtain the ratio (%) of the sum of the respective cross-sectional areas of the cured resin-filled pores to the entire area of the cross section of the separator. In practice, with respect to each of ten or more

different cross-sectional portions of the separator which each include a number of cured resin-filled pores, the ratio (%) of the sum of the respective cross-sectional areas of the cured resin-filled pores to the entire area of the cross section of each of the different portions of the separator is obtained in substantially the same manner as mentioned above, and the average value of the obtained ratios is defined as the porosity of the separator.

In the present invention, the above-mentioned separator may have an ion conductive property attributed to a factor other than the voids of the aggregate form of particles of at least one insulating substance.

Examples of methods for obtaining such separators, which have an ion conductive property attributed to a factor other than the voids of the aggregate form of particles, include a method in which porous particles of at least one insulating substance are employed; a method in which use is made of particles of at least one insulating substance which has, in the skeletal structure thereof, voids which allow the molecules of the electrolyte to pass therethrough (e.g., a zeolite); a method in which use is made of insulating substance particles and/or another substance used in a mixture of the particles, which can be swollen with an electrolyte.

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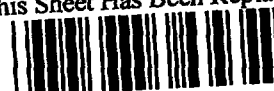
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tic liquid {e.g., polyacrylonitrile, poly(methyl methacrylate) and poly(vinylidene fluoride)}; and a method in which use is made of particles of at least one insulating substance and/or another substance used in a mixture of the particles, wherein the insulating substance and/or another substance is a material, e.g., a composite of an alkaline metal salt with poly(ethylene oxide), poly(propylene oxide), a polyphosphazene or the like, namely a material obtained by impregnating a solid with a solution of an electrolyte in a solvent, and removing the solvent by evaporation from the impregnated solid.

In the embodiment mentioned in item 8 above, use is made of a porous separator comprising an aggregate form of particles of at least two different insulating substances. In the embodiment mentioned in item 9 above, use is made of a porous separator comprising at least two layers respectively comprised of different aggregate forms of particles. In the embodiment mentioned in item 10 above, use is made of a porous separator comprising a first separator layer comprising at least one layer of an aggregate form of particles of at least one inorganic insulating substance and a second separator layer comprising at least one layer of an aggregate form of particles of at least one organic

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insulating substance. The term "different" used herein is intended to indicate that the chemical compositions are different and that the properties, such as melting point, are different despite the fact that the chemical compositions are the same. According to each of the above-mentioned embodiments, it is possible to impart the separator with the ability to function as a fuse. As an example of the batteries according to the embodiment of item 8 above there can be mentioned a battery in which the layer of an aggregate form of particles comprises a mixture of particles of an inorganic oxide having a high melting point (e.g., 1,000 °C or more) and particles of a resin having a low melting point (e.g., 200 °C or less). As an example of the batteries according to the embodiment of item 10 above, there can be mentioned a battery in which the separator comprises a first separator layer of an aggregate form of particles of an inorganic oxide having a high melting point (e.g., 1,000 °C or more) and a second separator layer of an aggregate form of particles of a resin having a low melting point (e.g., 200 °C or less), wherein the first separator layer is directly formed, in an immobilized form, on the cathode active material layer and the second separator layer is directly formed, in an immobilized form, on the anode active material layer.

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When the battery according to the embodiment of each of items 8 and 10 above is caused to have a high temperature, only the resin particles contained in the separator are melted and the resultant molten resin closes the voids of the separator to thereby shut off the current (i.e., the separator functions as a fuse), so that the safety of the battery can be secured.

With respect to the type of the battery of the present invention, there is no particular limitation, and the battery of the present invention may be, for example, a primary battery, such as a manganese dioxide-lithium battery and a graphite fluoride-lithium battery; a secondary battery using an aqueous electrolytic liquid, such as a lead storage battery, a nickel-cadmium battery and a nickel-hydrogen battery; or a secondary battery using a non-aqueous electrolytic liquid, such as a lithium ion secondary battery.

With respect to the casing usable in the battery of the present invention, there is no particular limitation. Examples of casings include a can made of aluminum, stainless steel, iron or nickel; a plated can made of iron; a casing formed from a material having a laminate structure; and a casing formed from a resin film.

In the case of a battery of the present invention,

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which is a primary battery, the positive electrode, the negative electrode and the electrolyte may be those which are prepared by conventional techniques. For example, when the battery of the present invention is a manganese dioxide-lithium battery, use can be made of a positive electrode prepared using manganese dioxide, a negative electrode prepared using metallic lithium, and an electrolyte prepared by dissolving a lithium salt in an organic solvent. When the battery of the present invention is a graphite fluoride-lithium battery, use can be made of a positive electrode prepared using a graphite fluoride, the same negative electrode as in the above-mentioned manganese dioxide-lithium battery, and the same electrolyte as in the above-mentioned manganese dioxide-lithium battery.

Also, in the case of the battery of the present invention which is a secondary battery, the positive electrode, the negative electrode and the electrolyte may be those which are prepared by conventional techniques. For example, when the battery of the present invention is a lead storage battery, use can be made of PbO_2 as a cathode active material, Pb as an anode active material, and an aqueous solution of H_2SO_4 as an electrolytic liquid. When the battery of the present invention is a nickel-cadmium battery, use can be made

of NiOOH as a cathode active material, Cd as an anode active material, and, as an electrolytic liquid, an aqueous solution of KOH which contains LiOH or NaOH in a small amount. When the battery of the present invention is a nickel-hydrogen battery, use can be made of the same cathode active material as in the nickel-cadmium battery, hydrogen (e.g., a metal alloy having hydrogen occluded therein) as an anode active material, and the same electrolytic liquid as in the above-mentioned nickel-cadmium battery.

With respect to the battery of the present invention, which is a lithium ion secondary battery, a detailed explanation is made below (the explanation is made mainly about the cathode active material, the anode active material, and the electrolyte).

In the lithium ion secondary battery, as a current collector for the positive electrode, for example, a metallic foil, such as an aluminum foil, a titanium foil, or a stainless steel foil, can be used. Of the above-mentioned metallic foils, an aluminum foil is preferred. As a current collector for the negative electrode, for example, a metallic foil, such as a copper foil, a nickel foil, or a stainless steel foil, can be used. Of the above-mentioned metallic foils, a copper foil is preferred.

In the lithium ion secondary battery, as a cathode active material, a composite metal oxide of Li and a transition metal (such as Co, Ni, Mn, and Fe), and a composite metal oxide of Li, a transition metal and a non-transition metal can be used. Examples of composite metal oxides include a lithium-containing composite metal oxide having a lamellar structure and having the ability to electrochemically intercalate and deintercalate Li ions. Examples of lithium-containing composite metal oxides include LiCoO_2 as disclosed in Unexamined Japanese Patent Application Laid-Open Specification No. 55-136131 (corresponding to U.S. Patent No. 4,357,215); $\text{Li}_x\text{Ni}_y\text{Co}_{(1-y)}\text{O}_2$ wherein $0 \leq x \leq 1$, and $0 \leq y \leq 1$, as disclosed in Unexamined Japanese Patent Application Laid-Open Specification No. 3-49155; and $\text{Li}_x\text{Mn}_2\text{O}_4$ wherein $0 \leq x \leq 1$.

These compounds can be easily obtained by a calcination reaction of a lithium compound, such as lithium hydroxide, lithium oxide, lithium carbonate, lithium nitrate or the like, with a metal oxide, a metal hydroxide, a metal carbonate, a metal nitrate or the like and, if desired, with other metal compounds.

In the lithium ion secondary battery, as an anode active material, a carbonaceous material, such as a coke, a graphite, and an amorphous carbon, can be used.

The above-mentioned carbonaceous material may be in various forms, such as crushed particles, lamellar particles and spherical particles. With respect to the type of carbonaceous material, there is no particular limitation, and various types of carbonaceous materials can be used. Examples of carbonaceous materials include a carbon or graphite material having a large surface area as disclosed in Unexamined Japanese Patent Application Laid-Open Specification No. 58-35881 (corresponding to U.S. Patent No. 4,617,243), a calcination-carbonized product of a phenolic resin and the like as disclosed in Unexamined Japanese Patent Application Laid-Open Specification No. 58-209864, and a calcination-carbonized product of a condensed polycyclic hydrocarbon compound as disclosed in Unexamined Japanese Patent Application Laid-Open Specification No. 61-111907 (corresponding to U.S. Patent No. 4,725, 422).

With respect to the non-aqueous electrolytic liquid used in the lithium ion secondary battery, there is no particular limitation. The non-aqueous electrolytic liquid can be prepared by dissolving the electrolyte as mentioned below in an organic solvent. Examples of electrolytes include LiClO_4 , LiBF_4 , LiAsF_6 , $\text{CF}_3\text{SO}_3\text{Li}$, $(\text{CF}_3\text{SO}_3)_2\text{N}\cdot\text{Li}$, LiPF_6 , LiI , LiAlCl_4 , NaClO_4 ,

NaBF₄, NaI, (n-Bu)₄NClO₄, (n-Bu)₄NBF₄ and KPF₆. It is preferred that the concentration of the electrolyte in the organic electrolytic liquid is from about 0.1 to about 2.5 mol/liter. Examples of organic solvents include ethers, ketones, lactones, nitriles, amines, amides, sulfur compounds, chlorinated hydrocarbons, esters, carbonates, nitro compounds, phosphoric ester compounds and sulfolane compounds. Among the above-mentioned organic solvents, ethers, ketones, nitriles, chlorinated hydrocarbons, carbonates and sulfolane compounds are preferred, and cyclic carbonates are especially preferred. Representative examples of cyclic carbonates include tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, anisol, monoglyme, acetonitrile, propionitrile, 4-methyl-2-pentanone, butyronitrile, valeronitrile, benzonitrile, 1,2-dichloroethane, γ -butyrolactone, dimethoxyethane, methyl formate, propylene carbonate, ethylene carbonate, diethyl carbonate, dimethyl carbonate, methyl ethyl carbonate, vinylene carbonate, dimethylformamide, dimethylsulfoxide, dimethylthioformamide, sulfolane, 3-methylsulfolane, trimethyl phosphate, triethyl phosphate, and mixtures thereof. The organic solvents usable in the present invention are not limited to those which are mentioned above.

With respect to a non-aqueous battery, such as the above-mentioned lithium ion secondary battery, the non-aqueous liquid used therein has a poor ion conductive property. Therefore, for the purpose of improving the efficiency of ion conduction between the positive electrode and the negative electrode, the conventional non-aqueous battery has a construction in which a plurality of unit cells as shown in Fig. 1(A) are laminated, or a construction in which a unit cell as shown in Fig. 1(A) is spirally wound into a spirally wound structure. The above-mentioned unit cell as shown in Fig. 1(A) comprises: positive electrode 11 comprising current collector foil 11a (for the positive electrode) having both surfaces thereof coated with respective cathode active material layers 11b, 11b; negative electrode 12 comprising current collector foil 12a (for the negative electrode) having both surfaces thereof coated with respective anode active material layers 12b, 12b; and resin film separator 13 disposed between cathode active material layer 11b and anode active material layer 12b. As already mentioned above, the use of resin film separator 13 has the following disadvantage. Since resin film separator 13 needs to be handled as an independent film during the production of the battery, the separator needs to have high me-

chanical strength so as to avoid breakage of the separator during the handling thereof. Therefore, the resin film separator needs to have a relatively large thickness so as to achieve high mechanical strength, and it is difficult to use a resin film separator having a thickness of less than 25 μm in a battery. When such a separator having a relatively large thickness is used in the above-mentioned non-aqueous battery having a construction as mentioned above, the amount of the active materials which can be accommodated in the battery per unit volume thereof becomes small due to the relatively large thickness of the separator. In contrast, when the porous separator used in the present invention is employed for producing a non-aqueous battery having a construction as mentioned above instead of resin film separator 13, it becomes possible to obtain a high performance battery, in which the amount of active materials which can be accommodated in the battery per unit volume thereof is markedly increased and the ion conduction between the positive electrode and the negative electrode is markedly improved. Further, the above-mentioned conventional non-aqueous battery, in which the resin film separator is used, is also disadvantageous in that the resin film separator which is a relatively expensive component

among the components of the battery needs to be used in a large amount, so that the production cost for the battery inevitably becomes high. On the other hand, the porous separator used in the present invention can be obtained at low cost. Therefore, by the use of the porous separator used in the present invention, it becomes possible to produce the above-mentioned high performance battery at low cost.

