UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
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Alexandria, Virginia 22313-1450
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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/061,427	02/07/2023	11575148	024607-02-5054-US	1915

24341 7590 01/18/2023

Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 307 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Patents Stakeholder Experience (OPSE), Stakeholder Support Division (SSD) at (571)-272-4200.

INVENTOR(s) (Please see PAIR WEB site http://pair.uspto.gov for additional inventors):

Jianjian YI, Ningde City, CHINA;
Xinzhi ZHANG, Ningde City, CHINA;
Zengbin WEI, Ningde City, CHINA;
Xinghua TAO, Ningde City, CHINA;

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

NINGDE AMPEREX TECHNOLOGY LIMITED, Ningde City, CHINA;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

IR103 (Rev. 10/09)

INFORMATION DISCLOSURE STATEMENT BY APPLICANT Substitute for Form 1449-PTO				*Electronically filed November 29, 2021*	
				Application Number	*17/061,427*
				Filing Date	*October 1, 2020*
				First Named Inventor	*Jianjian YI*
				Art Unit	*OPAP*
				Examiner Name	*Central Docket*
Sheet	1	of	1	Attorney Docket Number	*024607-02-5054-US*

U.S. PATENT DOCUMENTS

Examiner Initials	Cite No.	Document Number Number - Kind Code	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		2010/0015515 A1	01-21-2010	Takata et al.	
		2015/0050545 A1	02-19-2015	Murata et al.	
		2016/0181585 A1	~~06-23-216~~	Choi et al. 06/2016	
		2017/0194613 A1	07-06-2017	Murata et al.	

Change(s) applied to document, /B.P./ 10/7/2022

FOREIGN PATENT DOCUMENTS

Examiner Initials	Cite No.	Foreign Patent Document Country Code – Number - Kind Code *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T
		CN102939675A	02-20-2013	TOYOTA MOTOR CO LTD		
		CN103474602A	12-25-2013	SHENZHEN TAIBAI TECHNOLOGY CO LTD		
		CN104871341A	08-26-2015	MORIN BRIAN G		
		CN104999745A	10-28-2015	DAICEL CORP		
		CN205004376U	01-27-2016	SHENZHEN HONGTAI BATTERY TECH CO LTD		

NON PATENT LITERATURE DOCUMENTS

Examiner Initials	Cite No.	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published
		Office action, CN201810322931.1, 19AUG2021, 9 pgs.
		Yi, Office Action, 16/000,764, 22APR2020, 10 pgs.
		Yi, Notice of Allowance, 16/000,764, 24AUG2020, 8 pgs.

Examiner Signature	/GARY D HARRIS/	Date Considered	09/23/2022

DB2/ 42113168.1

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /G.D.H/

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US

CONFIRMATION NO. 1915

POA ACCEPTANCE LETTER

24341
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

OC000000137125173

Date Mailed: 01/03/2023

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 12/29/2022.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/tcouch/

PART B - FEE(S) TRANSMITTAL

Electronically filed December 29, 2022

Complete and send this form with applicable fee(s), to: Mail
Mail Stop ISSUE FEE
Commissioner of Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571) 273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advanced orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS

MORGAN, LEWIS & BOCKIUS LLP
1400 Page Mill Road
Palo Alto, CA 94304

Note: A certificate of mailing below can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing.

Certificate of Mailing

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)

(Signature)

(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTY'S DOCKET NO.	CONFIRMATION NO.
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US	1915

TITLE OF INVENTION POROUS FILM AND LITHIUM-ION BATTERY

APPLN. TYPE	ENTITY STATUS	ISSUE FEE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	0	$1200	01/04/2023

EXAMINER	ART UNIT	CLASS-SUB CLASS
HARRIS, GARY D	1727	429-209000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list (1) the names of up to 3 registered patent attorneys or agents OR, alternatively, (2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed

1. **Morgan, Lewis & Bockius LLP**
2.
3.

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: NINGDE AMPEREX TECHNOLOGY LIMITED

(B) RESIDENCE: (CITY and STATE OR COUNTRY) NINGDE CITY, FUJIAN, CHINA

Please check the appropriate assignee category or categories (will not be printed on the patent) ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:

☒ Issue Fee

☐ Advanced Order - # of Copies ____

4b. Payment of Fee(s): (**Please first reapply any previously paid issue fee shown above.**)

☐ A check in the amount of the fee(s) enclosed

☐ Payment by credit card. Form PTO-2038 is attached.

☒ The Director is hereby authorized to charge the required fee(s), or credit any overpayment, to Deposit Account Number 50-0310 (order no. 024607-02-5054-US).

5. **Change in Small Entity Status** (from status indicated above)

☐ a. Applicant certifying micro entity status. See 37 CFR 1.29. NOTE: Absent a valid certification of Micro Entity (see form PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

☐ Applicant asserting small entity status. See 37 CFR 1.27. NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

☐ Applicant changing to regular undiscounted fee status. NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be sign in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature: /Yalei Sun/ Date: December 29, 2022

Printed Name: Yalei Sun Registration No. 57,765

Electronic Patent Application Fee Transmittal

Application Number:	17061427
Filing Date:	01-Oct-2020
Title of Invention:	POROUS FILM AND LITHIUM-ION BATTERY
First Named Inventor/Applicant Name:	Jianjian YI
Filer:	Yalei Sun/Cheryl Rogers
Attorney Docket Number:	024607-02-5054-US

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
UTILITY APPL ISSUE FEE	1501	1	1200	1200

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**1200**

Electronic Acknowledgement Receipt	
EFS ID:	47293648
Application Number:	17061427
International Application Number:	
Confirmation Number:	1915
Title of Invention:	POROUS FILM AND LITHIUM-ION BATTERY
First Named Inventor/Applicant Name:	Jianjian YI
Customer Number:	24341
Filer:	Yalei Sun
Filer Authorized By:	
Attorney Docket Number:	024607-02-5054-US
Receipt Date:	29-DEC-2022
Filing Date:	01-OCT-2020
Time Stamp:	17:07:19
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1200
RAM confirmation Number	E2022BSH07493646
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	024607-02-5054-US_Issue_Fee.pdf	113463 0f6617882f87596e93c12531f179919fccd4c1aa	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	37522 fb1ab5f3d56a733994e474e107fc9034e511b227	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	150985		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

POWER OF ATTORNEY TO PROSECUTE APPLICATIONS BEFORE THE UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

I hereby revoke all previous powers of attorney given in the application identified in the attached statement under 37 CFR 3.73(c).

I hereby appoint the practitioners of Morgan, Lewis & Bockius LLP, Customer Number **24341** as attorneys or agents to represent the undersigned and to transact all business before the United States Patent and Trademark Office (USPTO) in connection with any and all patent applications and patents assigned only to the undersigned according to the USPTO assignment records or assignment documents attached to this form in accordance with 37 C.F.R. § 3.73(c), said appointment to be to the exclusion of the inventor(s) and their attorney(s) in accordance with the provisions of 37 C.F.R. § 3.71, provided that, if any one of these attorneys ceases being affiliated with the law firm of Morgan, Lewis & Bockius LLP as partner, counsel, or employee, then the appointment of that attorney and all powers derived therefrom shall terminate on the date such attorney ceases being so affiliated.

Please change the correspondence address for the application identified in the attached statement under 37 CFR 3.73(c) to the address associated with Customer Number **24341**.

Assignee Name and Address: **NINGDE AMPEREX TECHNOLOGY LIMITED**
No. 1, Xingang Road
Zhangwan Town, Jiaocheng Zone
Ningde City, Fujian Province
P.R. China 352100

SIGNATURE of Assignee of Record

The undersigned whose signature and title is supplied below is authorized to act on behalf of the assignee.

Signature Liangxin Yang

Name Liangxin Yang Date Feb. 24th, 2021

Title IP Manager Telephone

A copy of this form, together with a statement under 37 C.F.R. § 3.73(c) (Form PTO/SB96 or equivalent) is required to be filed in each application in which this form is used. The statement under 37 C.F.R. § 3.73(c) may be completed by one of the practitioners appointed in this form if the appointed practitioner is authorized to act on behalf of the assignee and must identify the application in which this Power of Attorney is to be filed.

DB2/ 40409063.1

ASSIGNMENT

WHEREAS, WE, Jianjian YI, citizen of China, residing in Ningde City, CN; Xinzhi ZHANG, citizen of China, residing in Ningde City, CN; Zongbin WEI, citizen of China, residing in Ningde City, CN, and Xinghua TAO, citizen of China, residing in Ningde City, CN, ASSIGNORS, are the inventors of the invention in POROUS FILM AND LITHIUM-ION BATTERY, described in an application for a Patent of the United States;

which is executed on even date herewith

which is identified by Morgan, Lewis & Bockius LLP docket no. 034607-02-5054-US

which was filed on October 1, 2020, Application No. 17/061,827

which claims priority on U.S. Provisional Patent Application No(s.) .....

We hereby authorize and request our attorney, Yaire Sun, of Morgan, Lewis & Bockius LLP, to insert here in parenthesis: (Application number October 1, 2020, filed 17/061,827) the filing date and application number of said application when known.

and WHEREAS, NINGDE AMPEREX TECHNOLOGY LIMITED, ASSIGNEE, having a place of business at 1 Xingang Road, Zhangwan Town, Jiaocheng District, Ningde City, Fujian Province, 352100, China, is desirous of obtaining my entire right, title and interest in, to and under the said invention and the said application;

NOW, THEREFORE, let it be known that for and in consideration of the sum of One Dollar ($1.00) to me paid and other good and valuable consideration, the receipt and sufficiency of which are hereby acknowledged, we, the said ASSIGNORS, have sold, assigned, transferred and set over, and by these presents do hereby sell, assign, transfer and set over, unto the said ASSIGNEE, its successors, legal representatives and assigns, our entire right, title and interest in, to and under the said invention, and the said United States application and all divisions, renewals and continuations thereof, and any substitute applications therefore, and all Patents of the United States which may be granted thereon and all reissues and extensions thereof; the said United States provisional patent application(s), if any, on which the said United States application claims priority; and all applications for industrial property protection, including, without limitation, all applications for patents, utility models, and designs which may hereafter be filed for said invention in any country or countries foreign to the United States, together with the right to file such applications and the right to claim for the same the priority rights derived from said United States application and said United States provisional patent application(s), if any, under the Patent Laws of the United States, the International Convention for the Protection of Industrial Property, or any other international agreement or the domestic laws of the country in which any such application is filed, as may be applicable; and all forms of industrial property protection, including, without limitation, patents, utility models, inventors' certificates and designs which may be granted for said invention in any country or countries foreign to the United States and all extensions, renewals and reissues thereof;

AND WE HEREBY authorize and request the Commissioner of Patents and Trademarks of the United States, and any Official of any country or countries foreign to the United States, whose duty it is to issue patents or other evidence of forms of industrial property protection on applications as aforesaid, to issue the same to the said ASSIGNEE, its successors, legal representatives and assigns, in accordance with the terms of this instrument.

AND WE HEREBY covenant and agree that we have full right to convey the entire interest herein assigned, and that we have not executed, and will not execute, any agreement in conflict herewith.

AND WE HEREBY further covenant and agree that we will communicate to the said ASSIGNEE, its successors, legal representatives and assigns, any facts known to us respecting said invention, and testify in any legal proceeding, sign all lawful papers, execute all divisional, continuing, reissue and foreign applications, make all rightful oaths, and generally do everything possible to aid the said ASSIGNEE, its successors, legal representatives and assigns, to obtain and enforce proper protection for said invention in all countries.

IN TESTIMONY WHEREOF, We hereunto set our hands and seals the day and year set opposite our respective signatures.

Date September 23, 2020 Jianjian YI L.S.
Jianjian YI

Date September 23, 2020 Xinzhi Zhang L.S.
Xinzhi ZHANG

Date September 23, 2020 ZengBin WEI L.S.
ZengBin WEI

Date September 23, 2020 Xinghua Tao L.S.
Xinghua TAO

Electronic Acknowledgement Receipt	
EFS ID:	47291821
Application Number:	17061427
International Application Number:	
Confirmation Number:	1915
Title of Invention:	POROUS FILM AND LITHIUM-ION BATTERY
First Named Inventor/Applicant Name:	Jianjian YI
Customer Number:	24341
Filer:	Yalei Sun
Filer Authorized By:	
Attorney Docket Number:	024607-02-5054-US
Receipt Date:	29-DEC-2022
Filing Date:	01-OCT-2020
Time Stamp:	12:46:15
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		024607-02-5054-US_Assignee_Statement.pdf	995352 736479b765ba4fa931bc6ebc2e0abef812f08009	yes	4

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Assignee showing of ownership per 37 CFR 3.73	1	1
	Power of Attorney	2	2
	Miscellaneous Incoming Letter	3	4
Warnings:			
Information:			
	Total Files Size (in bytes):	995352	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Electronically filed December 29, 2022

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:	Jianjian YI, et al.	Confirmation No.:	1915
Serial No.:	17/061,427	Art Unit	1727
Filed:	October 1, 2020	Examiner:	HARRIS, Gary D.
For:	POROUS FILM AND LITHIUM-ION BATTERY	Attorney Docket No.:	024607-02-5054-U S

STATEMENT UNDER 37 C.F.R. § 3.73(c)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

NINGDE AMPEREX TECHNOLOGY LIMITED, a corporation, states that it is the assignee of the entire right, title and interest in the patent application/patent identified above by virtue of an assignment from the inventor(s) of the parent of the patent application/patent identified above.

The assignment was recorded in the United States Patent and Trademark Office on _____ at Reel _____, Frame _____, or for which a copy thereof is attached.

The undersigned is authorized to act on behalf of the assignee.

Date: December 29, 2022

/Yalei Sun/ 57,765
Yalei Sun (Reg. No.)

MORGAN, LEWIS & BOCKIUS LLP
1400 Page Mill Road
Palo Alto, CA 94304
(650) 843-4000

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

24341 7590 10/04/2022

Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

EXAMINER
HARRIS, GARY D

ART UNIT	PAPER NUMBER
1727	

DATE MAILED: 10/04/2022

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US	1915

TITLE OF INVENTION: POROUS FILM AND LITHIUM-ION BATTERY

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$0.00	$1200	01/04/2023

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PTOL-85 (Rev. 02/11)

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

24341 7590 10/04/2022
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US	1915

TITLE OF INVENTION: POROUS FILM AND LITHIUM-ION BATTERY

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$0.00	$1200	01/04/2023

EXAMINER	ART UNIT	CLASS-SUBCLASS
HARRIS, GARY D	1727	429-209000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/AIA/122 or PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/AIA/47 or PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑Issue Fee ❑Publication Fee (if required) ❑Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

Zhuhai CosMX Battery Co. - EX1002
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
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UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US	1915

24341 7590 10/04/2022

Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

EXAMINER	
HARRIS, GARY D	

ART UNIT	PAPER NUMBER
1727	

DATE MAILED: 10/04/2022

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

PTOL-85 (Rev. 02/11)

Notice Requiring Inventor's Oath or Declaration	Application No. 17/061,427	Applicant(s) Jianjian YI	
	Examiner HARRIS, GARY D	Art Unit 1727	

This notice is an attachment to the Notice of Allowability (PTOL-37), or the Notice of Allowability For A Design Application (PTOL-37D).

An inventor's oath or declaration in compliance with 37 CFR 1.63 or 1.64 executed by or with respect to each inventor has not yet been submitted.

An oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each inventor (for any inventor for which a compliant oath, declaration, or substitute statement has not yet been submitted) MUST be filed no later than the date on which the issue fee is paid. See 35 U.S.C. 115(f). Failure to timely comply will result in ABANDONMENT of this application.

A properly executed inventor's oath to declaration has not been received for the following inventor(s):

If applicant previously filed one or more oaths, declarations, or substitute statements, applicant may have received an informational notice regarding deficiencies therein.

The following deficiencies are noted:

INFORMAL ACTION PROBLEMS

Questions relating to this Notice should be directed to the Application Assistance Unit at 571-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 17/061,427	Applicant(s) Yl et al.	
	Examiner GARY D HARRIS	Art Unit 1727	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to documents submitted on 11/29/2021.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-19 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☑ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☑ All b) ☐ Some* c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☑ Certified copies of the priority documents have been received in Application No. 16/000,764 .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☑ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 11/29/2021.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☐ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/GARY D HARRIS/
Primary Examiner, Art Unit 1727

Zhuhai CosMX Battery Co. - EX1002
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.

POROUS FILM AND LITHIUM-ION BATTERY

Primary Examiner: Gary Harris Art Unit: 1727 September 23, 2022

DETAILED ACTION

Notice of Pre-AIA or AIA Status

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Priority

Receipt is acknowledged of certified copies of papers submitted under 35 U.S.C. 119(a)-(d), which papers have been placed of record in the file.

Information Disclosure Statement

The information disclosure statements (IDS) submitted on 11/29/2021 was considered by the examiner.

Drawings

The drawings were received on 10/01/2020. These drawings are acceptable.

Allowable Subject Matter

Claims 1-19 are allowed.

The following is an examiner's statement of reasons for allowance:

The art made of record Murata et al. US 2017/0194613 discloses a porous film (membrane, see abstract and title), comprising: a binder (see abstract); and inorganic particles [0073-0075]. The porous film comprises pores formed by the binder [0086] given pores are found within the binder and porous layer. The pores at least comprise a part of the inorganic particles (filler). However, Murata fails to teach, suggest or render obvious the particles sizes and ranges as required in the independent claims 1 & 10.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to GARY D HARRIS whose telephone number is (571)272-6508. The examiner can normally be reached on Mon-Sat. 5:30AM-8PM EST (flex).

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Barbara Gilliam can be reached on (571)272-1330. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/GARY D HARRIS/
Primary Examiner, Art Unit 1727

Notice of References Cited	Application/Control No. 17/061,427	Applicant(s)/Patent Under Reexamination YI et al.	
	Examiner GARY D HARRIS	Art Unit 1727	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-20170194613-A1	07-2017	Murata; Hiroshi	H01M50/42	1/1
	B					
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/061,427	YI et al.
	Examiner	**Art Unit**
	GARY D HARRIS	1727

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS										
☐ Claims renumbered in the same order as presented by applicant			☐ CPA	☐ T.D.	☐ R.1.47					
CLAIM		**DATE**								
Final	Original	09/23/2022								
	1	=								
	2	=								
	3	=								
	4	=								
	5	=								
	6	=								
	7	=								
	8	=								
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	10	=								
	11	=								
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	17	=								
	18	=								
	19	=								

Zhuhai CosMX Battery Co. - EX1002
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
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Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/061,427	YI et al.
	Examiner	**Art Unit**
	GARY D HARRIS	1727

CPC								
Symbol							**Type**	**Version**
H01M	/	10	/	0525			F	2013-01-01
H01M	/	4	/	623			I	2013-01-01
H01M	/	4	/	583			I	2013-01-01
H01M	/	4	/	661			I	2013-01-01
H01M	/	50	/	403			I	2021-01-01
H01M	/	50	/	409			I	2021-01-01
H01M	/	2004	/	028			A	2013-01-01
H01M	/	2004	/	027			A	2013-01-01

CPC Combination Sets								
Symbol							**Type**	**Set**	**Ranking**	**Version**
	/		/							

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	19	
/GARY D HARRIS/ Primary Examiner, Art Unit 1727	23 September 2022	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20220923

Zhuhai CosMX Battery Co. - EX1002
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Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	17/061,427	YI et al.
	Examiner	**Art Unit**
	GARY D HARRIS	1727

INTERNATIONAL CLASSIFICATION					
CLAIMED					
H01M	/	10	/	0525	
NON-CLAIMED					
	/		/		

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**
429	209

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	19	
/GARY D HARRIS/ Primary Examiner, Art Unit 1727	23 September 2022	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20220923

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Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
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	Examiner	Art Unit
	GARY D HARRIS	1727

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	10	10	19	19										
2	2	11	11												
3	3	12	12												
4	4	13	13												
5	5	14	14												
6	6	15	15												
7	7	16	16												
8	8	17	17												
9	9	18	18												

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	19	
/GARY D HARRIS/ Primary Examiner, Art Unit 1727	23 September 2022	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office Part of Paper No.: 20220923

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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
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	Examiner	Art Unit
	GARY D HARRIS	1727

CPC - Searched*		
Symbol	Date	Examiner
H01M10/0525 H01M4/583 H01M4/623 H01M4/661 H01M50/403 H01M50/409 H01M2004/027 H01M2004/028 H01M50/426 H01M50/443 H01M50/491 H01M50/417 H01M50/431 H01M50/446 Y02E60/10 H01M50/44	09/23/2022	gh

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner
429	209	09/23/2022	gh

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
Assignee, inventor name and key word search based on H01M10/0525 H01M4/583 H01M4/623 H01M4/661 H01M50/403 H01M50/409 H01M2004/027 H01M2004/028 H01M50/426 H01M50/443 H01M50/491 H01M50/417 H01M50/431 H01M50/446 Y02E60/10 H01M50/44 (see search history).	09/23/2022	gh

/GARY D HARRIS/ Primary Examiner, Art Unit 1727	

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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
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Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
H01M	H01M10/0525 H01M4/583 H01M4/623 H01M4/661 H01M50/403 H01M50/409 H01M2004/027 H01M2004/028 H01M50/426 H01M50/443 H01M50/491 H01M50/417 H01M50/431 H01M50/446 Y02E60/10 H01M50/44	09/23/2022	gh
429	209	09/23/2022	gh

/GARY D HARRIS/ Primary Examiner, Art Unit 1727	

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L11	13,241	NINGDE near3 AMPEREX	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/09/23 16:09
L12	1,131,641	(H01M10/0525 or H01M4/583 or H01M4/623 or H01M4/661 or H01M50/403 or H01M50/409 or H01M2004/027 or H01M2004/028 or H01M50/426 or H01M50/443 or H01M50/491 or H01M50/417 or H01M50/431 or H01M50/446 or Y02E60/10 or H01M50/44).cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/09/23 16:09
L13	3,793	429/209.ccls.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/09/23 16:09
L14	1,132,664	12, 13	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/09/23 16:09
L15	862,795	Yi.in.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/09/23 16:10
L16	248	11 and 15	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/09/23 16:10

L17	213	14 and 16	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/09/23 16:10
L18	9	17 and (porous, porosity) with (film, layer, coat$3).clm.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/09/23 16:11
S2	2	(US-1234567-$ | US-28676403-$).DID.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 10:13
S3	5	(AI-1234567-$ | CN-103474602-$ | CN-205004376-$ | JP-1234567-$).DID.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 10:14
S4	2	"16000764"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 10:21
S5	19,457	porous with inorganic with particle	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:20
S6	67,912	(porous, pores, porosity) with binder	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:20

S7	119,978	(porous, pores, porosity) with (nanometer, nm)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:21
S8	137,888	(porous, pores, porosity) with size with (micro, micron, micro$1meter ".mu.m")	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:23
S9	5,978	S5 and S6	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:24
S10	7,350	S6 and S7	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:24
S11	19,936	S7 and S8	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:25
S12	1,316	S9 and S10	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:25
S13	2,183	S10 and S11	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:25

S14	507	S12 and S13	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:25
S15	189,519	(H01M10/0525 or H01M2/145 or H01M4/661 or H01M4/583 or H01M2/164 or H01M4/623 or H01M2004/027 or H01M2004/028 or H01M2/166 or H01M2/1646 or H01M2/1653 or H01M2/16 or H01M2/1606).cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:26
S16	3,783	429/209.ccls.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:26
S17	191,425	S15 S16	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:26
S18	207	S14 and S17	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:27
S19	195	S18 and (alumina, silica, magnesia, titanium adj oxide, hafnium adj dioxide, tin adj oxide, cerium adj dioxide, nickel adj oxide, zirconia)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:30
S20	41	S18 and (magnesium adj hydroxide, calcium adj hydroxide, barium adj sulfate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:33

S21	58	S18 and (zinc adj oxide, calcium adj oxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:34
S22	196	S19 S20	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:35
S23	196	S21 S22	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:37
S24	189	S23 and (porous, pores, porosity) with binder same (film, layer, coat$3)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:38
S25	1	S24 and (porous, pores, porosity) with (nanometer, nm) with wall adj thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:39
S26	1	S24 and (porous, pores, porosity) with (nanometer, nm) same wall adj thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:40
S27	85	S24 and (porous, pores, porosity) with (nanometer, nm) same thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:40

S28	46	S27 and (porous, pores, porosity) with (average, avg) with size with (micro, micron, micro$1meter".mu.m")	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:41
S29	46	S28 and (polyvinylidene adj fluoride, vinylidene adj fluoride$1hexafluoropropylene adj copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic adj acid, polyacrylic adj acid adj salt, sodium adj carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl adj ether, polymethyl adj methacrylate, polytetrafluoroethylene, polyhexafluoropropylene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:44
S30	35	S28 and binder same (polyvinylidene adj fluoride, vinylidene adj fluoride$1hexafluoropropylene adj copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic adj acid, polyacrylic adj acid adj salt, sodium adj carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl adj ether, polymethyl adj methacrylate, polytetrafluoroethylene, polyhexafluoropropylene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:45
S31	1	S30 and ("Dv10", "Dv50")	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:47
S32	15	S30 and particle adj size same range	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:48
S33	1	S31 and particle adj size same range.clm.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2020/04/17 11:52

			DERWENT; IBM_TDB			
S34	1	S31 and (porous, pores, porosity) with binder same (film, layer, coat$3).clm.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 11:53
S35	2	"16000764"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/04/17 14:06
S38	1,602,014	"11" and (binder, polyvinylidene adj fluoride, vinylidene adj fluoride$1hexafluoropropylene adj copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic adj acid, polyacrylic adj acid adj salt, sodium adj carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl adj ether, polymethyl adj methacrylate, polytetrafluoroethylene, polyhexafluoropropylene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/08/17 14:30

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	145,878	(H01M10/0525 or H01M4/583 or H01M4/623 or H01M4/661 or H01M50/403 or H01M50/409 or H01M2004/027 or H01M2004/028 or H01M50/426 or H01M50/443 or H01M50/491 or H01M50/417 or H01M50/431 or H01M50/446 or Y02E60/10 or H01M50/44).cpc.	US-PGPUB; USPAT	OR	ON	2022/09/23 15:39
L2	2,101	429/209.ccls.	US-PGPUB; USPAT	OR	ON	2022/09/23 15:40
L3	146,144	1, 2	US-PGPUB; USPAT	OR	ON	2022/09/23 15:40
L4	33,893	3 and (porous, porosity) with (film, layer, coat$3)	US-PGPUB; USPAT	OR	ON	2022/09/23 15:41

L5	10,809	4 and (particle, powder) with (alumina, silica, magnesia, titanium adj oxide, hafnium adj dioxide, tin adj oxide, cerium adj dioxide, nickel adj oxide, zirconia, zinc adj oxide, calcium adj oxide, boehmite, aluminum adj hydroxide, magnesium adj hydroxide, calcium adj hydroxide, and barium adj sulfate)	US-PGPUB; USPAT	OR	ON	2022/09/23 15:43
L6	2,240	5 and (particle, powder) with (alumina, silica, magnesia, titanium adj oxide, hafnium adj dioxide, tin adj oxide, cerium adj dioxide, nickel adj oxide, zirconia, zinc adj oxide, calcium adj oxide, boehmite, aluminum adj hydroxide, magnesium adj hydroxide, calcium adj hydroxide, and barium adj sulfate) same particle adj size	US-PGPUB; USPAT	OR	ON	2022/09/23 15:49
L7	563	5 and (particle, powder) with (alumina, silica, magnesia, titanium adj oxide, hafnium adj dioxide, tin adj oxide, cerium adj dioxide, nickel adj oxide, zirconia, zinc adj oxide, calcium adj oxide, boehmite, aluminum adj hydroxide, magnesium adj hydroxide, calcium adj hydroxide, and barium adj sulfate) same particle adj size same ratio	US-PGPUB; USPAT	OR	ON	2022/09/23 15:50
L8	26	7 and (particle, powder) with (alumina, silica, magnesia, titanium adj oxide, hafnium adj dioxide, tin adj oxide, cerium adj dioxide, nickel adj oxide, zirconia, zinc adj oxide, calcium adj oxide, boehmite, aluminum adj hydroxide, magnesium adj hydroxide, calcium adj hydroxide, and barium adj sulfate) same particle adj size same ratio.clm.	US-PGPUB; USPAT	OR	ON	2022/09/23 15:50
L9	137	7 and (particle, powder) with (alumina, silica, magnesia, titanium adj oxide, hafnium adj dioxide, tin adj oxide, cerium adj dioxide, nickel adj oxide, zirconia, zinc adj oxide, calcium adj oxide, boehmite, aluminum adj hydroxide, magnesium adj hydroxide, calcium adj hydroxide, and barium adj sulfate) same particle adj size same ratio same binder	US-PGPUB; USPAT	OR	ON	2022/09/23 15:51
L10	4	9 and (particle, powder) with (alumina, silica, magnesia, titanium adj oxide, hafnium adj dioxide, tin adj oxide, cerium adj dioxide, nickel adj oxide, zirconia, zinc adj oxide, calcium adj oxide, boehmite, aluminum adj hydroxide, magnesium adj hydroxide, calcium adj hydroxide, and barium adj sulfate) same particle adj size same ratio.clm.	US-PGPUB; USPAT	OR	ON	2022/09/23 15:52

S36	39,113	(H01M10/0525 H01M2/145 H01M4/661 H01M4/583 H01M2/164 H01M4/623 H01M2004/027 H01M2004/028 or H01M2/166 H01M2/1646 H01M2/1653 H01M2/16 H01M2/1606).cpc.	US-PGPUB; USPAT	OR	ON	2020/04/17 15:07
S37	2,101	429/209.ccls.	US-PGPUB; USPAT	OR	ON	2020/04/17 15:08
S39	2,101	429/209.ccls.	US-PGPUB; USPAT	OR	ON	2020/08/17 14:08
S40	41,066	(H01M10/0525 or H01M4/623 or H01M2/164 or H01M4/583 or H01M4/661 or H01M2/145 or H01M2004/028 or H01M2004/027 or H01M2/1653 or H01M2/1646 or H01M2/166 or H01M2/1606 or H01M2/16).cpc.	US-PGPUB; USPAT	OR	ON	2020/08/17 14:09
S41	41,066	(H01M10/0525 H01M4/623 H01M2/164 H01M4/583 H01M4/661 H01M2/145 H01M2004/028 H01M2004/027 H01M2/1653 H01M2/1646 H01M2/166 H01M2/1606 H01M2/16).cpc.	US-PGPUB; USPAT	OR	ON	2020/08/17 14:10
S42	17,012	(porous, pores, porosity, nano$1porous) with binder same (film, layer, coat$3)	US-PGPUB; USPAT	OR	ON	2020/08/17 14:21
S43	102,753	(porous, pores, porosity, nano$1porous) same (thick$4, diameter) with (nm, nanometer, micro, micron, micrometer)	US-PGPUB; USPAT	OR	ON	2020/08/17 14:23
S44	4,655	S42 and S43	US-PGPUB; USPAT	OR	ON	2020/08/17 14:24
S45	4,655	S44 and (size, diameter, thick$4) with (nm, nanometer, micro, micron, micrometer)	US-PGPUB; USPAT	OR	ON	2020/08/17 14:25
S46	34	S44 and (size, diameter, thick$4) with (nm, nanometer, micro, micron, micrometer) same Dv	US-PGPUB; USPAT	OR	ON	2020/08/17 14:26
S47	1,882	S44 and (size, diameter, thick$4) with (nm, nanometer, micro, micron, micrometer) same (volume, accumulation, Dv)	US-PGPUB; USPAT	OR	ON	2020/08/17 14:27
S48	390	S47 and (size, diameter, thick$4) with (micro, micron, micrometer) with (volume, accumulation, Dv)	US-PGPUB; USPAT	OR	ON	2020/08/17 14:28
S49	390	S48 and (binder, polyvinylidene adj fluoride, vinylidene adj fluoride$1hexafluoropropylene adj copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic adj acid, polyacrylic adj acid adj salt, sodium adj	US-PGPUB; USPAT	OR	ON	2020/08/17 14:30

		carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl adj ether, polymethyl adj methacrylate, polytetrafluoroethylene, polyhexafluoropropylene)				
S50	233	S48 and (binder, polyvinylidene adj fluoride, vinylidene adj fluoride$1hexafluoropropylene adj copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic adj acid, polyacrylic adj acid adj salt, sodium adj carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl adj ether, polymethyl adj methacrylate, polytetrafluoroethylene, polyhexafluoropropylene).clm.	US-PGPUB; USPAT	OR	ON	2020/08/17 14:31
S51	70	S50 and (size, diameter, thick$4) with (micro, micron, micrometer) with (volume, accumulation, Dv).clm.	US-PGPUB; USPAT	OR	ON	2020/08/17 14:32
S52	65	S51 and (diameter, size, thick$4) same range	US-PGPUB; USPAT	OR	ON	2020/08/17 14:33
S53	43	S52 and (diameter, size, thick$4) same range with (micro, micron, inch, inches)	US-PGPUB; USPAT	OR	ON	2020/08/17 14:34
S54	24	S53 and (diameter, size, thick$4) same range with (micro, micron, inch, inches).clm.	US-PGPUB; USPAT	OR	ON	2020/08/17 14:35
S55	4	S54 and (inorganic, alumina, silica, magnesia, titanium adj oxide, hafnium adj dioxide, tin adj oxide, cerium adj dioxide, nickel adj oxide, zirconia, zinc adj oxide, calcium adj oxide, boehmite, aluminum adj hydroxide, magnesium adj hydroxide, calcium adj hydroxide, barium adj sulfate) with (diameter, size, thick$4) same range with (micro, micron, inch, inches).clm.	US-PGPUB; USPAT	OR	ON	2020/08/17 14:38
S56	42,101	S39 S40	US-PGPUB; USPAT	OR	ON	2020/08/17 14:39
S57	0	S55 and S56	US-PGPUB; USPAT	OR	ON	2020/08/17 14:39
S58	6	S54 and S56	US-PGPUB; USPAT	OR	ON	2020/08/17 14:40