With respect to the method for producing the porous separator used in the present invention, there is no particular limitation. The porous separator can be produced, for example, by the method described below with reference to Fig. 2. Separator 13A can be produced by a method comprising forming cathode active material layers 11b and 11b on both surfaces of current collector foil 11a for a positive electrode by a conventional method, to thereby obtain positive electrode 11; forming a layer of an aggregate form of particles of at least one insulating substance on the surface of each cathode active material layer 11b, which layer of the aggregate form of particles serves as separator 13A. Specific examples of methods for forming separator 13A include a method in which particles of at least one insulating substance are uniformly coated on the surface of each cathode active material layer 11b, fol-

lowed by bonding the particles to the surface of each cathode active material layer 11b by means of a roll press, to thereby form a layer of an aggregated form of particles, which serves as separator 13A; and a method in which a dispersion of a mixture of particles of at least one insulating substance and a binder for the particles in a dispersion medium is uniformly coated in a predetermined thickness on the surface of each cathode active material layer 11b, followed by heating the coated dispersion to remove the dispersion medium by evaporation, to thereby form a layer of an aggregate form of particles which serves as separator 13A. In the case of the above-mentioned method in which a dispersion of the mixture of particles of at least one insulating substance and a binder is used, there is no particular limitation with respect to the dispersion medium as long as the following three requirements are satisfied; that is, (i) the particles of at least one insulating substance be insoluble in the dispersion medium, (ii) a binder for the particles be soluble in the dispersion medium, and (iii) the dispersion medium can be evaporated by heating at an appropriate temperature. Examples of dispersion media include ethyl acetate, ethylene glycol monoethyl ether (2-ethoxyethanol), 1-methyl-2-pyrrolidone (NMP), N,N-

dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and water. With respect to the time and temperature for the removal of the dispersion medium by heating, there is no particular limitation, as long as the particles of the insulating substance are not deformed or melted. However, the removal of the dispersion medium by heating is generally conducted at a temperature of from 50 to 200 °C for 5 to 30 minutes. Further, with respect to the solids (particles of the insulating substance) content of the above-mentioned dispersion, there is no particular limitation. However, it is preferred that the solids content is from 40 to 60 % by weight, based on the weight of the dispersion.

The porous separator obtained by the above-mentioned methods, in which the morphology of each of the particles constituting the aggregate form thereof is the same as that before the particles are fabricated into the aggregate from thereof, is fundamentally different from a separator obtained by a method in which particles of an insulating substance are heated to thereby melt-bond (sinter) the particles to each other. In the present invention, each of the particles constituting the aggregate form thereof maintains its original morphology (i.e., the morphology of the particle

before the fabrication of the particles into the aggregated form thereof), in which the particles are not melt-bonded to each other and no chemical bond is formed between the particles.

5 When a unit cell having a structure as shown in Fig. 2 (which comprises a positive electrode having separators 13A, 13A on both sides thereof, and a negative electrode formed of a current collector 12a having anode active material layers 12b and 12b on both sides
10 of current collector 12a) is used in the battery of the present invention, for example, such a unit cell can be used in the form of a spirally wound structure in which the unit cell is spirally wound so that the negative electrode of the wound unit cell is positioned on the
15 side of the outer surface of each wind of the spirally wound structure, or in the form of a laminate structure in which a plurality of the unit cells are laminated so that each positive electrode 11 is positioned opposite to negative electrode 12 through separator 13A (i.e.,
20 in this laminate structure, each separator 13A is disposed between positive electrode 11 and negative electrode 12, wherein two opposite surfaces of the separator face cathode active material layer 11b and anode active material layer 12b, respectively).

25 As already mentioned above, with respect to sepa-

rator 13A as shown in Fig. 2, which is directly formed, in an immobilized form, on the active material layer of the electrode, such a separator need not be handled as an independent film during the production of a battery.

5 Therefore, the separator may have an extremely small thickness, and the lower limit of the thickness of the separator is not particularly limited as long as a predetermined porosity of the separator can be achieved and maintained, and occurrence of short-circuiting can
10 be prevented. Separator 13A having an extremely small thickness can be obtained by using particles of the insulating substance having an appropriate average particle diameter. For example, by using particles of the insulating substance, which have an average parti-
15 cle diameter of 1 μm or less, separator 13A having a thickness of from 5 to 10 μm and a porosity of about 60 % can be obtained.

Further, in the case of the above-mentioned separator 13A which is obtained by using a mixture of a
20 binder and the particles of insulating substance, and which is directly formed, in an immobilized form, on the surface of an active material layer of an electrode, such a separator has high flexibility so that it continues to be stably positioned on the active materi-
25 al layer of the electrode without suffering slippage

during the production of a battery. This is advantageous from the viewpoint of the efficiency in the production of a battery. It is difficult to obtain a separator having such high flexibility by a conventional technique, for example, by a method in which the particles of the insulating substance are melt-bonded (sintered) to each other to form a separator.

Next, in order to illustratively show the construction of the battery of the present invention, an explanation is made below about various embodiments of the present invention with reference to Figs. 2 to 6.

The unit cell shown in the above-mentioned Fig. 2, has a structure in which separators 13A, 13A are formed, in an immobilized form, on the respective cathode active material layers 11b, 11b which are formed on both surfaces of current collector foil 11a for positive electrode 11. Alternatively, the battery of the present invention may comprise a unit cell having a structure as shown in Fig. 3, in which separators 13B, 13B are formed, in an immobilized form, on the respective anode active material layers 12b, 12b which are formed on both surfaces of current collector foil 12a for negative electrode 12.

Further, the battery of the present invention may comprise a unit cell having a structure as shown in

Fig. 4, in which separators 13A, 13B are respectively formed, in an immobilized form, on one of the two cathode active material layers 11b, 11b which are formed on both surfaces of current collector 11a for positive electrode 11, and on one of the two anode active material layers 12b, 12b which are formed on both surfaces of current collector 12a for negative electrode 12, wherein cathode active material layer 11b (having separator 13A formed thereon) and anode active material layer 12b (free of separator) are arranged opposite to each other through separator 13A.

Further, the battery of the present invention may comprise a unit cell having a structure as shown in Fig. 5, in which separators 13A, 13A are formed, in an immobilized form, on the respective cathode active material layers 11b, 11b which are formed on both surfaces of current collector 11a for positive electrode 11; separators 13B, 13B are formed, in an immobilized form, on the respective anode active material layers 12b, 12b which are formed on both surfaces of current collector 12a for negative electrode 12, wherein either of cathode active material layers 11b, 11b and either of anode active material layers 12b, 12b are arranged opposite to each other through separators 13A and 13B to thereby form unit cell 1. In this instance,

two separators 13A, 13A (formed on the respective cathode active material layers 11b, 11b which are formed on both surfaces of current collector 11a for positive electrode 11) may be the same or different, and two separators 13B, 13B (formed on the respective anode active material layers 12b, 12b which are formed on both surfaces of current collector 12a for negative electrode 12) may be the same or different. The battery comprising the unit cell having a structure as shown in Fig. 5 has a double-separator structure (comprised of separators 13A, 13B) formed between the cathode active material layer and the anode active material layer. Therefore, such a battery is especially advantageous for the following reason. Even when either or each of separator 13A and separator 13B of the above-mentioned double-separator structure suffers from pin hole phenomenon (i.e., a phenomenon in which holes extending along the thicknesswise direction of a separator are formed), by virtue of the above-mentioned double-separator structure, there is almost no probability that a hole formed in one of the two separators communicates to a hole formed in the other of the two separators to form a through-hole extending through both of the two separators. Therefore, the above-mentioned battery is substantially free from the danger of occurrence of a

short-circuiting between cathode active material layer 11b and anode active material layer 12b.

Further, the battery of the present invention may comprise a unit cell having a structure as shown in Fig. 6, in which separator 13C is formed, in an immobilized form, on both of cathode active material layer 11b and anode active material layer 12b. Examples of methods for producing separator 13C include:

a method comprising:

coating a dispersion of a mixture of particles of an insulating substance and a binder for the particles in a dispersion medium on the surface of an active material layer of an electrode selected from the positive electrode and the negative electrode,

immediately after coating the surface of the active layer with the dispersion, laminating the resultant electrode (having the active material layer thereof coated with the dispersion) to the remaining other electrode so that the cathode active material layer and the anode active material layer are arranged opposite to each other through the above-mentioned coated dispersion, and

removing, by evaporation, the dispersion medium by heating, so that separator 13C is formed, in an immobilized form, on both of the cathode active material

layer and the anode active material layer;

a method comprising:

coating the above-mentioned dispersion on the surface of an active material layer of an electrode selected from the positive electrode and the negative electrode,

drying the coated dispersion to form a separator layer on the active material layer,

laminating the electrode having the active material layer (on which the separator layer is formed) to the remaining other electrode so that the cathode active material layer and the anode active material layer are arranged opposite to each other through the separator layer, to thereby obtain a laminate structure comprised of the positive electrode, the negative electrode and the separator layer disposed between the positive electrode and the negative electrode; and

pressing the obtained laminate structure by means of a hot press under temperature conditions at which the binder for the particles can be melted, so that separator 13C is formed, in an immobilized form, on both of the cathode active material layer and the anode active material layer; and

a method comprising:

coating the above-mentioned dispersion on the surface of an active material layer of an electrode selected from the positive electrode and the negative electrode,

5 drying the coated dispersion to form a separator layer on the active material layer,

coating a solvent, which is capable of dissolving the above-mentioned binder, on the separator layer,

10 laminating the electrode having the active material layer (on which the separator layer is formed) to the remaining other electrode so that the cathode active material layer and the anode active material layer are arranged opposite to each other through the separator layer, to thereby obtain a laminate structure
15 comprised of the positive electrode, the negative electrode and the separator layer disposed between the positive electrode and the negative electrode;
and

20 pressing and heating the obtained laminate structure, so that separator 13C is formed, in an immobilized form, on both of the cathode active material layer and the anode active material layer.

25 In the battery of the present invention, as shown in Figs. 2 to 6, the unit cell may comprise a plurality of cathode active material layers and a plurality of

anode active material layers. Alternatively, as shown in Figs. 7(a) to (c) (which are referred to in the Examples below), the unit cell may comprise a single cathode active material layer and a single anode active material layer, and such a unit cell may be used in the form of a laminate structure in which a plurality of unit cells are laminated, or in the form of a spirally wound structure in which a unit cell is spirally wound.

With respect to the method for producing the battery of the present invention, there is no particular limitation. However, as a preferred example of methods for producing the battery of the present invention, there can be mentioned a method comprising:

(1) individually providing a positive electrode comprising a cathode active material layer and a negative electrode comprising an anode active material layer;

(2) coating a dispersion of a mixture of particles of an insulating substance and a binder for the particles in a dispersion medium on at least one active material layer selected from the group consisting of the cathode active material layer and the anode active material layer;

(3) removing, by evaporation, the dispersion medium of the dispersion coated on the at least one

active material layer to form a layer of an aggregate of the particles, wherein the particles are bound together by means of the binder, thereby providing a porous separator formed directly, in an immobilized form, on the at least one active material layer, wherein the layer of an aggregate form of particles has a three dimensional network of voids; and

(4) disposing the positive electrode and the negative electrode, at least one of which has the porous separator formed on the active material layer thereof, in a casing so that the cathode active material layer and the anode active material layer are arranged opposite to each other through the porous separator formed on the at least one active material layer, operatively with an electrolyte contained in the casing.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinbelow, the present invention will be described in detail with reference to the following Examples and Comparative Examples, which should not be construed as limiting the scope of the present invention.

Example 1

Using sample unit cells each having a structure as shown in Fig. 7(a), the charge/discharge cycle characteristics of the battery of the present invention were examined.

Sheet electrodes were individually produced as follows.

(Positive electrode)

LiCoO_2 as a cathode active material, a lamellar graphite and acetylene black, each as a filler, and a fluororubber (a copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene: manufactured and sold, under the tradename "Miraflon", by Asahi Chemical Industry Co., LTD., Japan) as a binder (LiCoO_2 /lamellar graphite/acetylene black/fluororubber weight ratio: 100/2.5/2.5/1.96) were mixed in a mixed solvent of ethyl acetate and ethyl cellosolve (ethyl acetate/ethyl cellosolve volume ratio: 1/3) to thereby

obtain a slurry for coating. The obtained slurry was applied to one surface of aluminum foil 11a (a current collector) having a thickness of 15 μm , followed by drying. The resultant coated aluminum foil was pressed by means of a calender roll, to thereby obtain positive electrode 11 having 88 μm -thick cathode active material layer 11b.

(Negative electrode)

A needle coke as a negative active material, carboxymethyl cellulose as a dispersing agent and a styrene-butadiene latex as a binder (needle coke/carboxymethyl cellulose/styrene-butadiene latex weight ratio: 100/0.8/2.0) were mixed in purified water to thereby obtain a slurry for coating. The obtained slurry was applied to one surface of copper foil 12a (a current collector) having a thickness of 18 μm , followed by drying. The resultant coated copper foil was pressed by means of a calender roll, to thereby obtain negative electrode 12 having 124 μm -thick anode active material layer 12b.

(Aggregate form of particles of an insulating substance)

An aggregate form of particles of an insulating substance was prepared by the method described below using the materials described below.

(Materials used)

Particles of an insulating substance: Particles of α - Al_2O_3 having an average particle diameter of 0.5 μm .

5 Binder: A fluororubber (Miraflon, manufactured and sold by Asahi Chemical Industry Co., LTD., Japan).

Solvent: A mixed solvent of ethyl acetate and ethyl cellosolve (ethyl acetate/ethyl cellosolve volume ratio: 1/3).

10 (Preparation method)

A fluororubber (Miraflon) was dissolved in a mixed solvent of ethyl acetate and ethyl cellosolve to obtain a solution having a fluororubber content of 4.3 % by weight. Then, to the obtained fluororubber solution
15 were added particles of α - Al_2O_3 to obtain a slurry having a solids content of 45.3 % by weight. Using a doctor blade, the obtained slurry was applied, in a predetermined uniform thickness, to the surface of cathode active material layer 11b of positive electrode
20 11, followed by drying in an oven at 120 °C for 15 minutes, to thereby obtain separator 13A, wherein separator 13A was composed of a layer of an aggregate form of particles of α - Al_2O_3 , and was directly formed, in an immobilized form, on cathode active material
25 layer 11b. Separator 13A had a porosity of 52 %. The

porosity was measured by means of a mercury porosimeter (manufactured and sold by Shimadzu Corp., Japan) with respect to a sample separator prepared in substantially the same manner as in the preparation of separator 13A, except that the sample separator was formed on a dish made of an aluminum foil and then, the obtained sample separator was peeled off from the dish.

Positive electrode 11 having separator 13A (which was directly formed, in an immobilized form, on cathode active material layer 11b) was fabricated so as to have a surface area of 1.5 cm x 1.0 cm. Negative electrode 12 was fabricated so as to have a surface area of 1.55 cm x 1.05 cm. (These surface areas are of the face-to-face surfaces of both electrodes.)

Then, the obtained positive electrode sheet and the obtained negative electrode sheet were combined so that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separator 13A formed on cathode active material layer 11b, to thereby obtain a sample unit cell having a structure as shown in Fig. 7(a). (Example 1-A) In the obtained sample unit cell, the thickness of separator 13A was 25 μm .

Another sample unit cell having a structure as shown in Fig. 7(b) was obtained in substantially the

same manner as in Example 1-A, except that separator 13A was also formed on anode active material layer 12b. (Example 1-B) In the obtained sample unit cell of Fig. 7(b), the total thickness of the separators respectively formed on cathode active material layer 11b and on anode active material layer 12b was 50 μm . Each of the obtained sample unit cells was immersed in an electrolytic liquid which had been prepared by dissolving LiBF_4 in a mixed solvent of propylene carbonate (PC), ethylene carbonate (EC) and γ -butyrolactone (γ -BL) (PC/EC/ γ -BL volume ratio: 1/1/2, and LiBF_4 concentration: 1.0 mol/liter), and the charge/discharge cycle test was conducted under the following conditions.

(Charge/discharge conditions)

Temperature : 25 $^{\circ}\text{C}$

(1st cycle)

Charge : The charging operation was conducted for 8 hours, in which the operation was started at a current density of 1.0 mA/cm^2 and, after the voltage of the unit cell became 4.2 V, the current density was controlled so as to maintain the voltage at 4.2 V.

Discharge: The discharging operation was conducted at a current density of 1.0 mA/cm^2 {corresponding to 1/3C, wherein C indicates the discharge rate (1.0C corresponds to a discharge current at which a fully

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charged battery can complete discharging in 1 hour))
until the voltage of the unit cell became 2.7 V.
(2nd to 15th cycles)

5 Charge : The charging operation was conducted
for 6 hours, in which the operation was started at a
current density of 1.0 mA/cm^2 and, after the voltage of
the unit cell became 4.2 V, the current density was
controlled so as to maintain the voltage at 4.2 V.

10 Discharge: The discharging operation was conducted
at a current density of 1.0 mA/cm^2 (corresponding to
1/3C) until the voltage of the unit cell became 2.7 V.
(16th and 17th cycles)

15 Charge : The charging operation was conducted
under substantially the same conditions as in the 2nd
to 15th cycles.

Discharge: The discharging operation was conducted
at a current density of 3.0 mA/cm^2 (corresponding to
1.0C) until the voltage of the unit cell became 2.7 V.
(18th cycle)

20 Charge : The charging operation was conducted
under substantially the same conditions as in the 2nd
to 15th cycles.

25 Discharge: The discharging operation was conducted
under substantially the same conditions as in the 2nd
to 15th cycles.

(19th cycle)

Charge : The charging operation was conducted under substantially the same conditions as in the 2nd to 15th cycles.

5 Discharge: The discharging operation was conducted at a current density of 6.0 mA/cm^2 (corresponding to 2.0C) until the voltage of the unit cell became 2.7 V .

10 With respect to each of the sample unit cells, the discharge capacity lowering ratio (%) between the 15th cycle and the 16th cycle and the discharge capacity lowering ratio (%) between the 18th cycle and the 19th cycle were calculated. Results are shown in Table 1.

Comparative Example 1

15 Sample unit cells each having a structure as shown in Fig. 1(B) was prepared as follows.

20 Positive electrode 11 and negative electrode 12 were individually obtained in substantially the same manner as in Example 1. Positive electrode 11 and negative electrode 12 were fabricated so as to have a surface area of $1.5 \text{ cm} \times 1.0 \text{ cm}$ and a surface area of $1.55 \text{ cm} \times 1.05 \text{ cm}$, respectively. (These surface areas are of the face-to-face surfaces of both electrodes.) Then, the obtained positive electrode sheet, the ob-
25 tained negative electrode sheet and separator 13 {a

microporous polyethylene (PE) film having a thickness of 25 μm and a porosity of 48 %} were combined so that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separator 13, to thereby obtain a sample unit cell having a structure as shown in Fig. 1(B). (Comparative Example 1-A)

Another sample unit cell was obtained in substantially the same manner as in Comparative Example 1-A, except that use was made of a microporous PE film having a thickness of 34 μm and a porosity of 63 % as separator 13. (Comparative Example 1-B)

The porosity of each of the above-mentioned microporous PE films was calculated by the following formula:

$$\text{Porosity} = \left(\frac{\text{total volume of pores in the microporous film}}{\text{volume of the microporous film}} \right) \times 100$$

wherein the total volume of pores is the value obtained by subtracting the weight of the microporous film in the dry state thereof from the weight of the microporous film in the wet state thereof in which the microporous film is impregnated with water.

Each of the obtained sample unit cells was im-

mersed in the same electrolytic liquid as in Example 1,
and the charge/discharge cycle test was conducted under
the same conditions as in Example 1. With respect to
each of the obtained sample unit cells, the discharge
capacity lowering ratio (%) between the 15th cycle and
the 16th cycle and the discharge capacity lowering
ratio (%) between the 18th cycle and the 19th cycle
were calculated. Results are shown in Table 1.

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Table 1

	Discharge capacity E ₁₅ at the 15th cycle (current density: 1/3C) (mAh)	Discharge capacity E ₁₆ at the 16th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 15th cycle and the 16th cycle (%)	Discharge capacity E ₁₈ at the 18th cycle (current density: 1/3C) (mAh)	Discharge capacity E ₁₉ at the 19th cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 18th cycle and the 19th cycle (%)
Example 1-A	4.326	4.017	-7.1	4.311	2.354	-45.4
Example 1-B	4.342	4.076	-6.1	4.303	1.553	-63.9
Comparative Example 1-A	4.350	3.959	-9.0	4.337	1.341	-69.1
Comparative Example 1-B	4.383	4.058	-7.4	4.364	1.502	-65.6

Discharge capacity lowering ratio (%) between the (n-1)-th cycle and the n-th cycle : $[E_n - E_{(n-1)}] / E_{(n-1)} \times 100$.

As can be seen from Table 1, the sample unit cell obtained in Example 1-A had a markedly small discharge capacity lowering ratio (%) between the 18th cycle (in which the discharge current density was 1/3C) and the 19th cycle (in which the discharge current density was 1.0C), as compared to the sample unit cell obtained in Comparative Example 1-A in which the separator used had the same thickness as that of the separator used in Examples 1-A. That is, the battery of the present invention has improved discharge characteristics at a high current density, which are superior to those of a battery using a conventional microporous PE film separator. The reason for this is presumed to be as follows. The separator used in the present invention, which comprises a layer of an aggregate form of particles of at least one insulating substance, has a unique pore structure in which the morphology of the pores and the distribution of the pore diameters are different from those of the conventional microporous PE film separator, and the above-mentioned unique pore structure of the separator used in the present invention is more effective for achieving a high ion conductive property than the pore structure of the above-mentioned conventional separator. It is presumed that, due to such a high ion conductive property of the separator,

the sample unit cell using the separator used in the present invention exhibits improved discharge characteristics at a high current density. This can be confirmed by the fact that the sample unit cell obtained in Example 1-B (which had a separator having a thickness which is much larger than those of the separators respectively obtained in Comparative Examples 1-A and 1-B), exhibited excellent discharge characteristics, as compared to the sample unit cells respectively obtained in Comparative Examples 1-A and 1-B.

Further, the sample unit cell obtained in Example 1-A has a markedly small discharge capacity lowering ratio (%) between the 18th cycle (in which the discharge current density was 1/3C) and the 19th cycle (in which the discharge current density was 2.0C), as compared to the sample unit cell obtained in Comparative Example 1-B which had a porosity which is higher than that of the separator used in the sample unit cell of Example 1-A and had a thickness which is larger than that of the separator used in the unit cell of Example 1-A. The reason for this is as follows. Although the separator used in the sample unit cell of Example 1-A had a porosity which is lower than that of the conventional separator used in the sample unit cell of Comparative Example 1-B, the separator used in the sample

unit cell of Example 1-A had a thickness which is much smaller than that of the conventional separator used in the sample unit cell of Comparative Example 1-B (which necessarily has a large thickness so as to avoid break-
5 age of the separator during the handling thereof). Due to such a small thickness of the separator, the ion conductive property of the separator was improved, so that the sample unit cell obtained in Example 1-A exhibited improved discharge characteristics at a high
10 discharge current density.

Example 2

Using a sample unit cell having a structure as shown in Fig. 7(b) and a sample unit cell having a
15 structure as shown in Fig. 7(c), the charge/discharge cycle characteristics of the battery of the present invention were examined in substantially the same manner as in Example 1.

Sheet electrodes were individually produced as
20 follows.

(Positive electrode)

LiCoO_2 as a cathode active material, a lamellar graphite and acetylene black, each as a filler, and a fluororubber as a binder (LiCoO_2 /lamellar
25 graphite/acetylene black/fluororubber weight ratio:

100/2.5/2.5/1.96) were mixed in a mixed solvent of ethyl acetate and ethyl cellosolve (ethyl acetate/ethyl cellosolve volume ratio: 1/3) to thereby obtain a paste for coating. The obtained paste was applied to one surface of aluminum foil 11a (a current collector) having a thickness of 15 μm , followed by drying. The resultant coated aluminum foil was pressed by means of a calender roll, to thereby obtain positive electrode 11 having 87 μm -thick cathode active material layer 11b.

(Negative electrode)

A mesophase pitch carbon fiber graphite and a lamellar graphite, each as an anode active material, carboxymethyl cellulose as a dispersing agent and a latex as a binder (mesophase pitch carbon fiber graphite/lamellar graphite/carboxymethyl cellulose/latex weight ratio: 90/10/1.4/1.8) were mixed in purified water to thereby obtain a paste for coating. The obtained paste was applied to one surface of copper foil 12a (a current collector) having a thickness of 12 μm , followed by drying. The resultant coated copper foil was pressed by means of a calender roll, to thereby obtain negative electrode 12 having 81 μm -thick anode active material layer 12b.

(Aggregate form of particles of an insulating sub-

stance)

An aggregate form of particles of an insulating substance was prepared by the method described below using the materials described below.

5 (Materials used)

Particles of an insulating substance: Particles of α - Al_2O_3 having an average particle diameter of 1.0 μm .

10 Binder: Polyvinylidene fluoride (PVDF) (KF#1100, manufactured and sold by Kureha Chemical Industry Co., Ltd., Japan).

Solvent: 1-methyl-2-pyrrolidone (NMP).

(Preparation method)

15 Particles of α - Al_2O_3 and particles of PVDF (α - Al_2O_3 /PVDF weight ratio: 100/5) were mixed with each other to obtain a powder mixture. Then, to the obtained powder mixture was added NMP to obtain a slurry having a solids content of 56.8 % by weight.

20 Using a doctor blade, the obtained slurry was applied, in a predetermined uniform thickness, to each of the surface of cathode active material layer 11b of positive electrode 11 and the surface of anode active material layer 12b of negative electrode 12, followed by drying in an oven at 120 °C for 15 minutes, to
25 thereby obtain separators 13A and 13B, wherein each of

separators 13A and 13B was composed of a layer of an aggregate form of particles of α -Al₂O₃, and separators 13A and 13B were directly formed, in an immobilized form, on cathode active material layer 11b and anode active material layer 12b, respectively. Each of separators 13A and 13B had a porosity of 52 %. The porosities of separators 13A and 13B were measured by means of a mercury porosimeter (manufactured and sold by Shimadzu Corp., Japan) with respect to sample separators prepared in substantially the same manner as in the preparation of separator 13A and the preparation of separator 13B, respectively, except that each of the sample separators was formed on a dish made of an aluminum foil and then, peeled off from the dish.