9/23/2022 4:11:40 PM
C:\Users\gharris\Documents\EAST\Workspaces\17061427.wsp

INFORMATION DISCLOSURE STATEMENT BY APPLICANT Substitute for Form 1449-PTO				*Electronically filed November 29, 2021*	
				Application Number	*17/061,427*
				Filing Date	*October 1, 2020*
				First Named Inventor	*Jianjian YI*
				Art Unit	*OPAP*
				Examiner Name	*Central Docket*
Sheet	1	of	1	Attorney Docket Number	*024607-02-5054-US*

U.S. PATENT DOCUMENTS					
Examiner Initials	Cite No.	Document Number Number - Kind Code	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		2010/0015515 A1	01-21-2010	Takata et al.	
		2015/0050545 A1	02-19-2015	Murata et al.	
		2016/0181585 A1	06-23-216	Choi et al.	
		2017/0194613 A1	07-06-2017	Murata et al.	

FOREIGN PATENT DOCUMENTS						
Examiner Initials	Cite No.	Foreign Patent Document Country Code – Number - Kind Code *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T
		CN102939675A	02-20-2013	TOYOTA MOTOR CO LTD		
		CN103474602A	12-25-2013	SHENZHEN TAIBAI TECHNOLOGY CO LTD		
		CN104871341A	08-26-2015	MORIN BRIAN G		
		CN104999745A	10-28-2015	DAICEL CORP		
		CN205004376U	01-27-2016	SHENZHEN HONGTAI BATTERY TECH CO LTD		

NON PATENT LITERATURE DOCUMENTS		
Examiner Initials	Cite No.	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published
		Office action, CN201810322931.1, 19AUG2021, 9 pgs.
		Yi, Office Action, 16/000,764, 22APR2020, 10 pgs.
		Yi, Notice of Allowance, 16/000,764, 24AUG2020, 8 pgs.

Examiner Signature	/GARY D HARRIS/	Date Considered	09/23/2022

DB2/ 42113168.1

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /G.D.H/

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BIB DATA SHEET

CONFIRMATION NO. 1915

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
17/061,427	10/01/2020	429	1727	024607-02-5054-US

APPLICANTS

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Xinzhi ZHANG, Ningde City, CHINA;
Zengbin WEI, Ningde City, CHINA;
Xinghua TAO, Ningde City, CHINA;

**** CONTINUING DATA ***************************

This application is a CON of 16/000,764 06/05/2018 PAT 10833355

**** FOREIGN APPLICATIONS ***************************

CHINA 201810322931.1 04/11/2018

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ****

Foreign Priority claimed ☑ Yes ☐ No 35 USC 119(a-d) conditions met ☑ Yes ☐ No Verified and Acknowledged /GARY D HARRIS/ Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
		CHINA	2	19	2

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Palo Alto, CA 94304-1124
UNITED STATES

TITLE

POROUS FILM AND LITHIUM-ION BATTERY

FILING FEE RECEIVED		
1880	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

BIB (Rev. 05/07).

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				Art Unit	*OPAP*
				Examiner Name	*Central Docket*
Sheet	1	of	1	Attorney Docket Number	*024607-02-5054-US*

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		2010/0015515 A1	01-21-2010	Takata et al.	
		2015/0050545 A1	02-19-2015	Murata et al.	
		2016/0181585 A1	06-23-216	Choi et al.	
		2017/0194613 A1	07-06-2017	Murata et al.	

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		CN103474602A	12-25-2013	SHENZHEN TAIBAI TECHNOLOGY CO LTD		
		CN104871341A	08-26-2015	MORIN BRIAN G		
		CN104999745A	10-28-2015	DAICEL CORP		
		CN205004376U	01-27-2016	SHENZHEN HONGTAI BATTERY TECH CO LTD		

NON PATENT LITERATURE DOCUMENTS		
Examiner Initials	Cite No.	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published
		Office action, CN201810322931.1, 19AUG2021, 9 pgs.
		Yi, Office Action, 16/000,764, 22APR2020, 10 pgs.
		Yi, Notice of Allowance, 16/000,764, 24AUG2020, 8 pgs.

Examiner Signature		Date Considered	

DB2/ 42113168.1

Espacenet

CN102939675A Non-aqueous electrolyte secondary battery

Applicants: TOYOTA MOTOR CO LTD

Inventors: UEKI TOMOYOSHI,SHIMAMURA HARUNARI,FUKUMOTO YUSUKE

Classifications:
IPC ***H01M10/052; H01M10/0566; H01M10/058; H01M2/16;***

CPC **H01M10/052 (EP,US); H01M10/0566 (EP,US); H01M10/0587 (EP,US); H01M10/44 (KR); H01M4/626 (US); H01M50/40 (KR); H01M50/409 (KR); H01M50/431 (EP,US); H01M50/60 (KR);** Y02E60/10 (EP,US); Y02P70/50 (EP);

Priorities: JP2010060139W 2010-06-15

Application: CN201080067406A·2010-06-15

Publication: CN102939675A·2013-02-20

Published as: CN102939675A;**CN102939675B; JP5720965B2; JPWO2011158335A1; KR101536063B1; KR20130043655A; US2013084503A1; US9190668B2; WO2011158335A1**

Non-aqueous electrolyte secondary battery

Abstract

Disclosed is a non-aqueous electrolyte secondary battery provided with an electrode body formed by placing a positive pole sheet and a negative pole sheet (20) one over the other with a separator sheet (40) interposed, wherein a porous layer (42) comprising an inorganic filler and binder is formed on at least one surface of the separator sheet (40), the surface of the porous layer (42) is unevenly formed, and the maximum difference in height of the recesses and protrusions of an uneven surface (42a) is 0.2 [mu]m to 1.7 [mu]m.

Zhuhai CosMX Battery Co. - EX1002
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CN102939675A Non-aqueous electrolyte secondary battery

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Technical field

The present invention relates to a non-aqueous electrolyte secondary battery, and more particularly, to a non-aqueous electrolyte secondary battery with improved durability against high-speed charge and discharge.

Background technique

In recent years, lithium-ion batteries, nickel-metal hydride batteries, and other non-aqueous electrolyte secondary batteries have become increasingly important as power sources for vehicles, personal computers, and mobile terminals. In particular, a light-weight lithium ion battery capable of obtaining a high energy density is expected to be used as a high-output power source for vehicle installation. In a typical structure of such a lithium ion battery, lithium ions reciprocate between the positive electrode and the negative electrode, and thereby charge and discharge. As a prior art related to a lithium ion battery, for example, Patent Document 1 is cited.

Existing technical literature

Patent Literature

Patent Document 1: Japanese Patent Application Publication No. 2002-008730

Summary of the invention

Therefore, among the uses of lithium ion batteries, a use is assumed in which the high-speed discharge (rapid discharge) is repeated. A lithium-ion battery used as a power source of a vehicle (for example, a lithium-ion battery mounted on a hybrid vehicle that uses a lithium-ion battery as a power source in combination with another power source with a different operating principle such as an internal combustion engine) is A representative example of a lithium ion battery in such a use state. However, it is known that conventional general lithium-ion batteries exhibit high durability against low-rate charge-discharge cycles, but in a charge-discharge mode in which high-speed discharge is repeated, performance degradation (increased battery resistance) is likely to occur Wait).

Patent Document 1 describes a technique for forming a thin layer of 20 μm or less for holding an electrolyte on a substrate of a separator, thereby making up for the shortage of electrolyte between the positive and negative electrodes, and thereby improving The discharge capacity of the battery. However, in this technique, even if the discharge capacity of the battery can be improved, the durability of the charge-discharge mode resistant to repeated high-speed discharge (for example, rapid discharge at a level required in a lithium-ion battery for vehicle power sources, etc.) cannot be improved Sex.

The present invention is made in view of the above-mentioned problems, and its main object is to provide a non-aqueous electrolyte secondary battery capable of improving durability against high-speed charge and discharge.

The inventor of the present application focused on the following situation: In a non-aqueous electrolyte secondary battery having an electrode body in which a positive electrode and a negative electrode are superposed through a separator, if the non-aqueous electrolyte for vehicle power source is continuously repeated With the high-speed discharge and charge assumed in the secondary battery, it was found that the battery resistance increased significantly. Therefore, the inventors have analyzed in detail the influence of this high-speed charge and discharge repetition on the non-aqueous electrolyte secondary battery.

As a result, it was found that in a non-aqueous electrolyte secondary battery that repeatedly performs high-speed charge and discharge, the amount of electrolyte in the non-aqueous electrolyte immersed between the positive

and negative electrodes of the electrode body is reduced. During charging and discharging, part of the non-aqueous electrolyte immersed between the positive and negative electrodes of the electrode body is squeezed to the outside of the electrode, and the amount of electrolyte between the positive and negative electrodes falls below a necessary amount (that is, electrolyte depletion).

If the electrolyte depletion occurs between the positive and negative electrodes in this way, the amount of electrolytic solution in the positive and negative electrodes during charge and discharge is insufficient, so the high-speed charge and discharge performance of the entire battery decreases. In addition, since the battery reaction is concentrated in a portion with a relatively large amount of electrolyte (i.e., the remaining portion of the electrolyte in the positive and negative electrodes), the deterioration of this portion is promoted. These conditions are the main reasons that the durability of the non-aqueous electrolyte secondary battery withstands high-speed charge and discharge cycles (the battery resistance increases).

The present invention is based on the above finding, by eliminating or alleviating the shortage of the electrolyte between the positive and negative electrodes, to improve the durability of the non-aqueous electrolyte secondary battery against high-speed charge and discharge cycles.

That is, the non-aqueous electrolyte secondary battery provided by the present invention is a non-aqueous electrolyte secondary battery having an electrode body formed by superposing a positive electrode sheet and a negative electrode sheet through a separator. A porous layer is formed on the surface of at least one side of the separator, and the porous layer has an inorganic filler and a binder. The surface of the porous layer has **irregularities, and the maximum unevenness of the uneven surface is 0.2 μm to 1.7 μm.**

According to the structure of the present invention, the porous layer is formed on at least one surface of the separator, and the surface of the porous layer is formed with irregularities. Therefore, a large amount of non-aqueous electrolyte can be held on the uneven surface. Therefore, even if a part of the non-aqueous electrolyte immersed in the positive and negative electrodes due to high-speed charge and discharge is squeezed out of the positive and negative electrodes, the non-aqueous electrolyte held by the uneven surface can be quickly supplied into the positive and negative electrodes , So that the amount of electrolyte in the positive and negative electrodes is quickly restored. This can eliminate or alleviate the shortage of electrolyte in the positive and negative electrodes caused by high-speed charge and discharge, and can improve the durability against charge-discharge cycles.

Preferably, the maximum height difference of the uneven surface is 0.2 μm to 1.7 μm. If the maximum height difference of the uneven surface is less than 0.2 m, the liquid retention function of the uneven surface is reduced, and the above-mentioned cycle durability improvement effect may not be obtained. In addition, if the **maximum height difference of the uneven surface is higher than 1.7 μm, the balance of the amount of electrolyte** between the positive and negative electrodes is broken, and the battery reaction becomes uneven. Therefore, the cycle durability tends to decrease instead.

In a preferred embodiment disclosed herein, the porous layer has particles formed of an inorganic metal compound as the inorganic filler, and the cumulative particle size D10 of 10% in the particle size distribution **(volume basis) of the metal compound particles is 0.2μm or more. If the cumulative particle diameter D10 of** 10% of the metal compound particles is too small, the porous layer is formed by the aggregation of the minute metal compound particles with a small particle size, so the bonding between the metal compound particles is weak and the durability of the porous layer is reduced. Therefore, when the pressure caused by the expansion and contraction of the electrode body during high-speed charge and discharge is received, the uneven surface is easily damaged, and the above-mentioned cycle durability improvement effect may not be obtained.

In addition, preferably, in the particle size distribution (volume basis) of the metal compound particles, the particle diameter D90 accumulated 90% is 4 m or less. If such a collection of metal compound particles having a uniform particle size with a narrow particle size distribution forms a porous layer, the binding force between the metal compound particles is strong, and the durability of the porous layer is further improved. Therefore, even if the pressure caused by the expansion and contraction of the electrode body accompanying high-speed charge and discharge is received, the uneven surface is hardly damaged, and the above-mentioned cycle durability improvement effect can be obtained more reliably.

In a preferred mode disclosed herein, the metal compound particles are alumina or alumina hydrate. Since these metal compound particles have a high Mohs hardness, it is particularly preferable from the viewpoint of improving the durability of the porous layer formed using the particles.

In a preferred aspect disclosed herein, the binder content ratio in the porous layer, the amount of solid components contained in the porous layer (typically inorganic fillers, binders and other porous layers When the total amount of forming components (for example, a thickener) is 100% by mass, it is 1.5% by mass to 3% by mass. Thereby, the maximum height difference of the uneven surface can be easily controlled within the preferred range disclosed herein.

In a preferred mode disclosed herein, the porous layer is formed on the surface of the separator opposite the negative electrode sheet, and the uneven surface of the porous layer is formed at least opposite to the negative electrode active material layer containing the negative electrode active material of the negative electrode sheet Position. The negative electrode active material layer containing the negative electrode active material of the negative electrode sheet is likely to suffer from insufficient electrolyte due to high-speed charge and discharge. Therefore, it is particularly useful to form the uneven surface of the porous layer at a position opposed to the negative electrode active material layer.

Any of the non-aqueous electrolyte secondary batteries disclosed herein has performance suitable for batteries mounted on vehicles (for example, high output can be obtained), and in particular, has good durability against high-speed charge and discharge. Therefore, according to the present invention, it is possible to provide a vehicle having any of the non-aqueous electrolyte secondary batteries disclosed herein. In particular, it is possible to provide a vehicle (for example, an automobile) having the non-aqueous electrolyte secondary battery as a power source (typically, a power source for a hybrid vehicle or an electric vehicle).

Examples of preferred applications of the technology disclosed herein include non-aqueous electrolytes that can be used under charge and discharge cycles including high-speed discharge of 50A or more (eg, 50A to 250A) and further 100A or more (eg, 100A to 200A). Secondary batteries; large-capacity models with a theoretical capacity of 1 Ah or more (and further 3 Ah or more) and are thought to be able to withstand high-rate discharge including 10C or more (eg, 10C to 50C) and then 20C or more (eg, 20C to 40C) Used non-aqueous electrolyte secondary battery, etc.