Positive electrode 11 having separator 13A (which was directly formed, in an immobilized form, on the cathode active material layer 11b) was fabricated so as to have a surface area of 1.5 cm x 1.0 cm. Negative electrode 12 having separator 13B (which was directly formed, in an immobilized form, on anode active material layer 12b) was fabricated so as to have a surface area of 1.55 cm x 1.05 cm. (These surface areas are of the face-to-face surface of both electrodes.)

Then, the obtained positive electrode sheet and the obtained negative electrode sheet were combined so

that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separator 13A formed on cathode active material layer 11b and separator 13B formed on anode active material layer 12b, to thereby obtain a sample unit cell having a structure as shown in Fig. 7(b). (Example 2-A) In the obtained sample unit cell, the total thickness of separators 13A and 13B respectively formed on cathode active material layer 11b and anode active material layer 12b was 25 μm .

Another sample unit cell was obtained in substantially the same manner as in Example 2-A, except that the thickness of each of separators 13A and 13B was controlled so that the total thickness of separators 13A and 13B becomes 10 μm . (Example 2-B)

Using positive electrode 11, negative electrode 12 and a slurry (which is a material for the separator) each prepared in the same manner as in Examples 2-A and 2-B, still another sample unit cell having a structure as shown in Fig. 7(c) was prepared as follows. The above-mentioned slurry was applied to the surface of cathode active material layer 11b of positive electrode 11. Subsequently, positive electrode 11 and negative electrode 12 were combined so that cathode active

material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through the slurry coated on cathode active material layer 11b, followed by drying to remove, by
5 evaporation, the solvent contained in the slurry, to thereby obtain a laminate structure in which separator 13C was directly formed, in an immobilized form, on each of cathode active material layer 11b and anode active material layer 12b. The laminate structure was
10 fabricated so as to have a surface area of 1.5 cm x 1.0 cm, to thereby obtain a sample unit cell having a structure as shown in Fig. 7(c). (Example 2-C) In the obtained sample unit cell, the thickness of separator 13C was 25 μm .

15 Each of the obtained sample unit cells was immersed in an electrolytic liquid which had been prepared by dissolving LiPF_6 in a mixed solvent of ethylene carbonate (EC) and diethylene carbonate (DEC) (EC/DEC volume ratio: 1/1, and LiPF_6 concentration: 1.0
20 mol/liter), and the charge/discharge cycle test was conducted under the conditions as mentioned below.

In Comparative Example 2, a sample unit cell was prepared as follows. Positive electrode 11 and negative electrode 12 were individually obtained in substantially the same manner as in Example 2-A and
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Example 2-B. The obtained positive electrode 11 and the obtained negative electrode 12 were fabricated so as to have a surface area of 1.5 cm x 1.0 cm and a surface area of 1.55 cm x 1.05 cm, respectively. (These surface areas are of the face-to-face surface of both electrodes.) Then, the obtained positive electrode sheet and the obtained negative electrode sheet were combined so that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separator 13 which is a microporous polyethylene (PE) film having a thickness of 25 μ m and a porosity of 36 %, to thereby obtain a sample unit cell having a structure as shown in Fig. 1(B). Each of the obtained sample unit cells was immersed in the same electrolytic liquid as in Example 2, and the charge/discharge cycle test was conducted under the same conditions as in Example 2.

The porosity of the microporous PE film was calculated by the following formula:

$$\text{Porosity} = \left(\frac{\text{total volume of pores in the microporous film}}{\text{volume of the microporous film}} \right) \times 100$$

wherein the total volume of pores is the value obtained by subtracting the weight of the

microporous film in the dry state thereof from the weight of the microporous film in the wet state thereof in which the microporous film is impregnated with water.

5 With respect to each of the sample unit cells respectively obtained in Examples 2-A, 2-B and 2-C, and Comparative Example 2, the charge/discharge cycle test was conducted under the following conditions.

(Charge/discharge conditions)

10 Temperature: 25 °C

(1st cycle to 10th cycle)

Charge : The charging operation was conducted for 6 hours, in which the operation was started at a current density of 1.0 mA/cm² and, after the voltage of the unit cell became 4.2 V, the current density was controlled so as to maintain the voltage at 4.2 V.

Discharge: The discharging operation was conducted at a current density of 1.0 mA/cm² (corresponding to 1/3C) until the voltage of the unit cell became 2.7 V.

20 (11th cycle)

Charge : The charging operation was conducted under substantially the same conditions as in the 1st to 10th cycles.

Discharge: The discharging operation was conducted at a current density of 3.0 mA/cm² (corresponding to

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1.0C) until the voltage of the unit cell became 2.7 V.
(12th cycle)

5 Charge : The charging operation was conducted
under substantially the same conditions as in the 1st
to 10th cycles.

Discharge: The discharging operation was conducted
under substantially the same conditions as in the 1st
to 10th cycles.
(13th cycle)

10 Charge : The charging operation was conducted
under substantially the same conditions as in the 1st
to 10th cycles.

Discharge: The discharging operation was conducted
at a current density of 6.0 mA/cm^2 (corresponding to
15 2.0C) until the voltage of the unit cell became 2.7 V.

With respect to each of the sample unit cells
obtained in Examples 2-A, 2-B, 2-C and Comparative
Example 2, the discharge capacity lowering ratio (%)
between the 10th cycle and the 11th cycle and the
20 discharge capacity lowering ratio (%) between the 12th
cycle and the 13th cycle were calculated. Results are
shown in Table 2.

Table 2

	Discharge capacity E_{10} at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{11} at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E_{12} at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{13} at the 1st cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 2-A	5.027	4.944	-1.7	5.002	4.695	-6.1
Example 2-B	5.031	4.977	-1.1	5.005	4.821	-3.7
Example 2-C	5.011	4.933	-1.6	4.998	4.655	-6.9
Comparative Example 2	5.025	4.925	-2.0	5.000	4.425	-11.5

Discharge capacity lowering ratio (%) between the (n-1)-th cycle and the n-th cycle : $[E_n - E_{(n-1)}] / E_{(n-1)} \times 100$.

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As can be seen from Table 2, the sample unit cell obtained in Example 2-A had a markedly small discharge capacity lowering ratio (%) between the 12th cycle (in which the discharge current density was 1/3C) and the 13th cycle (in which the discharge current density was 2.0C), as compared to the sample unit cell obtained in Comparative Example 2 in which the separator used had the same thickness as that of the separator used in Examples 2-A. That is, the battery of the present invention has improved discharge characteristics at a high current density, which are superior to those of a battery using a conventional microporous PE film separator. The reason for this is presumed to be as follows. The separator used in the present invention, which comprises a layer of an aggregate form of particles of at least one insulating substance, has a unique pore structure in which the morphology of the pores and the distribution of the pore diameters are different from those of the conventional microporous PE film separator, and the above-mentioned unique pore structure of the separator used in the present invention is more effective for achieving a high ion conductive property than the pore structure of the above-mentioned conventional separator. It is presumed that, due to such a high ion conductive property of the separator,

the sample unit cell using the separator used in the present invention exhibits improved discharge characteristics at a high current density.

5 The sample unit cell obtained in Example 2-B exhibited even more improved discharge characteristics at a high current density than the sample unit cell obtained in Example 2-A. Such improved discharge characteristics can be presumed to be attributed to the small thickness of the separator used in the sample
10 cell of Example 1-B, which is even smaller than the thickness of the separator used in the sample unit cell of Example 1-A.

Further, the sample unit cell obtained in Example 2-C, which has a construction in which the separator
15 was directly formed, in an immobilized form, on each of the cathode active material layer and the anode active material layer, also exhibited improved discharge characteristics.

20 Example 3

A sample unit cell was obtained in substantially the same manner as in Example 2-A (Example 3), and another sample unit cell was obtained in substantially the same manner as in Comparative Example 2 (Compara-
25 tive Example 3). With respect to each of the obtained

sample unit cells, the charge/discharge cycle test was conducted under the conditions as mentioned below. In Example 3 and Comparative Example 3, the charge/discharge tests were conducted in order to demonstrate that the separator used in the battery of the present invention has not only an improved ion conductive property, but also an improved durability, as compared to a conventional separator.

(Charge/discharge conditions)

(1st cycle)

Charge : The charging operation was conducted for 6 hours, in which the operation was started at a current density of 1.0 mA/cm^2 and, after the voltage of the unit cell became 4.2 V, the current density was controlled so as to maintain the voltage at 4.2 V.

Discharge: The discharging operation was conducted at a current density of 1.0 mA/cm^2 (corresponding to 1/3C) until the voltage of the unit cell became 2.7 V.
(2nd to 200th cycles)

Charge : The charging operation was conducted for 3 hours, in which the operation was started at a current density of 3.0 mA/cm^2 and, after the voltage of the unit cell became 4.2 V, the current density was controlled so as to maintain the voltage at 4.2 V.

Discharge: The discharging operation was conducted.

at a current density of 3.0 mA/cm^2 (corresponding to 1.0C) until the voltage becomes 2.7 V.

With respect to each of the sample unit cells, the discharge capacity maintaining ratio {i.e., the ratio (%) of the discharge capacity at the 200th cycle to the discharge capacity at the 2nd cycle} were calculated. As a result, it was found that the discharge capacity maintaining ratio in Example 3 was 88.8 %, and that the ratio in Comparative Example 3 was 83.8 %. That is, although the thickness of the separator used in the sample unit cell of Example 3 was the same as that of the separator used in the sample unit cell of Comparative Example 3, the discharge capacity maintaining ratio of the sample unit cell of Example 3 was higher than that of the sample unit cell of Comparative Example 3. From the above, it is apparent that the separator used in the battery of the present invention, which comprises a layer of an aggregate form of particles of at least one insulating substance, has improved durability, as compared to the conventional microporous PE film separator.

Example 4

Using a sample unit cell having a structure as shown in Fig. 7(b), the charge/discharge cycle charac-

teristics of the battery of the present invention were examined in substantially the same manner as in Examples 1 and 2.

(Electrodes)

5 Sheet electrodes were individually produced in substantially the same manner as in Examples 2-A, 2-B and Example 3.

(Aggregate form of particles of an insulating substance)

10 An aggregate form of particles of an insulating substance was prepared by the method described below using the materials described below.

(Materials used)

15 Particles of an insulating substance: Zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 29.

Binder: Polyvinylidene fluoride (PVDF) (KF#1100, manufactured and sold by Kureha Chemical Industry Co., Ltd., Japan).

Solvent: 1-methyl-2-pyrrolidone (NMP).

20 (Preparation method)

 Particles of a zeolite and particles of PVDF (zeolite/PVDF weight ratio: 100/5) were mixed with each other to obtain a powder mixture. Then, to the obtained powder mixture was added NMP to obtain a slurry
25 having a solids content of 55.0 % by weight.

Using a doctor blade, the obtained slurry was applied, in a predetermined uniform thickness, to each of the surface of cathode active material layer 11b of positive electrode 11 and the surface of anode active material layer 12b of negative electrode 12, followed by drying in an oven at 120 °C for 15 minutes, to thereby obtain separators 13A and 13B, wherein each of separators 13A and 13B was comprised of a layer of an aggregate form of particles of a zeolite, and separators 13A and 13B were directly formed, in an immobilized form, on cathode active material layer 11b and anode active material layer 12b, respectively. Each of the obtained separators 13A and 13B had a porosity of 50 %. The porosities of separators 13A and 13B were measured by means of a mercury porosimeter (manufactured and sold by Shimadzu Corp., Japan) with respect to sample separators prepared in substantially the same manner as in the preparation of separator 13A and the preparation of separator 13B, respectively, except that each of the sample separators was formed on a dish made of an aluminum foil and then, peeled off from the dish.

Positive electrode 11 having separator 13A (which was directly formed, in an immobilized form, on cathode active material layer 11b) was fabricated so as to have a surface area of 1.5 cm x 1.0 cm. Negative electrode

12 having separator 13B (which was directly formed, in an immobilized form, on anode active material layer 12b) was fabricated so as to have a surface area of 1.55 cm x 1.05 cm. (These surface areas are of the face-to-face surfaces of both electrodes.)

Then, the obtained positive electrode sheet and the obtained negative electrode sheet were combined so that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separators 13A and 13B respectively formed on cathode active material layer 11b and anode active material layer 12b, to thereby obtain a sample unit cell having a structure as shown in Fig. 7(b). In the obtained sample unit cell, the total thickness of the separator respectively formed on cathode active material layer 11b and anode active material layer 12b was 25 μm . The obtained sample unit cell was immersed in an electrolytic liquid which had been prepared by dissolving LiPF_6 in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC/DEC volume ratio: 1/1, LiPF_6 concentration: 1.0 mol/liter), and the charge/discharge cycle test was conducted under the same conditions as in Example 2. (Example 4)

With respect to the obtained sample unit cell, the

discharge capacity lowering ratio (%) between the 10th cycle and the 11th cycle and the discharge capacity lowering ratio (%) between the 12th cycle and the 13th cycle were calculated. Results are shown in Table 3.