BRIEF DESCRIPTION

FIG. 1 is a side view schematically showing a lithium secondary battery according to an embodiment of the present invention.

FIG. 2 is a cross-sectional view taken along the line II-II of FIG. 1.

Fig. 3 is a diagram schematically showing an electrode body of a lithium secondary battery according to an embodiment of the present invention.

4 is an enlarged cross-sectional view showing a main part of a lithium secondary battery according to an embodiment of the present invention.

FIG. 5 is a diagram for explaining the measurement method of the film resistance in one test example.

6 is a side view schematically showing a vehicle having a lithium secondary battery according to an embodiment of the present invention.

detailed description

Hereinafter, embodiments of the present invention will be described with reference to the drawings. In the following drawings, components and parts that perform the same function are denoted by the same reference symbols. In addition, the dimensional relationship (length, width, thickness, etc.) in each figure does not reflect the actual dimensional relationship. In addition, for matters other than those specifically mentioned in this specification, if they are necessary for implementing the present invention (for example, the structure and manufacturing method of an electrode body having a positive electrode and a negative electrode, the structure and manufacturing method of a separator or an electrolyte Methods, general technologies related to the construction of non-aqueous electrolyte secondary batteries and other batteries, etc.), can be grasped as a design matter for those skilled in the art based on the prior art in this field.

It is not intended to be particularly limited, but the following is a non-aqueous electrolyte lithium secondary battery (lithium ion battery) in the form of a wound electrode body (wound electrode body) and a non-aqueous electrolyte solution packed in a cylindrical container) As an example to explain the present invention in detail.

The schematic structure of the lithium ion battery of one embodiment of the present invention is shown in FIGS. 1 to 3. The lithium-ion battery 100 has a structure in which an elongated positive electrode sheet 10 and an elongated negative electrode sheet 20 are wound through an elongated separator 40 (wound electrode body) 80, Along with a non-aqueous electrolyte not shown in the figure, it is put into a container 50 in a shape (cylindrical shape) that can accommodate the wound electrode body 80.

The container 50 has a bottomed cylindrical container body 52 with an open upper end, and a lid 54 for closing the opening thereof. As the material constituting the container 50, metal materials such as aluminum, steel, Ni-plated SUS, etc. (Ni-plated SUS in this embodiment) are preferably used. Alternatively, it may be a container 50 molded from a resin material such as PPS or polyimide resin. A positive terminal 70 electrically connected to the positive electrode 10 of the wound electrode body 80 is provided on the upper surface of the container 50 (that is, the lid 54). On the lower surface of the container 50, a negative electrode terminal 72 electrically connected to the negative electrode 20 of the wound electrode body 80 is provided (in this embodiment, the container body 52 also serves.). Inside the container 50, the wound electrode body 80 is housed together with a non-aqueous electrolyte not shown in the figure.

The wound electrode body 80 of the present embodiment is the same as the wound electrode body of a general lithium ion battery except for the structure of the separator 40 described below. As shown in FIG. 3, the wound electrode body 80 is assembled The pre-stage has a strip-shaped (band-shaped) sheet structure.

The positive electrode sheet 10 has a structure in which a positive electrode active material layer 14 containing a positive electrode active material is held on both surfaces of a long sheet-shaped foil-shaped positive electrode current collector 12. However, the positive electrode active material layer 14 is not attached to an edge (the lower edge portion in the figure) extending along the widthwise end of the positive electrode sheet 10, but the positive electrode current collector 12 is exposed to a certain width. The non-forming part of the positive electrode active material layer is formed.

Like the positive electrode sheet 10, the negative electrode sheet 20 has a structure in which a negative electrode active material layer 24 containing a negative electrode active material is held on both sides of a long foil-shaped negative electrode current collector 22. However, the negative electrode active material layer 24 is not attached to an edge (the upper edge portion in the figure) extending along the widthwise end of the negative electrode sheet 20, but the negative electrode current collector 22 is exposed to a certain width. The negative electrode active material layer non-formed portion is formed.

When the wound electrode body 80 is produced, as shown in FIG. 3, the positive electrode sheet 10 and the negative electrode sheet 20 are laminated via the separator 40. At this time, the positive electrode sheet 10 and the negative electrode are made so that the positive electrode active material layer non-forming portion of the positive electrode sheet 10 and the negative electrode active material layer non-forming portion of the negative electrode sheet 20 extend from both sides in the width direction of the separator 40 respectively The pieces 20 are slightly shifted and overlapped in the width direction. The wound electrode body 80 can be produced by winding the laminated body thus superposed.

At the central portion of the wound electrode body 80 in the winding axis direction, a wound core portion 82 (ie, the positive electrode active material layer 14 of the positive electrode sheet 10, the negative electrode active material layer 24 of the negative electrode sheet 20, and the separator 40 are closely laminated section). In addition, at both ends of the wound electrode body 80 in the winding axis direction, the electrode active material layer non-forming portions of the positive electrode sheet 10 and the negative electrode sheet 20 extend from the winding core portion 82 outward, respectively. A positive electrode lead terminal 74 and a negative electrode are attached to the positive electrode side overhanging portion (ie, the non-forming portion of the positive electrode active material layer 14) 84 and the negative electrode side overhanging portion (ie, the non-forming portion of the negative electrode active material layer 24) The lead terminal 76 is electrically connected to the above-mentioned positive electrode terminal 70 and negative electrode terminal 72 (in this case, the container body 52 also serves.).

The constituent elements constituting the wound electrode body 80 can be the same as the wound electrode body of a conventional lithium ion battery except for the separator 40, and are not particularly limited. For example,

the positive electrode sheet 10 can be formed by applying a positive electrode active material layer 14 mainly composed of a positive electrode active material for a lithium ion battery to a long positive electrode current collector 12. As the positive electrode current collector 12, aluminum foil and other metal foils suitable for the positive electrode can be suitably used. As the positive electrode active material, one or two or more kinds of materials conventionally used in lithium ion batteries can be used, and there is no particular limitation. As a preferred object of use of the technology disclosed herein, lithium nickel oxide (LiMn 2 O 4), lithium cobalt oxide (LiCoO 2), lithium manganese oxide (LiNiO 2), etc., as constituent metal elements, include lithium and A transition metal element oxide (lithium transition metal oxide) as a main component of the positive electrode active material.

The negative electrode sheet 20 can be formed by applying a negative electrode active material layer 24 mainly composed of a negative electrode active material for a lithium ion battery to a long negative electrode collector 22. As the negative electrode current collector 22, copper foil and other metal foils suitable for the negative electrode can be suitably used. The negative electrode active material can use one or two or more of the materials conventionally used in lithium ion batteries, and is not particularly limited. Preferred examples include carbon-based materials such as graphite carbon and amorphous carbon, lithium-containing transition metal oxides, transition metal nitrides, and the like.

As a preferred separator 40 used between the positive and negative electrode sheets 10 and 20, a porous polyolefin-based resin can be mentioned. For example, a porous separator made of synthetic resin (e.g. made of polyolefin such as polyethylene) is preferably used. The separator 40 is impregnated with a non-aqueous electrolyte.

Here, in this embodiment, as shown in FIG. 3, a porous layer 42 is formed on at least one surface of the separator 40 constituting the wound electrode body. In this embodiment, the porous layer 42 is formed on the surface of the separator opposed to the negative electrode sheet 20. The porous layer 42 is composed of an inorganic filler and a binder, and the inorganic filler and the inorganic filler and the separator are bonded together by the binder.

In this way, the porous layer 42 is formed on the surface of the separator opposed to the negative electrode sheet 20, whereby heat generation during internal short circuit can be suppressed. That is, it is conceivable that when foreign substances are mixed into the wound electrode body and a slight internal short circuit occurs, the heat will cause the separator 40 to shrink and the internal short circuit will expand (and thus the battery generates heat), but by providing the porous layer 42 in this way, the internal short circuit can be prevented Expansion to suppress heat generation.

As the inorganic filler constituting the porous layer 42, it is preferable to use a material having heat resistance and having stable electrochemical properties in the range of use of the battery. Examples of such inorganic fillers include particles formed of inorganic metal compounds. As preferred examples, alumina (Al 2 O 3), alumina hydrate (for example, boehmite (Al 2 O 3 · H 2 O)), magnesium hydroxide (Mg (OH) 2), magnesium carbonate (MgCO 3) etc. One or more of these inorganic metal compound materials can be used. Among them, aluminum oxide or aluminum oxide hydrate has a high Mohs hardness, so it is preferable in terms of improving the durability of the porous layer.

The binder used in the porous layer 42 is a binder for binding the inorganic filler. The material constituting the binder itself is not particularly limited, and various materials can be used in a wide range. As a preferable example, an acrylic resin can be mentioned. As the acrylic resin, acrylic acid, methacrylic acid, acrylamide, methacrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, methacrylate, methyl methacrylate, acrylic acid are preferably used A homopolymer obtained by polymerizing monomers such as ethylhexyl ester and butyl acrylate. In addition, the acrylic resin may be a copolymer obtained by polymerizing two or more of the comonomers. Furthermore, it may be a material obtained by mixing two or more of the above-mentioned homopolymer and copolymer. In addition to the above-mentioned acrylic resin, polyvinylidene fluoride, polytetrafluoroethylene (PTFE), polyacrylonitrile, polymethyl methacrylate, and the like can also be used.

Next, the wound electrode body 80 of this embodiment will be described in detail together with FIG. 4. 4 is a schematic cross-sectional view showing an enlarged section of a section cut along the winding axis of the wound electrode body 80 of the present embodiment, showing the separator 40 and the porous layer 42 formed on the surface of the separator 40 3. The negative electrode sheet 20 opposed to the porous layer 42.

As shown in FIG. 4, the negative electrode active material layer 24 in the negative electrode sheet 20 is composed of negative electrode active material particles 26 and a binder not shown in the figure, and the negative electrode active material particles 26 and the negative electrode active material are separated by the binder The particles 26 and the negative electrode current collector 22 are bonded together. Between adjacent negative electrode active material particles 26, a plurality of pores 28 are formed in a portion that is not bound by the binder, and a non-aqueous electrolyte solution (that is, the non-aqueous electrolyte solution penetrates into the negative electrode active material layer is maintained in the pores 28 Inside).

Here, in the conventional lithium secondary battery, if the discharge and charging of a short time (pulse shape) are continuously repeated at a high speed as imagined by a lithium secondary battery for a vehicle power source, there is a non-immersion in the negative electrode active material layer 24 A part of the aqueous electrolyte is squeezed out of the negative electrode active material layer 24, and the amount of electrolyte in the negative electrode active material layer 24 is reduced to a necessary amount or less (that is, electrolyte depletion occurs).

In this way, if the electrolyte depletion occurs in the negative electrode active material layer 24, the amount of electrolyte in the negative electrode active material layer 24 is insufficient during charge and discharge, and the high-speed charge and discharge performance of the entire battery decreases. In addition, in a portion where the amount of electrolyte is relatively large (i.e., the portion where the electrolyte remains in the negative electrode active material layer 24), the battery reaction is concentrated, thereby promoting the deterioration of this portion. These conditions can be the cause of the reduction in the durability of the lithium secondary battery against high-speed charge and discharge cycles (increasing the battery resistance).

In contrast, in the present embodiment, a porous layer 42 having an inorganic filler and a binder is formed on the surface of the separator 40. The surface of the porous layer 42 has irregularities, and the maximum unevenness of the uneven surface 42a is 0.2 m to 1.7 m. In this embodiment, the porous layer 42 is formed on the surface of the separator 40 opposed to the negative electrode sheet 20, and the uneven surface 42a of the porous layer 42 is formed at least on the negative electrode active material layer containing the negative electrode active material in the negative electrode sheet 20 24 relative position.

According to this structure, the porous layer 42 is formed on the surface of the separator 40 opposed to the negative electrode sheet 20, and the surface of the porous layer 42 is formed with irregularities, so that a large number of non-condensed portions 44 can be maintained in the concave portions 44 of the uneven surface 42a Water electrolyte. Therefore, even if a part of the non-aqueous electrolyte immersed in the negative electrode active material layer 24 is pushed out of the negative electrode active material layer 24 due to high-speed charge and discharge, the non-aqueous electrolysis held in the concave portion 44 of the uneven surface 42a The liquid is quickly supplied to the negative electrode active material layer 24, and the amount of electrolyte in the negative electrode active material layer can be quickly recovered. Thereby, the shortage of electrolyte in the negative electrode active material layer due to high-speed charge and discharge can be eliminated or alleviated, and the durability against charge and discharge cycles can be improved.

Preferably, the maximum height difference δ of the uneven surface is 0.2 μm to 1.7 μm. If the maximum height difference δ of the uneven surface is less than 0.2 μm, the liquid retention function of the uneven surface is reduced, and the above-mentioned cycle durability improvement effect may not be obtained. In addition, if the **maximum height difference δ of the uneven surface is higher than 1.7 μm, the balance of the amount of** electrolyte between the positive and negative electrodes is broken, and the battery reaction becomes uneven. Therefore, on the contrary, there is a tendency to lower the cycle durability. It is appropriate that the maximum **height difference δ of the uneven surface is approximately 0.2 μm to 1.7 μm, preferably 0.3 μm to 1.5 μm, and particularly preferably 0.5 μm to 1.5 μm.**

In addition, preferably, the thickness d (including the maximum thickness of the uneven surface) d of the porous layer 42 may be approximately 2 to 50 μm. If the porous layer 42 is too thick, since the porous layer itself functions as a resistance component, the cycle durability tends to decrease. In addition, if the porous layer 42 is too thin, the above-mentioned effect of suppressing heat generation during internal short circuit may not be obtained. The thickness d of the porous layer is suitably approximately 2 to 50 m, preferably 2 to 10 m, and particularly preferably 3 to 7 m.

In addition, preferably, the porosity of the porous layer 42 is approximately 40% to 70%. If the porosity of the porous layer 42 is too small, the porous layer itself acts as a resistance component, which tends to lower the cycle durability. In addition, if the porosity of the porous layer 42 is too large, there is a case where the aforementioned heat generation suppression effect during internal short circuit cannot be obtained. In addition,

the porosity can be determined by, for example, the mass of the porous layer measured by an electronic balance, its apparent volume (for example, the thickness of the porous layer measured by SEM observation × area), and inorganic fillers, binders, and other porous layer structures The true density of the components is calculated.

The maximum height difference δ of the uneven surface can be adjusted by changing the particle size (average particle size, particle size distribution (wide or narrow)) of the metal compound particles used in the porous layer. Generally, as the particle size increases, the filling efficiency decreases, so the maximum height difference of the uneven surface tends to increase. Therefore, by changing the particle size (average particle size, particle size distribution) of the metal compound particles, the maximum height difference of the uneven surface can be controlled. That is, by appropriately selecting the particle size (average particle size, particle size distribution) of the metal compound particles, it is possible to form a porous layer having a maximum height difference of the uneven surface satisfying 0.2 μm≤δ≤1.7μm.

Although not particularly limited, the average particle diameter D50 of the metal compound particles by laser diffraction or scattering method is preferably approximately 0.4 m to 2 m. Thereby, the maximum height difference δ of the uneven surface can be easily controlled within the preferred range disclosed herein.

In addition, it is preferable that in the particle size distribution (volume basis) of the metal oxide particles measured by laser diffraction or scattering method, the cumulative 10% particle diameter D10 is 0.2 m or more. If the cumulative particle diameter D10 of the metal compound particles is too small, the porous layer 42 is formed by the collection of fine metal compound particles with a small particle size, so the bonding between the metal compound particles is weak and the durability of the porous layer 42 low. Therefore, when subjected to pressure due to expansion and contraction of the wound electrode body accompanied by high-speed charge and discharge, the uneven surface 42a is easily damaged, and the above-mentioned cycle durability improvement effect may not be obtained. The cumulative 10% particle size D10 of the metal compound particles is suitably approximately 0.2 μm or more, preferably 0.24 μm or more, and particularly preferably 0.3 μm or more.

In addition, it is preferable that in the particle size distribution (volume basis) of the metal oxide particles measured by laser diffraction or scattering method, the cumulative 90% particle size D90 is 4 m or less. If the porous layer 42 is formed by a collection of metal compound particles having a uniform particle size with a narrow particle size distribution, the bonding between the metal compound particles is strong, and the durability of the porous layer 42 is further improved. Therefore, even if the pressure caused by the expansion and contraction of the wound electrode body undergoes high-speed charge and discharge, the uneven surface 42a is hardly damaged, and the above-mentioned cycle durability improvement effect can be obtained more reliably. It is appropriate that the cumulative 90% particle diameter D90 of the metal compound particles is approximately 4 m or less, preferably 3.5 m or less, and particularly preferably 2.9 m or less.

As another method of realizing the uneven surface that can satisfy the preferred maximum height difference δ disclosed herein, a method of appropriately selecting the formation conditions when forming the porous layer can be cited. For example, the porous layer is obtained by dispersing metal oxide particles, a binder, and other porous layer forming components (for example, a thickener) in an appropriate solvent, and coating the obtained coating for forming a porous layer After the cloth is spread on one side or both sides of the separator, the coating is dried by drying air to form. In this case, by selecting the drying conditions such as the drying temperature and the drying wind speed, the maximum height difference δ of the uneven surface can be controlled. That is, by appropriately selecting drying conditions such as drying temperature and drying wind speed, a porous layer having a maximum height difference δ of the uneven surface satisfying 0.2 μm ≤ δ ≤ 1.7 μm can be formed. Although not particularly limited, the above drying temperature may be set substantially at 40 ° C or higher (for example, 40 ° C to 80 ° C). In addition, the above-mentioned drying wind speed may be set substantially at or above 17 m / s (for example, 17 m / s to 22 m / s). Thereby, the maximum height difference of the uneven surface can be easily controlled within the preferable range disclosed here.

In addition, as a method of adjusting the maximum height difference δ of the uneven surface within an appropriate range, a method of changing the solid content rate and binder amount of the coating material for forming the porous layer can be cited. If the solid content rate and binder amount of the paint for forming a porous layer increase, the viscosity increases, so the smoothness of the coated surface deteriorates. Therefore, the maximum height difference δ of the uneven surface tends to increase. Therefore, by changing the solid content rate of the paint for forming the porous layer and the amount of the binder, the maximum height difference δ of the uneven surface can be controlled. That is, by appropriately selecting the solid content rate of the coating material for forming the porous layer and the amount of the binder, a porous layer having a maximum height difference δ of the uneven surface satisfying 0.2 μm ≤ δ ≤ 1.7 μm can be formed. Although not

particularly limited, the solid content rate of the paint for forming a porous layer is preferably about 40% by mass or more (typically 40-50% by mass). In addition, when the content ratio of the binder is 100% by mass, the solid content (typically the total amount of the inorganic filler, binder, and other porous layer-forming components) contained in the paint for forming the porous layer is 100% by mass It is preferably about 1.5% by mass or more (typically 1.5 to 4.5% by mass). As a result, the maximum height difference of the uneven surface can be easily controlled within the preferred range disclosed herein. In addition, the method of controlling the **maximum height difference δ of the above-mentioned uneven surface can be used individually or in** combination.

In addition, examples of the solvent used for the above-mentioned porous layer forming paste include N-methylpyrrolidone (NMP), pyrrolidone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, toluene, and dimethyl. Organic solvents such as formamide and dimethylacetamide, or a combination of two or more of them. Or, it may be water or a mixed solvent mainly composed of water. As a solvent other than water constituting the mixed solvent, one or two or more organic solvents (lower alcohols, lower ketones, etc.) that can be homogeneously mixed with water can be appropriately selected and used.

In addition, the coating material for forming the porous layer may contain, in addition to the inorganic filler and the binder, one or two or more materials that can be used as necessary. As an example of such a material, a polymer functioning as a thickener for the paint for forming a porous layer can be cited. As the polymer functioning as a thickener, for example, carboxymethyl cellulose (CMC) is preferably used. The content ratio of the tackifier is preferably about 1.5% by mass or less, and more preferably about 1% by mass or less (for example, about 0.5 to 1%) when the solid content contained in the paint for forming a porous layer is 100% by mass. quality%).

Such a porous layer-forming paint is applied on the surface of the separator 40, and the porous layer 42 is formed on the surface of the separator 40 by drying. At this time, the particle size (particle size distribution) of the inorganic filler contained in the coating material for forming the porous layer, the amount of binder, the solid content rate, and / or The drying conditions when the paint is dried (for example, the drying temperature and the drying wind speed), and the porous layer 42 may be formed according to the set conditions. As a result, **a porous layer having a maximum height difference δ of the uneven surface satisfying 0.2 μm ≤ δ ≤ 1.7 μm can** be formed.

After the porous layer 42 is formed on the surface of the separator 40 in this way, the positive electrode sheet 10 and the negative electrode sheet 20 are wound through the two separator sheets to produce a wound electrode body 80. Then, the wound electrode body 80 is loaded into the container body 52, and an appropriate non-aqueous electrolyte is arranged (injected) into the container body 52. As the non-aqueous electrolyte solution that is loaded together with the wound electrode body 80 in the container body 52, the same non-aqueous electrolyte solution as that used in conventional lithium ion batteries can be used, and is not particularly limited. The non-aqueous electrolyte typically has a composition containing a supporting electrolyte in an appropriate non-aqueous solvent. As the non-aqueous solvent, for example, ethylene carbonate (EC), methyl ethyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), propylene carbonate (PC) and the like can be used. In addition, as the supporting electrolyte, for example, lithium salts such as LiPF 6, LiBF 4, LiAsF 6, LiCF 3 SO 3, and LiClO 4 are preferably used. For example, the following non-aqueous electrolyte solution can be preferably used: LiPF 6 as a supporting electrolyte is contained in a mixed solvent containing EC, EMC, and DMC in a volume ratio of 3: 4: 3 at a concentration of about 1 mol / liter.

The non-aqueous electrolyte solution described above is loaded into the container body 52 together with the wound electrode body 80, and the opening of the container body 52 is sealed by the lid body 54 to complete the construction (assembly of the lithium ion battery 100 of this embodiment). In addition, the sealing procedure of the container body 52 and the arrangement (injection) procedure of the electrolytic solution can be carried out in the same manner as conventionally performed in the manufacture of lithium ion batteries. Thereafter, the battery is adjusted (initial charge and discharge). Processes such as air extraction and quality inspection can also be performed as needed.

Hereinafter, the test examples related to the present invention will be described, but this does not mean that the present invention is limited to the contents shown in the following test examples.

□Test Example 1: Adjustment of particle size distribution of inorganic filler□

The metal compound powder as an inorganic filler was pulverized for 5 minutes at a wind pressure of 0.2 MPa using a jet mill (manufactured by ヘソカワミクロン Inc.), and classified to 4 m or less using an air jet powder classifying device (manufactured by Kang マエンジニアリング). The particle size distributions D10 and D90 of the obtained metal compound powder were measured by a laser diffraction and scattering type particle size distribution measuring device (manufactured by Nikkiso Co., Ltd.).

In addition, in this test, as shown in Table 1, five kinds of metal compound powders of magnesium carbonate, magnesium hydroxide, boehmite, α-alumina, and titanium dioxide were used to prepare the accumulation in the particle size distribution (volume basis) in the above order. Metal compound powders with different 10% diameter D10 and cumulative 90% diameter D90 (Samples 1 to 15).

【Table 1】

□Test Example 2: Preparation of paint for forming a porous layer□

The coating for forming a porous layer was prepared using various metal compound powders prepared in the above Test Example 1. Specifically, for sample 1, magnesium carbonate powder as an inorganic filler, an aqueous acrylic binder solution (solid content rate of 45% by mass), and carboxymethyl cellulose (CMC) powder as a thickener are prepared, and The mass ratio of the inorganic filler, binder, and tackifier is 97.8: 1.5: 0.7, and is mixed in water so that the solid content rate becomes approximately 40% by mass. This mixture was pre-kneaded at a speed of 15,000 rpm for 5 minutes with a high-speed stirring and dispersing machine (manufactured by Cleac Corporation) at a speed of 15,000 rpm, and then was kneaded at a speed of 20,000 rpm for 15 minutes to prepare a coating for forming a porous layer.

In addition, Samples 2 to 15 are the same as Sample 1, except that the solid content rate and binder amount of the paint for forming the porous layer (binder content ratio of the total solid content in the paint for forming the porous layer) Different from Table 1, the paste for forming the porous layer was prepared in the same order as above.

□Test Example 3: Formation of porous layer□

The porous layer 42 was formed by applying various porous layer-forming paints prepared in the above Test Example 2 to one side of a long separator 40 (thickness 20 μm) by a gravure roll, and by drying. As the coating conditions, the moving speed A of the separator was 3 m / min, the rotating speed B of the gravure roll was 3.8 m / min, and the ratio of the rotating speed B of the gravure roll to the moving speed A of the separator (speed ratio = A / B) was 1.27, and it adjusted so that the coating amount of the coating material for porous layer formation may become about 0.7 mg / cm □2□ (based on solid content). In addition, the above-mentioned drying is performed by a hot air drying method using dry air. Specifically, the drying temperature and the drying air speed of the drying air are different from each sample as shown in Table 1, and the porous layer is formed in the above order. As the separator, a single-layer structure of polyethylene (PE) or a three-layer structure of polypropylene (PE) -polyethylene (PE) -polypropylene (PE) is used.

The cross sections of the porous layers of Samples 1 to 15 obtained above were observed with an electron microscope (SEM), and the maximum height difference δ of the surface irregularities (concavo-convex surfaces) was measured. Specifically, sampling is performed, and the distance (interval) between the highest position and the lowest position of the uneven surface within a reference length of 3 cm is taken as the maximum height difference δ. Sampling, select three parts at equal intervals in the TD direction (transverse direction), and select three parts at a distance of 3cm in the MD direction (machine direction, Machine Direction) (a total of 9 parts)). Then, the maximum height difference? Of the uneven surface within 3 cm of each reference length was measured, and the average value was determined.

□Test Example 4: Measurement of membrane resistance□

Using the separator 40 provided with the various porous layers 42 prepared in the above Test Example 3, a lithium secondary battery (laminated single cell) was produced, and its membrane resistance (Rs) was measured. Specifically, as shown in FIG. 5, the porous layer 42 and the separator 40 are impregnated with a non-aqueous electrolyte, and sandwiched between two copper plates 62 with an area of 35 mm 2 and a thickness of 1 mm to

produce a laminated single cell 60. As a non-aqueous electrolyte, a mixed solvent containing ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) at a volume ratio of 3: 4: 3 at about 1 mol / liter was used The concentration contains a non-aqueous electrolyte that supports the electrolyte LiPF 6. Then, a torque pressure of 50 cN.m was applied from above and below the copper plate 62, and the AC impedance of the laminated unit cell 60 was measured at 25 ° C, and the film resistance (Rs) was read from the obtained Cole-Cole diagram. The measurement conditions for AC impedance are 5 mV AC applied voltage and 10000 Hz to 1 Hz frequency range. In addition, the above-mentioned single cells are manufactured by using the separators sandwiched by the two copper plates 62 as one, two, and three pieces, respectively. Then, the resistance value was measured by the AC impedance method, the resistance value of the obtained single cell was plotted against the number of separators, and the membrane resistance (Rs) of each separator was obtained by linear approximation.

It can be seen from Table 1 that for samples 1 to 11 where the maximum height difference of the uneven surface is $0.2 \leq \delta \leq 1.7$, the film resistance is 1.6 Ω or less, and the film resistance is greatly reduced compared to samples 12 to 15. In particular, by making the maximum height difference 0.5 μm $\leq \delta \leq$ 1.5 μm, an extremely low film resistance of 1.2 Ω or less can be achieved.

□Test Example 5: High-speed durability test□

A lithium secondary battery was constructed using the separator 40 provided with the various porous layers 42 produced in Test Example 3 above, and its high-speed durability was evaluated. The lithium secondary battery is manufactured as follows.

Li 1.15 Ni 0.33 Mn 0.33 Co 0.33 O 2 powder as a positive electrode active material, acetylene black AB as a conductive material, and polyvinylidene fluoride PVdF as a binder in a mass ratio of these materials of 88: 10: 2 N-methylpyrrolidone (NMP) was mixed to prepare a paste for a positive electrode active material layer. This paste for a positive electrode active material layer was applied to both sides of a long sheet-shaped aluminum foil (positive electrode current collector 12) in a strip shape and dried, thereby producing a positive electrode active material provided on both sides of the positive electrode current collector 12层14 的cation film 10. The coating amount of the paste for the positive electrode active material layer was adjusted so that both sides were combined at approximately 17.2 mg / cm 2 (based on solid content).

In addition, graphite powder as a negative electrode active material, styrene-butadiene rubber SBR as a binder, and carboxymethyl cellulose CMC as a thickener were dispersed in water so that the mass ratio of these materials was 98.6: 0.7: 0.7. Thus, a paste for the negative electrode active material layer is prepared. This negative electrode active material layer paste was applied to both sides of a long sheet-shaped copper foil (negative electrode current collector 22) to prepare a negative electrode sheet 20 provided with a negative electrode active material layer 24 on both sides of the negative electrode current collector 22. The application amount of the paste for forming the negative electrode active material layer was adjusted so that the two sides were combined at approximately 11.1 mg / cm 2 (based on solid content).

Then, the positive electrode sheet 10 and the negative electrode sheet 20 are wound through the two separator sheets 40, thereby producing a wound electrode body 80. At this time, the porous layer 42 on the surface of the separator and the negative electrode sheet 20 are arranged to face each other. The thus-obtained wound electrode body 80 was loaded into the battery container 50 together with the non-aqueous electrolyte (here, a cylindrical type of 18650 was used.), And the opening of the battery container 50 was hermetically sealed. As a non-aqueous electrolyte, a mixed solvent containing ethylene carbonate EC, ethyl methyl carbonate EMC, and dimethyl carbonate DMC in a volume ratio of 3: 4: 3 containing a supporting electrolyte LiPF at a concentration of about 1 mol / liter 6 of non-aqueous electrolyte. In this way, the lithium secondary battery 100 is assembled. Then, an initial charge-discharge treatment (adjustment) was performed by a commonly used method to obtain a lithium secondary battery for evaluation.

The lithium secondary battery obtained in the above manner was subjected to a charge-discharge mode in which CC discharge at 20C was repeated for 10 seconds, and a charge-discharge cycle test was performed. Specifically, in a room temperature (approximately 25 ° C) environment, CC discharge was performed at 20C for 10 seconds, and after stopping for 5 seconds, a charge and discharge cycle of CC charging at 5C for 40 seconds was continuously repeated 10,000 times.

Then, the resistance increase rate was calculated from the IV resistance before the charge-discharge cycle test (the initial resistance of the lithium ion battery) and the IV resistance after the charge-discharge cycle test. Here,

the IV resistance before and after the charge-discharge cycle was calculated based on the voltage drop after discharge for 10 seconds when the pulse discharge was performed at 25 ° C and 30C. The resistance increase rate (%) is obtained by [(IV resistance after charge-discharge cycle test-IV resistance before charge-discharge cycle test) / IV resistance before charge-discharge cycle test] × 100. The results are shown in Table 1.

It can be seen from Table 1 that the samples 12 and 13 whose maximum height difference of the uneven surface is less than 0.2 have an increase rate of resistance exceeding 200%. In addition, the resistance increase rate of samples 14, 15 where the maximum height difference of the uneven surface exceeds 1.7 also exceeds 200%. On the other hand, the batteries of samples 1 to 11 with a maximum unevenness of 0.2≤δ≤1.7 on the uneven surface hardly increased even after 10,000 high-speed charge-discharge cycles were repeated, and the resistance increase rate was as low as 15% or less value. In particular, by making the maximum height difference 0.5 μm □ δ □ 1.5 μm, an extremely low resistance increase rate of 6% or less can be achieved. From this result, it was confirmed that by making the maximum height difference of the uneven surface 0.2≤δ≤1.7 (preferably 0.5 m≤δ≤1.5 m), the durability of the lithium secondary battery against high-speed charge and discharge can be improved.