5 In Table 3, the data shown as the results of Comparative Example 4 are the reproduction of the results of Comparative Example 2 shown in Table 2 above.

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Table 3

	Discharge capacity E_{10} at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{11} at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E_{12} at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{13} at the 1st cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 4	5.040	4.960	-1.6	5.009	4.771	-4.8
Comparative Example 4	5.025	4.925	-2.0	5.000	4.425	-11.5

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As can be seen from Table 3, the sample unit cell obtained in Example 4 had a markedly small discharge capacity lowering ratio (%) between the 12th cycle (in which the discharge current density was 1/3C) and the 13th cycle (in which the discharge current density was 2.0C), as compared to the sample unit cell obtained in Comparative Example 4 in which the separator used had the same thickness as that of the separator used in Example 4. That is, the battery of the present invention has improved discharge characteristics at a high current density, which are superior to those of a battery using a conventional microporous PE film separator. As already mentioned above, the reason for this is presumed to reside in that the separator used in the present invention has a unique pore structure which is more effective for achieving a high ion conductive property than the pore structure of the above-mentioned conventional separator, and that, due to such an improved ion conductivity of the separator, the sample unit cell using the separator of the present invention exhibits improved discharge characteristics at a high current density.

Example 5

Using a sample unit cell having a structure as

shown in Fig. 7(b), the charge/discharge cycle characteristics of the battery of the present invention were examined in substantially the same manner as in Examples 1, 2 and 4.

5 (Electrodes)

Sheet electrodes were individually produced in substantially the same manner as in Examples 2, 3 and 4.

10 (Aggregate form of particles of an insulating substance)

An aggregate form of particles of an insulating substance was prepared by the method described below using the materials described below.

(Materials used)

15 Particles of an insulating substance: Polypara-phenylene terephthalamide (aramide) (manufactured and sold, under the tradename "Twaron", by Nihon Aramide Kabushiki Kaisha).

20 Binder: Polyvinylidene fluoride (PVDF) (KF#1100, manufactured and sold by Kureha Chemical Industry Co., Ltd., Japan).

Solvent: 1-methyl-2-pyrrolidone (NMP).

(Preparation method)

25 Particles of aramide and particles of PVDF (aramide/PVD weight ratio: 100/5) were mixed with each

other to obtain a powder mixture. Then, to the obtained powder mixture was added NMP to obtain a slurry having a solids content of 50.0 % by weight.

Using a doctor blade, the obtained slurry was applied, in a predetermined uniform thickness, to the surface of cathode active material layer 11b of positive electrode 11 and the surface of anode active material layer 12b of negative electrode 12, followed by drying in an oven at 120 °C for 15 minutes, to thereby obtain separators 13A and 13B, wherein each of separators 13A and 13B was comprised of a layer of an aggregate form of particles of aramide, and separators 13A and 13B were directly formed, in an immobilized form, on cathode active material layer 11b and anode active material layer 12b, respectively. Each of the separators had a porosity of 50 %. The porosities of separators 13A and 13B were measured by means of a mercury porosimeter (manufactured and sold by Shimadzu Corp., Japan) with respect to sample separators prepared in substantially the same manner as in the preparation of separator 13A and the preparation of separator 13B, respectively, except that each of the sample separators was formed on a dish made of an aluminum foil and then, peeled off from the dish.

Positive electrode 11 having separator 13A (which

was directly formed, in an immobilized form, on cathode active material layer 11b) was fabricated so as to have a surface area of 1.5 cm x 1.0 cm. Negative electrode 12 having separator 13B (which was directly formed, in an immobilized form, on anode active material layer 12b) was fabricated so as to have a surface area of 1.55 cm x 1.05 cm. (These surface areas are of the face-to-face surfaces of both electrodes.)

Then, the obtained positive electrode sheet and the obtained negative electrode sheet were combined so that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separators 13A and 13B respectively formed on cathode active material layer 11b and anode active material layer 12b, to thereby obtain a sample unit cell having a structure as shown in Fig. 7(b). In the obtained sample unit cell, the total thickness of the separator respectively formed on cathode active material layer 11b and anode active material layer 12b was 25 μm . The obtained sample unit cell was immersed in an electrolytic liquid which had been prepared by dissolving LiPF_6 in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC/DEC volume ratio: 1/1, LiPF_6 concentration: 1.0 mol/liter), and the charge/discharge cycle

test was conducted under the same conditions as in Examples 2 and 4. (Example 5)

With respect to the sample unit cell, the discharge capacity lowering ratio (%) between the 10th cycle and the 11th cycle and the discharge capacity lowering ratio (%) between the 12th cycle and the 13th cycle were calculated. Results are shown in Table 4.

In Table 4, the data shown as the results of Comparative Example 5 are the reproduction of the results of Comparative Example 2 shown in Table 2 above.

Table 4

	Discharge capacity E_{10} at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{11} at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E_{12} at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{13} at the 1st cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 5	5.027	4.944	-1.7	5.003	4.766	-4.7
Comparative Example 5	5.025	4.925	-2.0	5.000	4.425	-11.5

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As can be seen from Table 4, the sample unit cell obtained in Example 5 had a markedly small discharge capacity lowering ratio (%) between the 12th cycle (in which the discharge current density was 1/3C) and the 13th cycle (in which the discharge current density was 2.0C), as compared to the sample unit cell of Comparative Example 5 in which the separator used had the same thickness as that of the separator used in Example 5.

Example 6.

Using a sample unit cell having a structure as shown in Fig 7(b), the charge/discharge cycle characteristics of the battery of the present invention were examined in substantially the same manner as in Examples 1, 2, 4 and 5.

(Electrodes)

Sheet electrodes were individually produced in substantially the same manner as in Examples 2, 3, 4 and 5.

(Aggregate form of particles of an insulating substance)

An aggregate form of particles of an insulating substance was prepared by the method described below using the materials described below.

(Materials for the positive electrode)

Particles of an insulating substance: Particles of α - Al_2O_3 having an average particle diameter of 1.0 μm .

5 Binder: Polyvinylidene fluoride (PVDF) (KF#1100, manufactured and sold by Kureha Chemical Industry Co., Ltd., Japan).

Solvent: 1-methyl-2-pyrrolidone (NMP).

(Preparation method)

10 Particles of α - Al_2O_3 and particles of PVDF (α - Al_2O_3 /PVDF weight ratio: 100/5) were mixed with each other to obtain a powder mixture. Then, to the obtained powder mixture was added NMP to obtain a slurry having a solids content of 56.8 % by weight.

15 Using a doctor blade, the obtained slurry was applied, in a predetermined uniform thickness, to the surface of cathode active material layer 11b of positive electrode 11, followed by drying in an oven at 120 °C for 15 minutes, to thereby obtain separator 13A, wherein separator 13A was comprised of a layer of an
20 aggregate form of particles of α - Al_2O_3 , and was directly formed, in an immobilized form, on cathode active material layer 11b. Separator 13A had a porosity of 52 %. The porosity was measured by means of a mercury porosimeter (manufactured and sold by Shimadzu Corp.,
25 Japan) with respect to a sample separator prepared in

substantially the same manner as in the preparation of separator 13A, except that the sample separator was formed on a dish made of an aluminum foil and then, the obtained sample separator was peeled off from the dish.

5 Positive electrode 11 having separator 13A (which was comprised of an aggregate form of particles of α - Al_2O_3 , and directly formed, in an immobilized form, on cathode active material layer 11b) was fabricated so as to have a surface area of 1.5 cm x 1.0 cm.

10 (Materials for the negative electrode)

 Particles of an insulating substance: Polyethylene.

 Binder: Carboxymethyl cellulose and latex.

 Solvent: Purified water.

15 (Preparation method)

 Carboxymethyl cellulose was dissolved in purified water to obtain an aqueous solution having a carboxymethyl cellulose content of 2.0 % by weight. Then, to the obtained aqueous solution of carboxymethyl cellulose were added the particles of polyethylene, and then
20 a latex having a solids content of 4.2 % by weight, to obtain a slurry (polyethylene/carboxymethyl cellulose/latex weight ratio: 100/1/2, solids content: 45.0 % by weight).

25 Using a doctor blade, the obtained slurry was

applied, in a predetermined uniform thickness, to the surface of anode active material layer 12b of negative electrode 12, followed by drying in an oven at 100 °C for 15 minutes, to thereby obtain separator 13B, wherein separator 13B was comprised of a layer of an aggregate form of particles of polyethylene, and was directly formed, in an immobilized form, on anode active material layer 12b. Separator 13B had a porosity of 50 %. The porosity was measured by means of a mercury porosimeter (manufactured and sold by Shimadzu Corp., Japan) with respect to a sample separator prepared in substantially the same manner as in the preparation of separator 13B, except that the sample separator was formed on a dish made of an aluminum foil and then, the obtained sample separator was peeled off from the dish.

Negative electrode 12 having separator 13B (which was composed of an aggregate form of particles of polyethylene, and directly formed, in an immobilized form, on anode active material layer 12b) was fabricated so as to have a surface area of 1.55 cm x 1.05 cm. (The surface areas of separators 13A and 13B are of the face-to-face surfaces of both electrodes.)

Then, the obtained positive electrode sheet and the obtained negative electrode sheet were combined so

that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separators 13A and 13B respectively formed on cathode active material layer 11b and anode active material layer 12b, to thereby obtain a sample unit cell having a structure as shown in Fig. 7(b). In the obtained sample unit cell, the total thickness of the separator respectively formed on cathode active material layer 11b and anode active material layer 12b was 25 μm . Each of the obtained sample unit cells was immersed in an electrolytic liquid which had been prepared by dissolving LiPF_6 in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC/DEC volume ratio: 1/1, LiPF_6 concentration: 1.0 mol/liter), and the charge/discharge cycle test was conducted under the same conditions as in Examples 2, 4 and 5. (Example 6)

With respect to the sample unit cell, the discharge capacity lowering ratio (%) between the 10th cycle and the 11th cycle and the discharge capacity lowering ratio (%) between the 12th cycle and the 13th cycle were calculated. Results are shown in Table 5.

In Table 5, the data shown as the results of Comparative Example 6 are the reproduction of the results of Comparative Example 2 shown in Table 2

above.

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Table 5

	Discharge capacity E_{10} at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{11} at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E_{12} at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{13} at the 1st cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 6	5.016	4.923	-1.9	4.998	4.732	-5.3
Comparative Example 6	5.025	4.925	-2.0	5.000	4.425	-11.5

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As can be seen from Table 5, the sample unit cell obtained in Example 6 had a markedly small discharge capacity lowering ratio (%) between the 12th cycle (in which the discharge current density was 1/3C) and the 13th cycle (in which the discharge current density was 2.0C), as compared to the sample unit cell obtained in Comparative Example 6 in which the separator used had the same thickness as that of the separator used in Examples 5. That is, the battery of the present invention has improved discharge characteristics at a high current density, which are superior to those of a battery using a conventional microporous PE film separator. As already mentioned above, the reason for this is presumed to reside in that the separator used in the present invention has a unique pore structure which is more effective for achieving a high ion conductive property than the pore structure of the above-mentioned conventional separator, and that, due to such an improved ion conductivity of the separator, the sample unit cell using the separator used in the present invention exhibits improved discharge characteristics at a high current density.

Further, in the case of the sample unit cell of Example 6, which has a double-separator structure (comprised of separator 13A and separator 13B) formed

between positive electrode 11 and negative electrode 12, in which separator 13A (formed on cathode active material layer 11a) comprises a layer of particles of an inorganic compound having a high melting point (2055 °C) and separator 13B (formed on anode active material layer 12a) comprises a layer of particles of a synthetic resin having a low melting point (140 °C), the double-separator structure also functions as a fuse. That is, when a battery having such a double-separator structure is caused to have a high temperature, only the resin particles contained in separator 13B are melted and the resultant molten resin closes the voids of separator 13A to thereby shut off the current (i.e., the double-separator structure functions as a fuse).

Example 7

Using a sample unit cell having a structure as shown in Fig. 7(b), the charge/discharge cycle characteristics of the battery of the present invention were examined in substantially the same manner as in Examples 1, 2, 4, 5 and 6.

Sheet electrodes were individually produced as follows.

(Positive electrode)

LiMn_2O_4 as a cathode active material, a lamellar

graphite as a filler and a fluororubber as a binder
(LiMn_2O_4 /lamellar graphite/fluororubber weight ratio:
100/6/1.96) were mixed in a mixed solvent of ethyl
acetate and ethyl cellosolve (ethyl acetate/ethyl
5 cellosolve volume ratio: 1/3) to thereby obtain a paste
for coating. The obtained paste was applied to one
surface of aluminum foil 11a (a current collector)
having a thickness of 15 μm , followed by drying. The
resultant coated aluminum foil was pressed by means of
10 a calender roll, to thereby obtain positive electrode
11 having a 112 μm -thick cathode active material layer
11b.

(Negative electrode)

A mesophase pitch carbon fiber graphite and a
15 lamellar graphite, each as an anode active material,
carboxymethyl cellulose as a dispersing agent, a latex
as a binder (mesophase pitch carbon fiber graphite/
lamellar graphite/carboxymethyl cellulose/latex weight
ratio: 90/10/1.4/1.8) were mixed in purified water to
20 thereby obtain a paste for coating. The obtained paste
was applied to one surface of copper foil 12a (a cur-
rent collector) having a thickness of 12 μm , followed
by drying. The resultant coated copper foil was
pressed by means of a calender roll, to thereby obtain
25 negative electrode 12 having 81 μm -thick anode active

material layer 12b.

(Aggregate form of particles of an insulating substance)

5 An aggregate form of particles of an insulating substance was prepared by the method described below using the materials described below.

(Materials used)

10 Particles of an insulating substance: Particles of α - Al_2O_3 having an average particle diameter of 1.0 μm .

Binder: Polyvinylidene fluoride (PVDF) (KF#1100, manufactured and sold by Kureha Chemical Industry Co., Ltd., Japan).

Solvent: 1-methyl-2-pyrrolidone (NMP).

15 (Preparation method)

20 Particles of α - Al_2O_3 and particles of PVDF (α - Al_2O_3 /PVD weight ratio: 100/5) were mixed with each other to obtain a powder mixture. Then, to the obtained powder mixture was added NMP to obtain a slurry having a solids content of 56.8 % by weight.

25 Using a doctor blade, the obtained slurry was applied, in a predetermined uniform thickness, to each of the surface of cathode active material layer 11b of positive electrode 11 and the surface of anode active material layer 12b of negative electrode 12, followed

by drying in an oven at 120 °C for 15 minutes, to
thereby obtain separators 13A and 13B, wherein each of
separators 13A and 13B was composed of a layer of an
aggregate form of particles of α -Al₂O₃, and separators
5 13A and 13B were directly formed, in an immobilized
form, on cathode active material layer 11b and anode
active material layer 12b, respectively. Each of
separators 13A and 13B had a porosity of 52 %. The
porosities of separators 13A and 13B were measured by
10 means of a mercury porosimeter (manufactured and sold
by Shimadzu Corp., Japan) with respect to sample sepa-
rators prepared in substantially the same manner as in
the preparation of separator 13A and the preparation of
separator 13B, respectively, except that each of the
15 sample separators was formed on a dish made of an
aluminum foil and then, peeled off from the dish.

Positive electrode 11 having separator 13A (which
was directly formed, in an immobilized form, on the
cathode active material layer 11b) was fabricated so as
20 to have a surface area of 1.5 cm x 1.0 cm. Negative
electrode 12 having separator 13B (which was directly
formed, in an immobilized form, on anode active materi-
al layer 12b) was fabricated so as to have a surface
area of 1.55 cm x 1.05 cm. (These surface areas are of
25 the face-to-face surface of both electrodes.)

Then, the obtained positive electrode sheet and the obtained negative electrode sheet were combined so that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separator 13A formed on cathode active material layer 11b and separator 13B formed on anode active material layer 12b, to thereby obtain a sample unit cell having a structure as shown in Fig. 7(b). In the obtained sample unit cell, the total thickness of the separators respectively formed on cathode active material layer 11b and anode active material layer 12b was 25 μm . The obtained sample unit cell was immersed in an electrolytic liquid which had been prepared by dissolving LiPF_6 in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC/DEC volume ratio: 1/1, and LiPF_6 concentration: 1.0 mol/liter), and the charge/discharge cycle test was conducted under the same conditions as in Examples 2, 4, 5 and 6. (Example 7)

In Comparative Example 7, a sample unit cell was prepared as follows. Positive electrode 11 and negative electrode 12 were individually obtained in substantially the same manner as in Example 7. The obtained positive electrode 11 and negative electrode 12 were fabricated so as to have a surface area of 1.5 cm

x 1.0 cm and a surface area of 1.55 cm x 1.05 cm, respectively. (These surface areas are of the face-to-face surface of both electrodes.) Then, the obtained positive electrode sheet, the obtained negative electrode sheet and separator 13 {a microporous polyethylene (PE) film having a thickness of 25 μ m and a porosity of 36 %} were combined so that cathode active material layer 11b and anode active material layer 12b were arranged in a positional relationship opposite to each other through separator 13 to thereby obtain a sample unit cell having the structure as shown in Fig. 1(B). The obtained sample unit cell was immersed in the same electrolytic liquid as in Example 2, and the charge/discharge cycle test was conducted under the same conditions as in Example 2.

With respect to each of the sample unit cell obtained in Example 7 and the sample unit cell obtained in Comparative Example 7, the discharge capacity lowering ratio (%) between the 10th cycle and the 11th cycle and the discharge capacity lowering ratio (%) between the 12th cycle and the 13th cycle were calculated. Results are shown in Table 6.

Table 6

	Discharge capacity E_{10} at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{11} at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E_{12} at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{13} at the 1st cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 7	4.957	4.755	-4.1	4.925	4.451	-9.6
Comparative Example 7	4.949	4.639	-6.3	4.910	4.009	-18.4

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As can be seen from Table 6, the sample unit cell obtained in Example 7 had a markedly small discharge capacity lowering ratio (%) between the 12th cycle (in which the discharge current density was 1/3C) and the 13th cycle (in which the discharge current density was 2.0C), as compared to the sample unit cell obtained in Comparative Example 7 in which the separator used had the same thickness as that of the separator used in Example 7. That is, the battery of the present invention has improved discharge characteristics at a high current density, which are superior to those of a battery using a conventional microporous PE film separator. As already mentioned above, the reason for this is presumed to reside in that the separator used in the present invention has a unique pore structure which is more effective for achieving a high ion conductive property than the pore structure of the above-mentioned conventional separator, so that, due to such an improved ion conductivity of the separator, the sample unit cell using the separator used in the present invention exhibits improved discharge characteristics at a high discharge current density.

INDUSTRIAL APPLICABILITY

The battery of the present invention is advanta-

geous not only in that the battery exhibits excellent
discharge characteristics even at a high discharge
current density without sacrificing safety, but also in
that a large amount of active materials can be accommo-
5 dated in the battery per unit volume thereof, as com-
pared to the amounts in the case of conventional bat-
teries, so that the battery of the present invention
can exhibit an extremely high performance, as compared
to conventional batteries. Further, the battery of the
10 present invention can exhibit such a high performance
even in a compact and light weight form.

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Claims

1. A battery comprising:

a casing,

an electrolyte contained in said casing,

5 a positive electrode comprising a cathode active material layer,

a negative electrode comprising an anode active material layer, and

10 a porous separator disposed between said positive electrode and said negative electrode, wherein two opposite surfaces of said porous separator face said cathode active material layer and said anode active material layer, respectively,

15 said positive electrode, said negative electrode and said separator being disposed in said casing, operatively with said electrolyte,

20 said porous separator comprising at least one layer of an aggregate form of particles of at least one insulating substance, wherein said at least one layer of the aggregate form of particles has a three-dimensional network of voids which function as pores in said porous separator and which are capable of passing ions therethrough.

25 2. The battery according to claim 1, wherein said

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porous separator further comprises a binder which is mixed with said particles to thereby bind said particles together.

- 5 3. The battery according to claim 1 or 2, wherein said porous separator is directly formed, in an immobilized form, on at least one active material layer selected from the group consisting of said cathode active material layer and said anode active material layer.
- 10
4. The battery according to any one of claims 1 to 3, wherein said porous separator has a porosity of 10 % or more as measured in the dry state of said porous separator.
- 15
5. The battery according to any one of claims 1 to 4, wherein said porous separator has an ion conductive property ascribed to a factor other than said voids of said aggregate form of particles.
- 20
6. The battery according to any one of claims 1 to 5, wherein said insulating substance is an inorganic substance.
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7. The battery according to any one of claims 1 to 5, wherein said insulating substance is an organic substance.
- 5 8. The battery according to any one of claims 1 to 7, wherein said aggregate form of particles comprises particles of at least two different insulating substances.
- 10 9. The battery according to any one of claims 1 to 8, wherein said porous separator comprises at least two layers respectively comprised of different aggregate forms of particles.
- 15 10. The battery according to any one of claims 1 to 9, wherein said separator comprises a first separator layer comprising at least one layer of an aggregate form of particles of at least one inorganic insulating substance and a second separator layer comprising at
- 20 least one layer of an aggregate form of particles of at least one organic insulating substance, said first separator layer being directly formed, in an immobilized form, on one active material layer selected from said cathode active material layer and said anode
- 25 active material layer, said second separator layer

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being directly formed, in an immobilized form, on the other active material layer remaining between said cathode active material layer and said anode active material layer.

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11. The battery according to any one of claims 1 to 10, wherein said electrolyte is a non-aqueous electrolyte.

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12. The battery according to claim 11, wherein said non-aqueous electrolyte contains lithium ions.

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13. The battery according to claim 11 or 12, wherein said cathode active material layer comprises lithium manganate.

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14. A method for producing a battery, comprising:
(1) individually providing a positive electrode comprising a cathode active material layer and a negative electrode comprising an anode active material layer;

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(2) coating a dispersion of a mixture of particles of at least one insulating substance and a binder for said particles in a dispersion medium on at least one active material layer selected from the group

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consisting of said cathode active material layer and said anode active material layer;

(3) removing, by evaporation, the dispersion medium of said dispersion coated on said at least one active material layer to form a layer of an aggregate form of said particles, wherein said particles are bound together by means of said binder, thereby providing a porous separator formed directly, in an immobilized form, on said at least one active material layer, wherein said layer of an aggregate form of particles has a three dimensional network of voids; and

(4) disposing said positive electrode and said negative electrode, at least one of which has the porous separator formed on the active material layer thereof, in a casing so that said cathode active material layer and said anode active material layer are arranged, operatively with an electrolyte contained in said casing, in a positional relationship opposite to each other through the porous separator formed on said at least one active material layer.

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ABSTRACT OF THE DISCLOSURE

Disclosed is a battery comprising a positive electrode comprising a cathode active material layer, a negative electrode comprising an anode active material layer, and a porous separator disposed between the positive electrode and the negative electrode, wherein the positive electrode, the negative electrode and the separator are disposed in a casing containing an electrolyte, and wherein the porous separator comprises at least one layer of an aggregate form of particles of at least one insulating substance, the layer of the aggregate form of particles having a three-dimensional network of voids which function as pores of the porous separator and which are capable of passing ions there-through. The battery of the present invention is advantageous not only in that the battery exhibits excellent discharge characteristics even at a high discharge current density without sacrificing safety, but also in that a large amount of active materials can be accommodated in the battery per unit volume thereof, as compared to the amounts in the case of conventional batteries, so that the battery can exhibit a high performance.

TITLE OF THE INVENTION

Novel battery and method for producing the same

BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a novel battery and a method for producing the same. More particularly, the present invention is concerned with a non-aqueous secondary battery comprising a positive electrode comprising a cathode active material layer, a
10 negative electrode comprising an anode active material layer, and a porous separator which is disposed between the positive electrode and the negative electrode and which is directly formed, in an immobilized form, on at least one active material layer selected from the
15 group consisting of the cathode active material layer and the anode active material layer, wherein the positive electrode, the negative electrode and the separator are disposed in a casing containing a non-aqueous electrolyte, and wherein the porous separator comprises
20 at least one layer of an aggregate form of particles of at least one insulating substance and a binder which is mixed with the particles to thereby bind the particles together, the layer of the aggregate form of particles having a three-dimensional network of voids which
25 function as pores in the porous separator and which are

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capable of passing ions therethrough. The present
invention is also concerned with a method for producing
the above-mentioned novel battery. The battery of the
present invention is advantageous not only in that the
5 battery exhibits excellent discharge characteristics
even at a high discharge current density without sacri-

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tion). Further, in a battery using a conventional separator, use must be made of a large amount of the separator which is produced by the above-mentioned cumbersome, costly method, so that the ratio of the cost for the separator to the total cost for the battery becomes relatively high. Therefore, especially in the case of the above-mentioned non-aqueous battery, such as the lithium ion secondary battery, in which the conventional resin film separator is used, a large area of separator is needed due to the above-mentioned unique construction of such a battery and the cost for the separator becomes disadvantageously high, thereby rendering high the production cost for the battery.