□Test Example 6: Internal short circuit test of foreign matter□

A lithium secondary battery was produced in the same manner as in Test Example 5 above, and a foreign matter internal short-circuit test was performed. The internal short circuit test for foreign objects was conducted in accordance with JISC8714 using L-shaped nickel-made small pieces having a height of 0.2 mm × a width of 0.1 mm and 1 mm on each side. Also, investigate whether there are abnormally smoked NG products. The results are shown in Table 1. Here, no smoke is indicated as ○, and no smoke is indicated as ×.

As shown in Table 1, samples 1 to 11 with a maximum height difference of the uneven surface of 0.2 ≤ δ ≤ 1.7 have no batteries that cause abnormal smoke, and can be confirmed as batteries with excellent safety.

The present invention has been described above through preferred embodiments, but such description is not a limiting matter, and of course various changes can be made.

For example, in the above-mentioned embodiment, the case where the porous layer 42 is formed on the surface of the separator 40 opposed to the negative electrode sheet 20 is shown, but it is not limited to this, and may also be formed on the surface of the separator opposed to the positive electrode sheet (Or on both sides of the separator).

In addition, as long as the structure is adopted in which the porous layer having the uneven surface satisfying the preferred maximum height difference δ value disclosed herein is provided on the surface of the separator, the shape of the constructed lithium secondary battery (The shape and size are not particularly limited. The outer package may be a sheet type composed of a laminate film or the like, and the battery case may be a cylindrical or rectangular parallelepiped battery, or a small button shape.

In addition, any of the lithium secondary batteries 100 disclosed herein has performance suitable for batteries mounted on vehicles (for example, high output can be obtained), and in particular, has good durability against high-speed charge and discharge. Therefore, according to the present invention, as shown in FIG. 6, a vehicle 1 having any of the lithium secondary batteries 100 disclosed herein can be provided. In particular, it is possible to provide a vehicle 1 (for example, an automobile) having the lithium secondary battery 100 as a power source (typically, a power source of a hybrid vehicle or an electric vehicle).

In addition, as a preferred use object of the technology disclosed herein, lithium that can be used under a charge-discharge cycle including high-speed discharge including 50A or more (for example, 50A to 250A) and more than 100A (for example, 100A to 200A) can be cited. Secondary battery 100; a large-capacity type with a theoretical capacity of 1 Ah or more (and further 3 Ah or more) and is thought to be a charge-discharge cycle capable of high-speed discharge including 10C or more (eg, 10C to 50C) and then 20C or more (eg, 20C to 40C) Lithium secondary batteries used below.

Industrial availability

According to the structure of the present invention, it is possible to provide a non-aqueous electrolyte secondary battery with improved durability against high-speed charge and discharge.

CN102939675A Non-aqueous electrolyte secondary battery

Data originating from sources other than the EPO may not be accurate, complete, or up to date.

The wording below is an initial machine translation of the original publication. To generate a version using the latest translation technology, go to the original language text and use Patent Translate.

1.A non-aqueous electrolyte secondary battery is a non-aqueous electrolyte secondary battery having an electrode body, the electrode body is formed by superposing a positive electrode sheet and a negative electrode sheet through a separator,

A porous layer is formed on the surface of at least one side of the separator, the porous layer has an inorganic filler and a binder,

The surface of the porous layer has irregularities, and the maximum height difference of the irregular surface is 0.2 μm to 1.7 μm.

2.The non-aqueous electrolyte secondary battery according to claim 1, wherein the porous layer has particles formed of an inorganic metal compound as the inorganic filler,

In the particle size distribution of the metal compound particles, the cumulative 90% particle size D90 is 4 μm or less.

3.The non-aqueous electrolyte secondary battery according to claim 2, wherein in the particle size distribution of the metal compound particles, a cumulative particle diameter D10 of 10% is 0.2 m or more.

4.The non-aqueous electrolyte secondary battery according to claim 2 or 3, wherein the metal compound particles are alumina or alumina hydrate.

5.The non-aqueous electrolyte secondary battery according to any one of claims 1 to 4, wherein the content of the binder in the porous layer is 100% by mass as the solid content contained in the porous layer %, It is 1.5% by mass to 3% by mass.

6.The non-aqueous electrolyte secondary battery according to any one of claims 1 to 5, wherein the porous layer is formed on a surface of the separator opposite to the negative electrode sheet, and the uneven surface of the porous layer is at least The negative electrode active material layer containing the negative electrode active material on the negative electrode sheet is formed at a position opposed to the negative electrode active material layer.

7.A vehicle equipped with the non-aqueous electrolyte secondary battery according to any one of claims 1 to 6.

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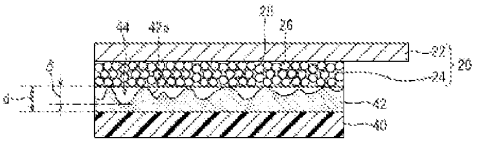
权利要求书 1 页 说明书 12 页 附图 3 页

(54)发明名称

非水电解液二次电池

(57)摘要

通过本发明得到的非水电解液二次电池，是具有电极体的非水电解液二次电池，所述电极体是正极片和负极片(20)介由隔离片(40)重合而成的，在隔离片(40)的至少一侧的表面上形成有多孔层(42)，多孔层具有无机填充剂和粘合剂，多孔层(42)的表面形成凹凸，该凹凸面(42a)的最大高低差为0.2μm～1.7μm。



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1. 一种非水电解液二次电池，是具有电极体的非水电解液二次电池，所述电极体是正极片和负极片介由隔离片重合而成的，

在所述隔离片的至少一侧的表面上形成有多孔层，所述多孔层具有无机填充剂和粘合剂，

所述多孔层的表面形成凹凸，该凹凸面的最大高低差为 0.2μm～1.7μm。

2. 根据权利要求 1 所述的非水电解液二次电池，所述多孔层，作为所述无机填充剂具有由无机金属化合物形成的粒子，

在所述金属化合物粒子的粒度分布中，累积 90%的粒径 D90 为 4μm 以下。

3. 根据权利要求 2 所述的非水电解液二次电池，在所述金属化合物粒子的粒度分布中，累积 10%的粒径 D10 为 0.2μm 以上。

4. 根据权利要求 2 或 3 所述的非水电解液二次电池，所述金属化合物粒子为氧化铝或氧化铝水合物。

5. 根据权利要求 1～4 的任一项所述的非水电解液二次电池，所述多孔层中的粘合剂含有比例，在将该多孔质层中所包含的固体成分量作为 100 质量%时，为 1.5 质量%～3 质量%。

6. 根据权利要求 1～5 的任一项所述的非水电解液二次电池，所述多孔层在所述隔离片的与负极片相对的表面上形成，该多孔层的凹凸面至少在与该负极片上的包含负极活性物质的负极活性物质层相对的位置上形成。

7. 一种车辆，搭载了权利要求 1～6 的任一项所述的非水电解液二次电池。

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非水电解液二次电池

技术领域

[0001] 本发明涉及非水电解液二次电池，详细地说，涉及耐高速充放电的耐久性提高了的非水电解液二次电池。

背景技术

[0002] 近年，锂离子电池、镍氢电池以及其他的非水电解液二次电池，作为车辆搭载用电源或个人电脑以及移动终端的电源重要性不断提高。尤其，轻量、能够得到高能密度的锂离子电池，期待其能够作为车辆搭载用高输出电源使用。在这种锂离子电池的一个典型的结构中，锂离子在正极和负极之间往返，并由此进行充电以及放电。作为与锂离子电池相关的现有技术，例如列举专利文献 1。

[0003] 现有技术文献

[0004] 专利文献

[0005] 专利文献 1：日本专利申请公开 2002 — 008730 号公报

发明内容

[0006] 因此，在锂离子电池的用途中，假想了一种用途，即在反复进行高速放电（急速放电）的状态下进行使用。作为车辆的动力源而被使用的锂离子电池（例如，搭载在作为动力源而并用锂离子电池和如内燃机等的工作原理不同的其他动力源的混合动力车辆上的锂离子电池），为被想成这样的使用状态的锂离子电池的代表例。但是，已知的是，以往的一般的锂离子电池，对于低速充放电循环，表现出较高的耐久性，但在反复进行高速放电的充放电模式下，容易引起性能劣化（电池电阻的上升等）。

[0007] 在专利文献 1 中，记载了一种技术，在隔离片的基材上形成用于保持电解液的 20 微米以下的薄层，由此，弥补正负极间的电解液不足，并由此改善电池的放电容量。但是，在该技术中，即使能够改善电池的放电容量，也无法提高耐反复高速放电（例如，在车辆动力源用的锂离子电池等中所要求的水平的急速放电）的充放电模式的耐久性。

[0008] 本发明是鉴于上述问题点作出的发明，其主要目的在于提供一种能够提高耐高速充放电的耐久性的非水电解液二次电池。

[0009] 本申请的发明者着眼于以下情况：在具有正极和负极介由隔离片重合而成的电极体的非水电解液二次电池中，若连续反复进行在车辆动力源用的非水电解液二次电池中所假定那样的高速放电和充电，则发现电池电阻会显著地上升。因此，发明者详细地解析了该高速充放电的反复对非水电解液二次电池的影响。

[0010] 其结果为，发现在反复进行高速充放电的非水电解液二次电池中，在电极体的正负极间浸入的非水电解液的电解液量降低的情况，更详细地说，因高速充放电，在电极体的正负极间浸入的非水电解液的一部分被挤到电极的外部，正负极间的电解液量下降到低于必要量（即发生电解液枯竭）。

[0011] 若这样在正负极间发生电解液枯竭，则由于充放电时正负极内的电解液量不足，

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所以，作为电池整体的高速充放电性能降低。另外，由于电池反应集中在电解液量相对多的部分（即正负极内的电解液残存部分），因此促进了该部分的劣化。这些情况都成为使非水电解液二次电池耐高速充放电循环的耐久性降低（电池电阻增大）的主要原因。

[0012] 本发明是基于上述发现，通过消除或缓和上述正负极间的电解液不足的这一途径，来使非水电解液二次电池耐高速充放电循环的耐久性提高的发明。

[0013] 即，由本发明提供的非水电解液二次电池是具有电极体的非水电解液二次电池，该电极体是正极片和负极片介由隔离片重合而成的。在上述隔离片的至少一侧的表面形成有多孔层，该多孔层具有无机填充剂和粘合剂。上述多孔层的表面形成凹凸，该凹凸面的最大高低差为 0.2μm～1.7μm。

[0014] 根据本发明的构造，在隔离片的至少一侧的表面上形成有多孔层，且该多孔层的表面形成凹凸，所以，能够在该凹凸面保持大量的非水电解液。因此，即使因高速充放电导致在正负极内浸入的非水电解液的一部分被挤到正负极的外部，也能够迅速地将凹凸面所保持的非水电解液向正负极内供给，从而使正负极内的电解液量迅速地恢复。由此，能够消除或缓和高速充放电导致的正负极内的电解液不足，能够使耐充放电循环的耐久性提高。

[0015] 优选地，上述凹凸面的最大高低差为 0.2μm～1.7μm。若凹凸面的最大高低差低于 0.2μm，则凹凸面的保液功能降低，存在无法得到上述那样的循环耐久性提高效果的情况。另外，若凹凸面的最大高低差高于 1.7μm，则正负极间的电解液量的平衡被打破，电池反应变得不均匀。因此，反而导致循环耐久性降低倾向。

[0016] 在这里公开的一个优选的方式中，上述多孔层，作为上述无机填充剂具有由无机金属化合物形成的粒子，在上述金属化合物粒子的粒度分布（体积基准）中，累积 10% 的粒径 D10 为 0.2μm 以上。若金属化合物粒子的累积 10% 的粒径 D10 过小，则由于通过粒径小的微小的金属化合物粒子的集合形成多孔层，所以，金属化合物粒子间的结合弱，多孔层的耐久性降低。因此，受到伴随高速充放电进行的电极体的膨胀收缩所产生的压力后，凹凸面容易损毁，存在无法得到上述那样的循环耐久性提高效果的情况。

[0017] 另外，优选地，在上述金属化合物粒子的粒度分布（体积基准）中，累积 90% 的粒径 D90 为 4μm 以下。若通过这样的粒度分布窄的粒径整齐的金属化合物粒子的集合形成多孔层，则金属化合物粒子间的结合力强，多孔层的耐久性进一步提高。因此，即使受到伴随高速充放电进行的电极体的膨胀收缩所产生的压力，凹凸面也难以损毁，能够更可靠地得到上述那样的循环耐久性提高效果。

[0018] 在这里公开的一个优选的方式中，上述金属化合物粒子为氧化铝或氧化铝水合物。由于这些金属化合物粒子的摩氏硬度高，所以，从利用该粒子形成的多孔层的耐久性提高这点考虑尤其优选。

[0019] 在这里公开的一个优选的方式中，上述多孔层中的粘合剂含有比例，在将该多孔质层中所包含的固体成分量（典型地是无机填充剂、粘合剂和其他的多孔层形成成分（例如增粘剂）的合计量）作为 100 质量％时，为 1.5 质量％～3 质量％。由此，能够容易地将凹凸面的最大高低差控制在这里公开的优选的范围内。

[0020] 在这里公开的一个优选的方式中，上述多孔层形成在上述隔离片的与负极片相对的表面，该多孔层的凹凸面至少形成在与该负极片的包含负极活性物质的负极活性物质层相对的位置上。负极片的包含负极活性物质的负极活性物质层，容易发生因高速充放电导

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致的电解液不足。因此，将多孔层的凹凸面形成在与负极活性物质层相对的位置上尤其有用。

[0021] 这里公开的任一种非水电解液二次电池，具有与作为搭载在车辆上的电池相适的性能（例如能够得到高输出），尤其具有耐高速充放电的良好耐久性。因此，根据本发明，能够提供具有这里公开的任一种非水电解液二次电池的车辆。尤其是，能够提供一种车辆（例如汽车），其具有该非水电解液二次电池作为动力源（典型地，混合动力车或电动车的动力源）。

[0022] 作为这里公开的技术的优选的适用对象例示有，被想成能够在包含 50A 以上（例如 50A～250A）进而 100A 以上（例如 100A～200A）的高速放电的充放电循环下使用的非水电解液二次电池；理论容量为 1Ah 以上（进而 3Ah 以上）的大容量型且被想成能够在包含 10C 以上（例如 10C ～ 50C）进而 20C 以上（例如 20C～40C）的高速放电的充放电循环下使用的非水电解液二次电池等。

附图说明

[0023] 图 1 是示意地表示本发明的一个实施方式的锂二次电池的侧视图。

[0024] 图 2 是图 1 的 II － II 线剖视图。

[0025] 图 3 是示意地表示本发明的一个实施方式的锂二次电池的电极体的图。

[0026] 图 4 是表示本发明的一个实施方式的锂二次电池的主要部分的放大剖视图。

[0027] 图 5 是用于说明一个试验例的膜电阻的测定方法的图。

[0028] 图 6 是示意地表示具有本发明的一个实施方式的锂二次电池的车辆的侧视图。

具体实施方式

[0029] 以下，边参照附图，边说明本发明的实施方式。在以下的附图中，对发挥相同作用的部件、部位标注相同的标记进行说明。此外，各图中的尺寸关系（长度、宽度、厚度等）并不反映实际的尺寸关系。另外，对于本说明书中特别提到的事项以外的事项，如果是在实施本发明时所必要的事项（例如，具有正极以及负极的电极体的构造以及制法、隔离片或电解质的构造以及制法、非水电解液二次电池以及其他的电池的构筑所涉及的一般的技术等），则能够基于该领域的现有技术、作为本领域技术人员的设计事项进行把握。

[0030] 并不意图进行特殊限定，但以下以将卷绕的电极体（卷绕电极体）和非水电解液装入圆筒型的容器中的形态的非水电解液锂二次电池（锂离子电池）为例对本发明进行详细地说明。

[0031] 将本发明的一个实施方式的锂离子电池的概要构造表示在图 1～3 中。该锂离子电池 100 具有以下构造，即长条状的正极片 10 和长条状的负极片 20 介由长条状的隔离片 40 而卷绕的形态的电极体（卷绕电极体）80，与图中未示出的非水电解液一起，被装入能够装纳该卷绕电极体 80 的形状（圆筒型）的容器 50 中。