SUMMARY OF THE INVENTION

The present inventors have made extensive and intensive studies with a view toward developing a battery which is free from the above-mentioned problems and which not only has high performance and high safety, but also can be produced at low cost. As a result, it has unexpectedly been found that a specific non-aqueous secondary battery as defined below is advantageous not only in that the battery exhibits excellent discharge characteristics even at a high discharge current density without sacrificing safety, but also in that a large amount of active materials can be accommo-

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dated in the battery per unit volume thereof, as compared to the amounts in the case of conventional batteries. Such a specific battery comprises a positive electrode comprising a cathode active material layer, a negative electrode comprising an anode active material layer, and a porous separator which is disposed between the positive electrode and the negative electrode and which is directly formed, in an immobilized form, on at least one active material layer selected from the group consisting of the cathode active material layer and the anode active material layer, wherein the positive electrode, the negative electrode and the separator are disposed in a casing containing a non-aqueous electrolyte, and wherein the porous separator comprises at least one layer of an aggregate form of particles of at least one insulating substance and a binder which is mixed with the particles to thereby bind the particles together, the layer of the aggregate form of particles having a three-dimensional network of voids which function as pores in the porous separator and which are capable of passing ions therethrough. The present invention has been completed, based on the above novel findings.

Accordingly, it is a primary object of the present invention to provide a high performance battery which

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is advantageous not only in that the battery exhibits
excellent discharge characteristics even at a high dis-
charge current density without sacrificing safety, but
also in that a large amount of active materials can be
5 accommodated in the battery per unit volume thereof, as
compared to the amounts in the case of conventional

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(21) 国際出願番号 PCT/JP96/02414 (22) 国際出願日 1996年8月28日(28.08.96) (30) 優先権データ 特願平7/219036 1995年8月28日(28.08.95) JP (71) 出願人 (米国を除くすべての指定国について) 旭化成工業株式会社 (ASAHI KASEI KOGYO KABUSHIKI KAISHA)[JP/JP] 〒530 大阪府大阪市北区堂島浜1丁目2番6号 Osaka, (JP) (72) 発明者：および (75) 発明者／出願人 (米国についてのみ) 山下昌哉(YAMASHITA, Masaya)[JP/JP] 〒194 東京都町田市成瀬1丁目7-10 Tokyo, (JP) 大木俊介(OKI, Shunsuke)[JP/JP] 〒211 神奈川県川崎市中原区上小田中1丁目37-7 Kanagawa, (JP) (74) 代理人 弁理士 片桐光治(KATAGIRI, Mitsuji) 〒107 東京都港区赤坂4丁目3番1号 共同ビル赤坂312号 Tokyo, (JP)		(81) 指定国 CA, CN, JP, KR, SG, US, 欧州特許 (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, HE, IT, LU, MC, NL, PT, SE). 添付公開書類 国際調査報告書 1pos copy
(54)Title: CELL AND PRODUCTION METHOD THEREOF (54)発明の名称 新規な電池およびその製造方法 (57) Abstract A cell comprising an electrolyte container in which a positive plate with a positive active material layer and a negative plate with a negative active material layer are disposed with a porous separator interposed. The porous separator comprises at least one layer of insulating particles, which has a three-dimensional network structure of pores so that pores may allow the passage of ions. The cell can exhibit excellent discharge characteristics at a high current density without spoiling safety, can increase the amounts of the active materials that can be stored per unit volume of the cell and can exhibit higher performance than the conventional cells.		

(57) 要約

電解質を含むケーシング内に、正極活物質層を含む正極、及び負極活物質層を含む負極が多孔性セパレータを介して配設されてなる電池において、該多孔性セパレータが、少なくとも1層の絶縁性物質粒子集合体層からなり、該絶縁性物質粒子集合体層が3次元網目空隙構造を有しており、それにより、該多孔性セパレータに、イオンが通過可能な孔が形成されるように構成された電池が開示される。本発明の電池は、安全性を損なうことなく、高い電流密度で優れた放電特性を発揮するだけでなく、従来の電池と比較して電池の単位体積あたりに収容できる活物質の量を多くすることができるなど、高い性能を発揮することができる。

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情報としての用途のみ

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12b : Anode active material layer

13 : Conventional separator

13A : Separator used in the present invention, which is
directly formed, in an immobilized form, on the
5 surface of a cathode active material layer.

13B : Separator used in the present invention, which is
directly formed, in an immobilized form, on the
surface of an anode active material layer.

13C : Separator used in the present invention, which is
10 directly formed, in an immobilized form, on each
of the surface of a cathode active material layer
and the surface of an anode active material layer.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

15 Essentially, according to the present invention,
there is provided a non-aqueous secondary battery
comprising:

a casing,
a non-aqueous electrolyte contained in the casing,
20 a positive electrode comprising a cathode active
material layer,
a negative electrode comprising an anode active
material layer, and
a porous separator disposed between the positive
25 electrode and the negative electrode, wherein two

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opposite surfaces of the porous separator face the cathode active material layer and the anode active material layer, respectively,

5 the positive electrode, the negative electrode and the separator being disposed in the casing, operatively with the electrolyte,

the porous separator comprising at least one layer of an aggregate form of particles of at least one insulating substance and a binder which is mixed with
10 the particles to thereby bind the particles together, which porous separator is directly formed, in an immobilized form, on at least one active material layer selected from the group consisting of the cathode active material layer and the anode active material
15 layer, wherein the at least one layer of the aggregate form of particles has a three-dimensional network of voids which function as pores in the porous separator and which are capable of passing ions therethrough.

For an easy understanding of the present invention,
20 the essential features and various preferred embodiments of the present invention are enumerated below.

1. A non-aqueous secondary battery comprising:
a casing,
25 a non-aqueous electrolyte contained in the casing,

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a positive electrode comprising a cathode active material layer,

a negative electrode comprising an anode active material layer,

5 a porous separator disposed between the positive electrode and the negative electrode, wherein two opposite surfaces of the porous separator face the cathode active material layer and the anode active material layer, respectively,

10 the positive electrode, the negative electrode and the separator being disposed in the casing, operatively with the electrolyte,

the porous separator comprising at least one layer of an aggregate form of particles of at least one
15 insulating substance and a binder which is mixed with the particles to thereby bind the particles together, which porous separator is directly formed, in an immobilized form, on at least one active material layer selected from the group consisting of the cathode
20 active material layer and the anode active material layer, wherein the at least one layer of the aggregate form of particles has a three-dimensional network of voids which function as pores in the porous separator and which are capable of passing ions therethrough.

25 2. The non-aqueous secondary battery according to

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item 1 above, wherein the porous separator has a porosity of 10 % or more as measured in the dry state of the porous separator.

5 3. The non-aqueous secondary battery according to item 1 or 2 above, wherein the porous separator has an ion conductive property ascribed to a factor other than the voids of the aggregate form of particles.

10 4. The non-aqueous secondary battery according to any one of items 1 to 3 above, wherein the insulating substance is an inorganic substance.

5. The non-aqueous secondary battery according to any one of items 1 to 3 above, wherein the insulating substance is an organic substance.

15 6. The non-aqueous secondary battery according to any one of items 1 to 5 above, wherein the aggregate form of particles comprises particles of at least two different insulating substances.

20 7. The non-aqueous secondary battery according to any one of items 1 to 6 above, wherein the porous separator comprises at least two layers respectively comprised of different aggregate forms of particles.

25 8. The non-aqueous secondary battery according to any one of items 1 to 7 above, wherein the separator comprises a first separator layer comprising at least one layer of an aggregate form of particles of at least one

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inorganic insulating substance and a second separator layer comprising at least one layer of an aggregate form of particles of at least one organic insulating substance, the first separator layer being directly
5 formed, in an immobilized form, on one active material layer selected from the cathode active material layer and the anode active material layer, the second separator layer being directly formed, in an immobilized form, on the other active material layer remaining
10 between the cathode active material layer and the anode active material layer.

9. The non-aqueous secondary battery according to any one of items 1 to 8 above, wherein the non-aqueous electrolyte contains lithium ions.

15 10. The non-aqueous secondary battery according to any one of items 1 to 9 above, wherein the cathode active material layer comprises lithium manganate.

11. A method for producing a non-aqueous secondary battery, comprising:

20 (1) individually providing a positive electrode comprising a cathode active material layer and a negative electrode comprising an anode active material layer;

25 (2) coating a dispersion of a mixture of particles of at least one insulating substance and a binder

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for the particles in a dispersion medium on at least one active material layer selected from the group consisting of the cathode active material layer and the anode active material layer;

5 (3) removing, by evaporation, the dispersion medium of the dispersion coated on the at least one active material layer to form a layer of an aggregate form of the particles, wherein the particles are bound together by means of the binder, thereby providing a
10 porous separator formed directly, in an immobilized form, on the at least one active material layer, wherein the layer of an aggregate form of particles has a three dimensional network of voids; and

 (4) disposing the positive electrode and the
15 negative electrode, at least one of which has the porous separator formed on the active material layer thereof, in a casing so that the cathode active material layer and the anode active material layer are arranged, operatively with a non-aqueous electrolyte
20 contained in the casing, in a positional relationship opposite to each other through the porous separator formed on the at least one active material layer.

 In the battery of the present invention, the porous separator used therein, which comprises an
25 aggregate form of particles of at least one insulating

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tic liquid {e.g., polyacrylonitrile, poly(methyl methacrylate) and poly(vinylidene fluoride)}; and a method in which use is made of particles of at least one insulating substance and/or another substance used in a mixture of the particles, wherein the insulating substance and/or another substance is a material, e.g., a composite of an alkaline metal salt with poly(ethylene oxide), poly(propylene oxide), a polyphosphazene or the like, namely a material obtained by impregnating a solid with a solution of an electrolyte in a solvent, and removing the solvent by evaporation from the impregnated solid.

In the embodiment mentioned in item 6 above, use is made of a porous separator comprising an aggregate form of particles of at least two different insulating substances. In the embodiment mentioned in item 7 above, use is made of a porous separator comprising at least two layers respectively comprised of different aggregate forms of particles. In the embodiment mentioned in item 8 above, use is made of a porous separator comprising a first separator layer comprising at least one layer of an aggregate form of particles of at least one inorganic insulating substance and a second separator layer comprising at least one layer of an aggregate form of particles of at least one organic

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insulating substance. The term "different" used herein is intended to indicate that the chemical compositions are different and that the properties, such as melting point, are different despite the fact that the chemical compositions are the same. According to each of the above-mentioned embodiments, it is possible to impart the separator with the ability to function as a fuse. As an example of the batteries according to the embodiment of item 6 above there can be mentioned a battery in which the layer of an aggregate form of particles comprises a mixture of particles of an inorganic oxide having a high melting point (e.g., 1,000 °C or more) and particles of a resin having a low melting point (e.g., 200 °C or less). As an example of the batteries according to the embodiment of item 8 above, there can be mentioned a battery in which the separator comprises a first separator layer of an aggregate form of particles of an inorganic oxide having a high melting point (e.g., 1,000 °C or more) and a second separator layer of an aggregate form of particles of a resin having a low melting point (e.g., 200 °C or less), wherein the first separator layer is directly formed, in an immobilized form, on the cathode active material layer and the second separator layer is directly formed, in an immobilized form, on the anode active material layer.

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When the battery according to the embodiment of each of items 6 and 8 above is caused to have a high temperature, only the resin particles contained in the separator are melted and the resultant molten resin closes the voids of the separator to thereby shut off the current (i.e., the separator functions as a fuse), so that the safety of the battery can be secured.

With respect to the type of the battery of the present invention, there is no particular limitation, and the battery of the present invention may be, for example, a primary battery, such as a manganese dioxide-lithium battery and a graphite fluoride-lithium battery; a secondary battery using an aqueous electrolytic liquid, such as a lead storage battery, a nickel-cadmium battery and a nickel-hydrogen battery; or a secondary battery using a non-aqueous electrolytic liquid, such as a lithium ion secondary battery.

With respect to the casing usable in the battery of the present invention, there is no particular limitation. Examples of casings include a can made of aluminum, stainless steel, iron or nickel; a plated can made of iron; a casing formed from a material having a laminate structure; and a casing formed from a resin film.

In the case of a battery of the present invention,

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same manner as in Example 1-A, except that separator 13B was also formed on anode active material layer 12b. (Example 1-B) In the obtained sample unit cell of Fig. 7(b), the total thickness of the separators respectively formed on cathode active material layer 11b and on anode active material layer 12b was 50 μm . Each of the obtained sample unit cells was immersed in an electrolytic liquid which had been prepared by dissolving LiBF_4 in a mixed solvent of propylene carbonate (PC), ethylene carbonate (EC) and γ -butyrolactone (γ -BL) (PC/EC/ γ -BL volume ratio: 1/1/2, and LiBF_4 concentration: 1.0 mol/liter), and the charge/discharge cycle test was conducted under the following conditions.

(Charge/discharge conditions)

Temperature : 25 $^{\circ}\text{C}$

(1st cycle)

Charge : The charging operation was conducted for 8 hours, in which the operation was started at a current density of 1.0 mA/cm^2 and, after the voltage of the unit cell became 4.2 V, the current density was controlled so as to maintain the voltage at 4.2 V.

Discharge: The discharging operation was conducted at a current density of 1.0 mA/cm^2 {corresponding to 1/3C, wherein C indicates the discharge rate (1.0C corresponds to a discharge current at which a fully

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Table 2

	Discharge capacity E_{10} at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{11} at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E_{12} at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{13} at the 13th cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 2-A	5.027	4.944	-1.7	5.002	4.695	-6.1
Example 2-B	5.031	4.977	-1.1	5.005	4.821	-3.7
Example 2-C	5.011	4.933	-1.6	4.998	4.655	-6.9
Comparative Example 2	5.025	4.925	-2.0	5.000	4.425	-11.5

Discharge capacity lowering ratio (%) between the (n-1)-th cycle and the n-th cycle : $[E_n - E_{(n-1)}] / E_{(n-1)} \times 100$.

Table 3

	Discharge capacity E_{10} at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{11} at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E_{12} at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E_{13} at the 13th cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 4	5.040	4.960	-1.6	5.009	4.771	-4.8
Comparative Example 4	5.025	4.925	-2.0	5.000	4.425	-11.5

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Table 4

	Discharge capacity E ₁₀ at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E ₁₁ at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E ₁₂ at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E ₁₃ at the 13th cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 5	5.027	4.944	-1.7	5.003	4.766	-4.7
Comparative Example 5	5.025	4.925	-2.0	5.000	4.425	-11.5

Table 5

	Discharge capacity E ₁₀ at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E ₁₁ at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E ₁₂ at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E ₁₃ at the 13th cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 6	5.016	4.923	-1.9	4.998	4.732	-5.3
Comparative Example 6	5.025	4.925	-2.0	5.000	4.425	-11.5

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Table 6

	Discharge capacity E ₁₀ at the 10th cycle (current density: 1/3C) (mAh)	Discharge capacity E ₁₁ at the 11th cycle (current density: 1.0C) (mAh)	Discharge capacity lowering ratio between the 10th cycle and the 11th cycle (%)	Discharge capacity E ₁₂ at the 12th cycle (current density: 1/3C) (mAh)	Discharge capacity E ₁₃ at the 13th cycle (current density: 2.0C) (mAh)	Discharge capacity lowering ratio between the 12th cycle and the 13th cycle (%)
Example 7	4.957	4.755	-4.1	4.925	4.451	-9.6
Comparative Example 7	4.949	4.639	-6.3	4.910	4.009	-18.4

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Claims

1. A non-aqueous secondary battery comprising:
a casing,
a non-aqueous electrolyte contained in said casing,
5 a positive electrode comprising a cathode active material layer,
a negative electrode comprising an anode active material layer, and
10 a porous separator disposed between said positive electrode and said negative electrode, wherein two opposite surfaces of said porous separator face said cathode active material layer and said anode active material layer, respectively,
15 said positive electrode, said negative electrode and said separator being disposed in said casing, operatively with said electrolyte,
said porous separator comprising at least one layer of an aggregate form of particles of at least one
20 insulating substance and a binder which is mixed with said particles to thereby bind said particles together, wherein said porous separator is directly formed, in an immobilized form, on at least one active material layer selected from the group consisting of said cathode
25 active material layer and said anode active material



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layer, and wherein said at least one layer of the aggregate form of particles has a three-dimensional network of voids which function as pores in said porous separator and which are capable of passing ions there-
5 though.

2. The battery according to claim 1, wherein said porous separator has a porosity of 10 % or more as measured in the dry state of said porous separator.

10 3. The battery according to claim 1 or 2, wherein said porous separator has an ion conductive property ascribed to a factor other than said voids of said aggregate form of particles.

15 4. The battery according to any one of claims 1 to 3, wherein said insulating substance is an inorganic substance.

20 5. The battery according to any one of claims 1 to 4, wherein said insulating substance is an organic substance.

25 6. The battery according to any one of claims 1 to 5, wherein said aggregate form of particles comprises



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particles of at least two different insulating substances.

5 7. The battery according to any one of claims 1 to 6, wherein said porous separator comprises at least two layers respectively comprised of different aggregate forms of particles.

10 8. The battery according to any one of claims 1 to 7, wherein said separator comprises a first separator layer comprising at least one layer of an aggregate form of particles of at least one inorganic insulating substance and a second separator layer comprising at least one layer of an aggregate form of particles of at least one organic insulating substance, said first separator layer being directly formed, in an immobilized form, on one active material layer selected from said cathode active material layer and said anode active material layer, said second separator layer
15 20 being directly formed, in an immobilized form, on the other active material layer remaining between said cathode active material layer and said anode active material layer.

25 9. The battery according to any one of claims 1 to 8,

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wherein said non-aqueous electrolyte contains lithium ions.

10. The battery according to any one of claims 1 to 9,
5 wherein said cathode active material layer comprises lithium manganate.

11. A method for producing a battery, comprising:

(1) individually providing a positive electrode
10 comprising a cathode active material layer and a negative electrode comprising an anode active material layer;

(2) coating a dispersion of a mixture of particles of at least one insulating substance and a binder
15 for said particles in a dispersion medium on at least one active material layer selected from the group consisting of said cathode active material layer and said anode active material layer;

(3) removing, by evaporation, the dispersion
20 medium of said dispersion coated on said at least one active material layer to form a layer of an aggregate form of said particles, wherein said particles are bound together by means of said binder, thereby providing a porous separator formed directly, in an immobilized form, on said at least one active material
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layer, wherein said layer of an aggregate form of particles has a three dimensional network of voids; and

(4) disposing said positive electrode and said negative electrode, at least one of which has the porous separator formed on the active material layer thereof, in a casing so that said cathode active material layer and said anode active material layer are arranged, operatively with an electrolyte contained in said casing, in a positional relationship opposite to each other through the porous separator formed on said at least one active material layer.



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item 1 above, wherein the porous separator has a porosity of 10 % or more as measured in the dry state of the porous separator.

5 3. The non-aqueous secondary battery according to item 1 or 2 above, wherein the porous separator has an ion conductive property ascribed to a factor other than the voids of the aggregate form of particles.

10 4. The non-aqueous secondary battery according to any one of items 1 to ²~~3~~ above, wherein the insulating substance is an inorganic substance.

5. The non-aqueous secondary battery according to any one of items 1 to 3 above, wherein the insulating substance is an organic substance.

15 6. The non-aqueous secondary battery according to any one of items 1 to 5 above, wherein the aggregate form of particles comprises particles of at least two different insulating substances.

20 7. The non-aqueous secondary battery according to any one of items 1 to 6 above, wherein the porous separator comprises at least two layers respectively comprised of different aggregate forms of particles.

25 8. The non-aqueous secondary battery according to any one of items 1 to 7 above, wherein the separator comprises a first separator layer comprising at least one layer of an aggregate form of particles of at least one

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inorganic insulating substance and a second separator layer comprising at least one layer of an aggregate form of particles of at least one organic insulating substance, the first separator layer being directly
5 formed, in an immobilized form, on one active material layer selected from the cathode active material layer and the anode active material layer, the second separator layer being directly formed, in an immobilized form, on the other active material layer remaining
10 ~~between the cathode active material layer and the anode active material layer.~~

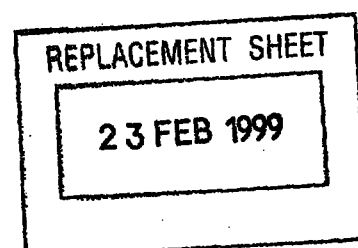
9. The non-aqueous secondary battery according to any one of items 1 to 8 above, wherein the non-aqueous electrolyte contains lithium ions.

15 10. The non-aqueous secondary battery according to any one of items 1 to 9 above, wherein the cathode active material layer comprises lithium manganate.

11. A method for producing a non-aqueous secondary battery, comprising:

20 (1) individually providing a positive electrode comprising a cathode active material layer and a negative electrode comprising an anode active material layer;

25 (2) coating a dispersion of a mixture of particles of at least one insulating substance and a binder





layer, and wherein said at least one layer of the aggregate form of particles has a three-dimensional network of voids which function as pores in said porous separator and which are capable of passing ions there-
5 though.

2. The battery according to claim 1, wherein said porous separator has a porosity of 10 % or more as measured in the dry state of said porous separator.

10 3. The battery according to claim 1 or 2, wherein said porous separator has an ion conductive property ascribed to a factor other than said voids of said aggregate form of particles.

15 4. The battery according to any one of claims 1 to ²~~3~~, wherein said insulating substance is an inorganic substance.

20 5. The battery according to any one of claims 1 to ³~~4~~, wherein said insulating substance is an organic substance.

25 6. The battery according to any one of claims 1 to 5, wherein said aggregate form of particles comprises



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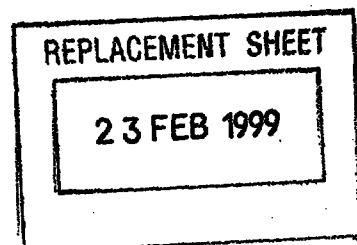
particles of at least two different insulating substances.

5 7. The battery according to any one of claims 1 to 6, wherein said porous separator comprises at least two layers respectively comprised of different aggregate forms of particles.

10 8. The battery according to any one of claims 1 to 7, wherein said separator comprises a first separator layer comprising at least one layer of an aggregate form of particles of at least one inorganic insulating substance and a second separator layer comprising at least one layer of an aggregate form of particles of at least one organic insulating substance, said first separator layer being directly formed, in an immobilized form, on one active material layer selected from said cathode active material layer and said anode active material layer, said second separator layer being directly formed, in an immobilized form, on the other active material layer, ~~remaining between said cathode active material layer and said anode active material layer.~~

15 20

25 9. The battery according to any one of claims 1 to 8,

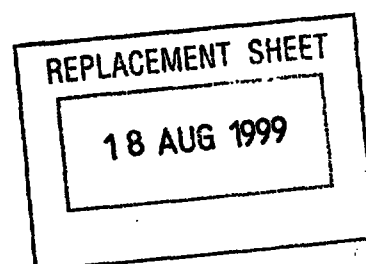


different cross-sectional portions of the separator which each include a number of cured resin-filled pores, the ratio (%) of the sum of the respective cross-sectional areas of the cured resin-filled pores to the entire area of the cross section of each of the different portions of the separator is obtained in substantially the same manner as mentioned above, and the average value of the obtained ratios is defined as the porosity of the separator.

10 In the present invention, the above-mentioned separator may have an ion conductive property attributed to a factor other than the voids of the aggregate form of particles of at least one insulating substance.

15 Examples of methods for obtaining such separators, which have an ion conductive property attributed to a factor other than the voids of the aggregate form of particles, include a method in which porous particles of at least one insulating substance are employed; a method in which use is made of particles of at least one insulating substance which has, in the skeletal structure thereof, voids which allow the molecules of the electrolyte to pass therethrough (e.g., a zeolite);

25



a method in which use is made of particles of a material {e.g., polyacrylonitrile, poly(methyl methacrylate) and poly(vinylidene fluoride)} which is swellable with an electrolytic liquid, wherein the swellable material is at least one insulating substance, a substance other than the insulating substance or a combination of the insulating substance and the other substance, the other substance being used in the form of a mixture with the insulating substance; and a method in which use is made of particles of a material, e.g., a composite of an alkaline metal salt with poly(ethylene oxide), poly(propylene oxide), a polyphosphazene or the like, namely a material obtained by impregnating a solid with a solution of an electrolyte in a solvent, and removing the solvent by evaporation from the impregnated solid, wherein the material is at least one insulating substance, a substance other than the insulating substance or a combination of the insulating substance and the other substance, the other substance being used in the form of a mixture with the insulating substance.

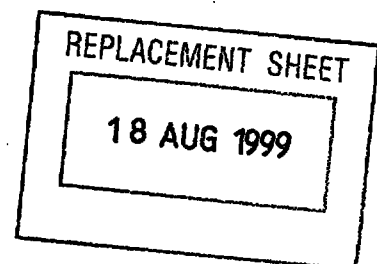
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In the embodiment mentioned in item 8 above, use
is made of a porous separator comprising an aggregate
5 form of particles of at least two different insulating
substances. In the embodiment mentioned in item 9
above, use is made of a porous separator comprising at
least two layers respectively comprised of different
aggregate forms of particles. In the embodiment men-
10 tioned in item 10 above, use is made of a porous sepa-
rator comprising a first separator layer comprising at
least one layer of an aggregate form of particles of at
least one inorganic insulating substance and a second
separator layer comprising at least one layer of an
15 aggregate form of particles of at least one organic

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layer, and wherein said at least one layer of the aggregate form of particles has a three-dimensional network of voids which function as pores in said porous separator and which are capable of passing ions there-
therethrough
5 ~~though~~.

2. The battery according to claim 1, wherein said porous separator has a porosity of 10 % or more as measured in the dry state of said porous separator.

3. The battery according to claim 1 or 2, wherein said porous separator has an ion conductive property ascribed to a factor other than said voids of said aggregate form of particles.

4. The battery according to any one of claims 1 to ³~~3~~, wherein said insulating substance is an inorganic substance.

5. The battery according to any one of claims 1 to ³~~4~~, wherein said insulating substance is an organic substance.

6. The battery according to any one of claims 1 to 5, wherein said aggregate form of particles comprises



* C L M S *

REPLACEMENT SHEET

18 AUG 1999