[0032] 容器 50 具有：上端开放的有底圆筒状的容器主体 52、用于封闭其开口部的盖体 54。作为构成容器 50 的材质，优选使用铝、钢、镀 Ni 的 SUS 等的金属材料（本实施方式中为镀 Ni 的 SUS）。或者，还可以为由 PPS、聚酰亚胺树脂等的树脂材料成型而成的容器 50。在容器 50 的上表面（即盖体 54）上，设有与卷绕电极体 80 的正极 10 电连接的正极端子 70。

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在容器 50 的下表面上，设有与卷绕电极体 80 的负极 20 电连接的负极端子 72（本实施方式中由容器主体 52 兼任。）。在容器 50 的内部，卷绕电极体 80 和图中未示出的非水电解液一起被装纳。

[0033] 本实施方式的卷绕电极体 80，除后述的隔离片 40 的构造以外，与通常的锂离子电池的卷绕电极体相同，如图 3 所示，在对卷绕电极体 80 进行组装的前阶段，具有长条状（带状）的片结构。

[0034] 正极片 10 具有在长条片状的箔状的正极集电体 12 的两面保持有包含正极活性物质的正极活性物质层 14 的结构。不过，正极活性物质层 14 没有附着在沿正极片 10 的宽度方向的端边延伸的一边缘（图中为下侧的边缘部分）上，而是使正极集电体 12 以一定的宽度露出、形成正极活性物质层非形成部。

[0035] 负极片 20 也与正极片 10 同样地，具有在长条片状的箔状的负极集电体 22 的两面保持有包含负极活性物质的负极活性物质层 24 的结构。不过，负极活性物质层 24 没有附着在沿负极片 20 的宽度方向的端边延伸的一边缘（图中为上侧的边缘部分）上，而是使负极集电体 22 以一定的宽度露出、形成负极活性物质层非形成部。

[0036] 在制作卷绕电极体 80 时，如图 3 所示，正极片 10 和负极片 20 介由隔离片 40 层叠。此时，以使正极片 10 的正极活性物质层非形成部分和负极片 20 的负极活性物质层非形成部分分别从隔离片 40 的宽度方向的两侧伸出的方式，使正极片 10 和负极片 20 在宽度方向上稍错开重合。通过对这样重合的层叠体进行卷绕，就能够制作卷绕电极体 80。

[0037] 在卷绕电极体 80 的卷绕轴方向的中央部分，形成有卷绕芯部分 82（即正极片 10 的正极活性物质层 14、负极片 20 的负极活性物质层 24 和隔离片 40 紧密层叠的部分）。另外，在卷绕电极体 80 的卷绕轴方向的两端部，正极片 10 以及负极片 20 的电极活性物质层非形成部分分别从卷绕芯部分 82 伸向外方。在该正极侧伸出部分（即正极活性物质层 14 的非形成部分）84 以及负极侧伸出部分（即负极活性物质层 24 的非形成部分）86 上，分别附设有正极引线端子 74 以及负极引线端子 76，并分别与上述的正极端子 70 以及负极端子 72（这里由容器主体 52 兼任。）电连接。

[0038] 构成该卷绕电极体 80 的构成要素，除了隔离片 40 以外，可以与以往的锂离子电池的卷绕电极体同样，没有特别限制。例如，正极片 10 能够通过向长条状的正极集电体 12 上赋予以锂离子电池用正极活性物质为主要成分的正极活性物质层 14 而形成。作为正极集电体 12，可以很好地使用铝箔、以及其他适合正极的金属箔。作为正极活性物质，能够使用一直以来锂离子电池所使用的物质中的一种或两种以上，没有特别限定。作为这里公开的技术的优选的使用对象，能够列举以锂镍氧化物（$LiMn_2O_4$）、锂钴氧化物（$LiCoO_2$）、锂锰氧化物（$LiNiO_2$）等作为构成金属元素含有锂和过渡金属元素的氧化物（锂过渡金属氧化物）作为主要成分的正极活性物质。

[0039] 负极片 20 能够通过向长条状的负极集电体 22 上赋予以锂离子电池用负极活性物质为主要成分的负极活性物质层 24 而形成。作为负极集电体 22，能够很好地使用铜箔以及其他的适合负极的金属箔。负极活性物质能够使用一直以来锂离子电池所使用的物质中的一种或两种以上，没有特别限定。作为优选例，能够列举石墨碳、无定形碳等的碳系材料、含锂过渡金属氧化物、过渡金属氮化物等。

[0040] 作为在正负极片 10、20 间所使用的优选的隔离片 40，能够列举由多孔质聚烯烃系

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树脂构成的。例如，优选使用合成树脂制（例如聚乙烯等的聚烯烃制）多孔质隔离片。在该隔离片 40 中含浸有非水电解液。

[0041] 这里，在本实施方式中，如图 3 所示，在构成卷绕电极体的隔离片 40 的至少一侧的表面上形成有多孔层 42。在本实施方式中，多孔层 42 形成在隔离片的与负极片 20 相对的表面上。多孔层 42 由无机填充剂和粘合剂构成，通过粘合剂使无机填充剂之间以及无机填充剂和隔离片之间结合在一起。

[0042] 这样在隔离片的与负极片 20 相对的表面上形成多孔层 42，由此，能够抑制内部短路时的发热。即，可以想到在异物混入卷绕电极体内从而发生微小的内部短路时，则该热会导致隔离片 40 收缩，内部短路扩大（进而电池发热），但通过这样设置多孔层 42，能够防止内部短路的扩大从而抑制发热。

[0043] 构成多孔层 42 的无机填充剂，优选使用具有耐热性、且在电池的使用范围内电化学性质稳定的材料。作为这样的无机填充剂，能够列举出由无机金属化合物形成的粒子。作为优选例，例示出氧化铝（Al_2O_3）、氧化铝水合物（例如勃姆石（$Al_2O_3 \cdot H_2O$））、氢氧化镁（$Mg(OH)_2$）、碳酸镁（$MgCO_3$）等。能够使用这些无机金属化合物材料中的一种或两种以上。其中，由于氧化铝或氧化铝水合物的摩氏硬度高，所以，在能够提高多孔层的耐久性方面优选。

[0044] 上述多孔层 42 所使用的粘合剂是用于将无机填充剂结合在一起的粘合剂，构成该粘合剂的材料本身没有特别限定，能够大范围地使用各种材料。作为优选例，能够列举丙烯酸系树脂。作为丙烯酸系树脂，优选使用将丙烯酸、甲基丙烯酸、丙烯酰胺、甲基丙烯酰胺、丙烯酸 2- 羟乙酯、甲基丙烯酸 2- 羟乙酯、甲基丙烯酸酯、甲基丙烯酸甲酯、丙烯酸乙基己酯、丙烯酸丁酯等单体一种聚合而成的均聚物。另外，丙烯酸系树脂还可以为将两种以上的上述共聚单体聚合而成的共聚物。而且，还可以是将上述均聚物及共聚物的两种以上进行混合后的材料。除了上述的丙烯酸系树脂，还能够使用聚偏氟乙烯、聚四氟乙烯（PTFE）、聚丙烯腈、聚甲基丙烯酸甲酯等。

[0045] 接下来，同图 4 一起对本实施方式的卷绕电极体 80 进行详细说明。图 4 是放大地表示沿本实施方式的卷绕电极体 80 的卷绕轴切出的截面的一部分的示意剖视图，示出了隔离片 40、形成在该隔离片 40 的表面上的多孔层 42、与该多孔层 42 相对的负极片 20。

[0046] 如图 4 所示，负极片 20 中的负极活性物质层 24 由负极活性物质粒子 26 和图中未示出的粘合剂构成，通过粘合剂将负极活性物质粒子 26 之间以及负极活性物质粒子 26 和负极集电体 22 之间结合在一起。在相邻的负极活性物质粒子 26 之间，在没有被粘合剂粘结的部位形成多个孔隙 28，在该孔隙 28 中保持有非水电解液（即非水电解液渗入负极活性物质层内）。

[0047] 这里，以往的锂二次电池，若以车辆动力源用的锂二次电池所想象那样的高速连续反复进行短时间（脉冲状）的放电和充电，则存在浸入负极活性物质层 24 内的非水电解液的一部分被向负极活性物质层 24 的外部挤出，负极活性物质层 24 内的电解液量减少到必要量以下（即发生电解液枯竭）的情况。

[0048] 这样，若在负极活性物质层 24 内发生电解液枯竭，则由于在充放电时负极活性物质层 24 内的电解液量不足，作为电池整体的高速充放电性能降低。另外，在电解液量相对较多的部分（即负极活性物质层 24 内的电解液残存部分）中，由于电池反应集中，促进了

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该部分的劣化。这些情况都能够成为使锂二次电池耐高速充放电循环的耐久性降低（使电池电阻增大）的要因。

[0049] 对此，在本实施方式中，在隔离片 40 的表面形成有具有无机填充剂和粘合剂的多孔层 42。多孔层 42 的表面形成凹凸，该凹凸面 42a 的最大高低差为 0.2μm~1.7μm。在本实施方式中，多孔层 42 形成在隔离片 40 的与负极片 20 相对的表面，该多孔层 42 的凹凸面 42a 至少形成在与该负极片 20 中的包含负极活性物质的负极活性物质层 24 相对的位置上。

[0050] 根据该构造，在隔离片 40 的与负极片 20 相对的表面上形成有多孔层 42，并且，该多孔层 42 的表面形成凹凸，所以，在该凹凸面 42a 的凹部 44 中能够保持大量的非水电解液。因此，即使因高速充放电导致负极活性物质层 24 内所浸入的非水电解液的一部分被挤到负极活性物质层 24 的外部，也能够使保持在凹凸面 42a 的凹部 44 中的非水电解液迅速供给负极活性物质层 24，能够使负极活性物质层内的电解液量迅速恢复。由此，能够消除或缓和因高速充放电引起的负极活性物质层内的电解液不足，能够使耐充放电循环的耐久性提高。

[0051] 优选地，上述凹凸面的最大高低差 δ 为 0.2μm~1.7μm。凹凸面的最大高低差 δ 若低于 0.2μm，则凹凸面的保液功能降低，存在不能得到上述那样的循环耐久性提高效果的情况。另外，若凹凸面的最大高低差 δ 高于 1.7μm，则正负极间的电解液量的平衡被打破，电池反应变得不均匀。因此，反而存在使循环耐久性降低的倾向。凹凸面的最大高低差 δ 大致为 0.2μm~1.7μm 比较适当，优选为 0.3μm~1.5μm，尤其优选 0.5μm~1.5μm。

[0052] 此外，优选地，上述多孔层 42 的厚度（包含凹凸面的最大厚度）d 可以大致为 2μm~50μm。若多孔层 42 过厚，则由于多孔层本身作为电阻成分发挥作用，会使循环耐久性有降低倾向。另外，若多孔层 42 过薄，则存在无法得到前述的内部短路时的发热抑制效果的情况。多孔层的厚度 d 大致为 2μm~50μm 是适当的，优选为 2μm~10μm，尤其优选为 3μm~7μm。

[0053] 另外，优选地，多孔层 42 的孔隙率为大致 40%~70%。若多孔层 42 的孔隙率过小，则由于多孔层本身作为电阻成分发挥作用，会导致循环耐久性有降低倾向。另外，若多孔层 42 的孔隙率过大，则存在无法得到前述的内部短路时的发热抑制效果的情况。此外，上述孔隙率能够通过例如由电子天平测定的多孔层的质量、其表观体积（例如通过 SEM 观察所测定的多孔层的厚度 × 面积）以及无机填充剂、粘合剂及其他多孔层构造成分的真密度经计算求出。

[0054] 上述凹凸面的最大高低差 δ 能够通过改变该多孔层所使用的金属化合物粒子的粒径尺寸（平均粒径、粒度分布（宽或窄））来调整。一般若粒子尺寸增大，则其充填效率降低，因此存在凹凸面的最大高低差增大的倾向。因此，通过改变金属化合物粒子的粒径尺寸（平均粒径、粒度分布），能够控制凹凸面的最大高低差。即，通过适当选择金属化合物粒子的粒径尺寸（平均粒径、粒度分布），能够形成凹凸面的最大高低差满足 0.2μm ≤ δ ≤ 1.7μm 的多孔层。

[0055] 虽没有特别限定，但金属化合物粒子的基于激光衍射、散射法的平均粒径 D50 优选为大致 0.4μm~2μm。由此，能够容易地将凹凸面的最大高低差 δ 控制在这里所公开的优选的范围内。

[0056] 另外，优选地，上述金属氧化物粒子的基于激光衍射、散射法测定的粒度分布（体

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积基准）中，累积 10% 的粒径 D10 为 0.2μm 以上。金属化合物粒子的累积 10% 的粒径 D10 若过小，则由于通过粒径小的微小的金属化合物粒子的集合形成多孔层 42，所以，金属化合物粒子间的结合弱，多孔层 42 的耐久性低。因此，受到伴随高速充放电的卷绕电极体的膨胀收缩所产生的压力时，凹凸面 42a 容易损毁，存在无法得到上述那样的循环耐久性提高效果的情况。金属化合物粒子的累积 10% 的粒径 D10 为大致 0.2μm 以上是适当的，优选为 0.24μm 以上，特别优选为 0.3μm 以上。

[0057] 另外，优选地，上述金属氧化物粒子的基于激光衍射、散射法测定的粒度分布（体积基准）中，累积 90% 的粒径 D90 为 4μm 以下。若通过这样粒度分布窄的粒径整齐的金属化合物粒子的集合来形成多孔层 42，则金属化合物粒子间的结合强，多孔层 42 的耐久性进一步提高。因此，即使受到伴随高速充放电进行的卷绕电极体的膨胀收缩所产生的压力，凹凸面 42a 也难以损毁，能够更可靠地得到上述那样的循环耐久性提高效果。金属化合物粒子的累积 90% 的粒径 D90 大致为 4μm 以下是适当的，优选为 3.5μm 以下，特别优选为 2.9μm 以下。

[0058] 作为实现能够满足这里公开的优选的最大高低差 δ 的值的凹凸面的其他的方法，能够列举适当选择形成多孔层时的形成条件的方法。例如，多孔层通过以下方式得到，即、将使金属氧化物粒子、粘合剂、其他的多孔层形成成分（例如增粘剂）分散在适当的溶剂中，将得到的多孔层形成用涂料涂布在隔离片的单面或两面上后，通过干燥风对该涂布物进行干燥，从而形成。该情况下，通过选择上述干燥温度以及干燥风速等的干燥条件，能够控制凹凸面的最大高低差 δ。即，通过适当选择干燥温度以及干燥风速等的干燥条件，能够形成凹凸面的最大高低差 δ 满足 0.2μm ≤ δ ≤ 1.7μm 的多孔层。虽无特别限定，但上述干燥温度可以大致设在 40℃以上（例如 40℃～80℃）。另外，上述干燥风速可以大致设在 17m/s 以上（例如 17m/s～22m/s）。由此，能够容易地将凹凸面的最大高低差控制在这里所公开的优选的范围内。

[0059] 此外，作为将凹凸面的最大高低差 δ 调整在适当的范围内的方法，能够列举改变上述多孔层形成用涂料的固体成分率以及粘合剂量的方法。若多孔层形成用涂料的固体成分率以及粘合剂量增多，则粘度增大，所以，涂布面的平滑性恶化。因此，凹凸面的最大高低差 δ 有增大倾向。因此，通过改变多孔层形成用涂料的固体成分率以及粘合剂量，能够控制凹凸面的最大高低差 δ。即，通过适当选择多孔层形成用涂料的固体成分率以及粘合剂量，能够形成凹凸面的最大高低差 δ 满足 0.2μm ≤ δ ≤ 1.7μm 的多孔层。虽无特别限定，但多孔层形成用涂料的固体成分率优选约为 40 质量％以上（典型地为 40～50 质量％）。另外，粘合剂的含有比例，在将多孔层形成用涂料中所包含的固体成分量（典型地是无机填充剂、粘合剂和其他的多孔层形成成分的合计量）作为 100 质量％时，优选约为 1.5 质量％以上（典型地为 1.5～4.5 质量％）。由此，能够容易地将凹凸面的最大高低差控制在这里所公开的优选的范围内。此外，控制上述的凹凸面的最大高低差 δ 的方法，能够分别单独或组合使用。

[0060] 此外，作为上述多孔层形成用糊剂所使用的溶剂，能够列举 N- 甲基吡咯烷酮（NMP）、吡咯烷酮、甲基乙基酮、甲基异丁基酮、环己酮、甲苯、二甲基甲酰胺、二甲基乙酰胺等有机系溶剂或它们中两种以上的组合。或者，还可以为水或以水为主体的混合溶剂。作为构成该混合溶剂的除水以外的溶剂，能够适当地选择使用能够与水均相混合的有机溶剂

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（低级醇、低级酮等）的一种或两种以上。

[0061] 另外，上述多孔层形成用涂料，除了无机填充剂和粘合剂以外，能够含有根据需要而能使用的一种或两种以上的材料。作为这样的材料的例子，能够列举发挥多孔层形成用涂料的增粘剂作用的聚合物。作为发挥增粘剂作用的聚合物，例如优选使用羧甲基纤维素（CMC）。该增粘剂的含有比例，在将多孔质层形成用涂料所含有的固体成分量作为 100 质量％时，优选约为 1.5 质量％以下，还优选约为 1 质量％以下（例如约 0.5～1 质量％）。

[0062] 将这样的多孔层形成用涂料涂布在隔离片 40 的表面上，并通过干燥，在隔离片 40 的表面形成多孔层 42。此时，以能够实现上述最大高低差 δ 的方式设定多孔层形成用涂料中所含有的无机填充剂的粒径（粒度分布）、粘合剂量、固体成分率及 / 或使多孔层形成用涂料干燥时的干燥条件（例如，干燥温度以及干燥风速的干燥条件），并根据该设定的条件形成多孔层 42 即可。由此，能够形成凹凸面的最大高低差 δ 满足 $0.2\mu m \leq \delta \leq 1.7\mu m$ 的多孔层。

[0063] 在这样将多孔层 42 形成在隔离片 40 的表面上后，将正极片 10 和负极片 20 介由两片隔离片卷绕，制作卷绕电极体 80。而且，将卷绕电极体 80 装入容器主体 52 中，向该容器主体 52 内配置（注入）适当的非水电解液。作为在容器主体 52 内与上述卷绕电极体 80 一起被装入的非水电解液，能够使用与以往的锂离子电池所使用的非水电解液同样的非水电解液，没有特别限定。该非水电解液，典型地具有在适当的非水溶剂中含有支持电解质的组成。作为上述非水溶剂，例如能够使用碳酸亚乙酯（EC）、碳酸甲乙酯（EMC）、碳酸二甲酯（DMC）、碳酸二乙酯（DEC）、碳酸亚丙酯（PC）等。另外，作为上述支持电解质，例如，优选使用 $LiPF_6$、$LiBF_4$、$LiAsF_6$、$LiCF_3SO_3$、$LiClO_4$ 等的锂盐。例如，能够优选使用如下非水电解液：使以 3 ：4 ：3 的体积比包含 EC 和 EMC 和 DMC 的混合溶剂中以约 1mol/ 升的浓度含有作为支持电解质的 $LiPF_6$。

[0064] 将上述非水电解液与卷绕电极体 80 一起装入容器主体 52 中，并通过盖体 54 将容器主体 52 的开口部密封，由此，完成本实施方式的锂离子电池 100 的构建（组装）。此外，容器主体 52 的密封程序以及电解液的配置（注入）程序能够与以往的锂离子电池的制造中进行的手法同样地进行。之后，进行该电池的调节（初期充放电）。还可以根据需要进行抽气、品质检查等的工序。

[0065] 以下，说明与本发明相关的试验例，但并不意味着将本发明限定在以下的试验例所示的内容中。

[0066] ＜试验例 1 ：无机填充剂的粒度分布调整＞

[0067] 利用气流粉碎机（ホソカワミクロン公司制）以风压 0.2MPa 将作为无机填充剂的金属化合物粉末粉碎 5 分钟，利用气流式粉体分级装置（クマエンジニアリング公司制）分级为 4μm 以下。通过激光衍射、散射式粒度分布测定装置（日机装公司制）测定得到的金属化合物粉末的粒度分布 D10、D90。

[0068] 另外，本试验中，如表 1 所示，使用碳酸镁、氢氧化镁、勃姆石、α－氧化铝、二氧化钛这 5 种金属化合物粉末，以上述顺序制作粒度分布（体积基准）中的累积 10％径 D10 以及累积 90％径 D90 各不相同的金属化合物粉末（试样 1～15）。

[0069] 【表 1】

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	多孔层					多孔层形成用糊剂				隔离片			评价试验		
	最大高低差δ [μm]	最大厚度 [μm]	填充剂的粒径(D10) [μm]	填充剂的粒径(D90) [μm]	填充剂的种类	固体成分率 [%]	粘合剂量 [%]	干燥温度 [℃]	干燥风速 [m·s⁻¹]	基材的种类	基材的孔隙率 [%]	基材的厚度 [μm]	膜电阻 [Ω]	电阻增加率 [%]	安全性
试样1	0.2	3.5	0.2	4	碳酸镁	40	1.5	40	17.2	PE	47	20	1.6	13	○
试样2	0.3	4	0.22	3.8	氢氧化镁	40	1.5	40	17.8	PE	47	20	1.4	11	○
试样3	0.5	4.5	0.24	3.5	勃姆石	41	1.8	45	18.6	PE	47	20	1.1	5.5	○
试样4	0.5	4.5	0.23	3.6	α－氧化铝	41	1.8	45	18.6	PE	47	20	1.2	6	○
试样5	0.75	4.7	0.25	3.4	α－氧化铝	41	1.9	70	18.9	PP/PE/PP	47	20	1.08	5	○
试样6	0.8	5	0.26	3.2	勃姆石	41	2	75	19.1	PP/PE/PP	47	20	1.05	4.8	○
试样7	1	5.5	0.3	2.9	氧化铝	42	2.1	80	19.4	PP/PE/PP	47	20	1.02	4	○
试样8	1.2	6	0.33	2.7	氧化铝	42	2.3	80	21	PP/PE/PP	47	20	0.97	3.5	○
试样9	1.5	6.5	0.35	2.5	勃姆石	43	2.5	80	21.3	PP/PE/PP	47	20	1	2	○
试样10	1.7	7	0.38	2.3	氢氧化镁	43	2.7	65	21.6	PP/PE/PP	47	20	1.2	10	○
试样11	1.7	7.2	0.37	2.4	二氧化钛	43	2.6	65	21.5	PP/PE/PP	47	20	1.1	9	○
试样12	0.1	9	0.1	6	二氧化钛	38	1	60	15.6	PP/PE/PP	47	20	2.2	230	×
试样13	0.12	4.3	0.15	4.1	α－氧化铝	38	1	35	16.0	PP/PE/PP	47	20	2.1	260	×
试样14	2	10	0.05	5	二氧化钛	38	1.2	30	15.6	PE	47	20	2.3	260	×
试样15	2.1	3.9	0.48	2	α－氧化铝	50	3.2	60	22.0	PP/PE/PP	47	20	2.4	310	×

[0071] ＜试验例 2：多孔层形成用涂料的调制＞

[0072] 利用上述试验例 1 制作的各种金属化合物粉末调制多孔层形成用涂料。具体来说，对于试样 1，准备作为无机填充剂的碳酸镁粉末、丙烯酸系粘合剂水溶液（固体成分率 45 质量％）、作为增粘剂的羧甲基纤维素（CMC）粉末，使无机填充剂、粘合剂和增粘剂的质量比为 97.8：1.5：0.7，以固体成分率成为约 40 质量％的方式在水中混合。通过高速搅拌分

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散机（クレアミックス;M テクニック公司制）对该混合物以 15000rpm 的速度预混炼 5 分钟，然后，以 20000rpm 的速度正式混炼 15 分钟，由此，调制多孔层形成用涂料。

[0073] 另外，对于试样 2~15，与试样 1 同样，不过，使多孔层形成用涂料的固体成分率和粘合剂量（粘合剂占多孔层形成用涂料中的总固体成分的含有比例）如表 1 那样不同，同时按上述顺序调制多孔层形成用糊剂。

[0074] ＜试验例 3：多孔层的形成＞

[0075] 利用上述试验例 2 制作的各种多孔层形成用涂料在长条状的隔离片 40（厚度 20μm）的单面通过凹版辊进行涂布，并通过干燥而形成多孔层 42。作为涂布条件，使隔离片的移动速度 A 为 3m/min，使凹版辊的旋转速度 B 为 3.8m/min，使凹版辊的旋转速度 B 相对隔离片的移动速度 A 的比率（速比＝A/B）为 1.27，以使多孔层形成用涂料的涂布量成为约 0.7mg/cm^2（固体成分基准）的方式进行调节。另外，上述干燥通过利用干燥风的热风干燥方式进行。具体来说，使干燥风的干燥温度以及干燥风速如表 1 那样各试样都不同，按上述顺序形成多孔层。作为隔离片，使用聚乙烯（PE）的单层结构或聚丙烯（PE）－聚乙烯（PE）－聚丙烯（PE）的 3 层结构。

[0076] 通过电子显微镜（SEM）观察上述得到的试样 1~15 的多孔层的截面，测定其表面凹凸（凹凸面）的最大高低差 δ。具体来说，进行取样，将基准长度 3cm 内的凹凸面的最高位置和最低位置之间的距离（间隔）作为最大高低差 δ。取样，在 TD 方向（横宽方向，Transverse Direction）上以均等间隔选择三个部位，在其 MD 方向（机器方向，Machine Direction）上以 3cm 基准长度的间隔选定三个部位（合计 9 个部位）。然后，对各基准长度 3cm 内的凹凸面的最大高低差 δ 进行测定，求出其平均值。

[0077] ＜试验例 4：膜电阻的测定＞

[0078] 利用没有上述试验例 3 制作的各种多孔层 42 的隔离片 40 制作锂二次电池（层合型单电池），测定其膜电阻（Rs）。具体来说，如图 5 所示，使多孔层 42 以及隔离片 40 中含浸非水电解液，并将其夹入面积 35mm^2、厚度 1mm 的两块铜板 62 之间，制作层合型单电池 60。作为非水电解液，使用使以 3:4:3 的体积比含有碳酸亚乙酯（EC）、碳酸二甲酯（DMC）和碳酸甲乙酯（EMC）的混合溶剂以约 1mol/ 升的浓度含有支持电解质 $LiPF_6$ 的非水电解液。然后，从铜板 62 的上下施加 50cN.m 的转矩压，并在 25℃下测定层合型单电池 60 的交流阻抗，从得到的 Cole－Cole 图读取膜电阻（Rs）。关于交流阻抗的测定条件，为交流施加电压 5mV、频率范围 10000Hz~1Hz。此外，上述单电池，以被两块铜板 62 夹持的隔离片为 1 片、2 片、3 片的方式分别制作。然后，通过交流阻抗法测定电阻值，将得到的单电池的电阻值相对于隔离片的片数作图，通过线性近似求出每一片隔离片的膜电阻（Rs）。

[0079] 从表 1 可知，关于凹凸面的最大高低差为 $0.2 \leqslant \delta \leqslant 1.7$ 的试样 1~11，膜电阻为 1.6Ω 以下，与试样 12~15 相比，膜电阻大幅度降低。尤其通过使最大高低差为 $0.5\mu m \leqslant \delta \leqslant 1.5\mu m$，能够实现 1.2Ω 以下极低的膜电阻。

[0080] ＜试验例 5：高速耐久性试验＞

[0081] 利用没有上述试验例 3 制作的各种多孔层 42 的隔离片 40 来构建锂二次电池，对其高速耐久性进行评价。锂二次电池以如下的方式制作。

[0082] 将作为正极活性物质的 $Li_{1.15}Ni_{0.35}Mn_{0.35}Co_{0.35}O_2$ 粉末和作为导电材料的乙炔黑 AB 和作为粘合剂的聚偏氟乙烯 PVdF 以这些材料的质量比为 88:10:2 的方式在 N- 甲基吡咯

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烷酮（NMP）中混合，并调制正极活性物质层用糊剂。将该正极活性物质层用糊剂以带状涂布在长条片状的铝箔（正极集电体 12）的两面并干燥，由此，制作在正极集电体 12 的两面设有正极活性物质层 14 的正极片 10。正极活性物质层用糊剂的涂布量以两面合起来约 17.2mg/cm^2（固体成分基准）的方式进行调节。

[0083] 另外，使作为负极活性物质的石墨粉末和作为粘合剂的丁苯橡胶 SBR 和作为增粘剂的羧甲基纤维素 CMC 以这些材料的质量比为 98.6 :0.7 :0.7 的方式在水中分散，从而调制负极活性物质层用糊剂。将该负极活性物质层用糊剂涂布在长条片状的铜箔（负极集电体 22）的两面，制作在负极集电体 22 的两面设有负极活性物质层 24 的负极片 20。负极活性物质层形成用糊剂的涂布量以两面合起来约 11.1mg/cm^2（固体成分基准）的方式进行调节。

[0084] 然后，将正极片 10 及负极片 20 介由两片隔离片 40 而卷绕，由此制作卷绕电极体 80。此时，以隔离片表面的多孔层 42 和负极片 20 相对的方式配置。将这样得到的卷绕电极体 80 与非水电解液一起装入电池容器 50 中（这里，使用 18650 型的圆筒型。），将电池容器 50 的开口部气密地封口。作为非水电解液，使用在以 3 :4 :3 的体积比含有碳酸亚乙酯 EC、碳酸甲乙酯 EMC 和碳酸二甲酯 DMC 的混合溶剂中以约 1mol/ 升的浓度含有支持电解质 $LiPF_6$ 的非水电解液。这样组装锂二次电池 100。然后，通过常用的方法进行初期充放电处理（调节）并得到评价用的锂二次电池。

[0085] 对由以上方式得到的锂二次电池分别作用反复以 20C 进行 10 秒钟的 CC 放电的充放电模式，进行充放电循环试验。具体来说，在室温（约 25℃）环境下，以 20C 进行 10 秒钟的 CC 放电，在停止 5 秒钟后，连续反复进行以 5C 进行 40 秒钟 CC 充电的充放电循环 10000 次。

[0086] 而且，根据上述充放电循环试验前的 IV 电阻（锂离子电池的初期的电阻）和充放电循环试验后的 IV 电阻算出电阻增加率。这里，充放电循环前后的 IV 电阻分别根据以 25℃、30C 进行脉冲放电时的放电 10 秒后的电压下降算出。此外，电阻增加率 (%) 通过［（充放电循环试验后的 IV 电阻－充放电循环试验前的 IV 电阻）/ 充放电循环试验前的 IV 电阻］×100 求出。将其结果表示在表 1 中。

[0087] 从表 1 可知，凹凸面的最大高低差低于 0.2 的试样 12、13，其电阻增加率超过 200%。另外，凹凸面的最大高低差超过 1.7 的试样 14、15，其电阻增加率也超过 200%。而凹凸面的最大高低差为 0.2 ≤ δ ≤ 1.7 的试样 1~11 的电池，即使在反复进行 10000 次高速充放电循环后，电阻也几乎不上升，电阻增加率显示为 15% 以下的低值。尤其，通过使最大高低差为 0.5μm ≤ δ ≤ 1.5μm，能够达成 6% 以下这样极低的电阻增加率。从该结果可以确认，通过使凹凸面的最大高低差为 0.2 ≤ δ ≤ 1.7（优选为 0.5μm ≤ δ ≤ 1.5μm），能够提高锂二次电池耐高速充放电的耐久性。

[0088] ＜试验例 6 ：异物内部短路试验＞

[0089] 与上述试验例 5 同样地制作锂二次电池，实施异物内部短路试验。异物内部短路试验是利用高度 0.2mm× 宽度 0.1mm 且各边 1mm 的 L 字形的镍制小片，依照 JISC8714 进行的。而且，对是否存在异常发烟的 NG 品进行调查。将结果表示在表 1 中。这里将没有发烟表示为○，将有发烟表示为 ×。

[0090] 如表 1 所示，凹凸面的最大高低差为 0.2 ≤ δ ≤ 1.7 的试样 1~11，完全没有导致

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异常发烟的电池，能够确认为安全性优良的电池。

[0091] 以上，通过优选的实施方式对本发明进行了说明，但这样的记载并非限定事项，当然能够进行各种改变。

[0092] 例如，在上述的实施方式中，示出了多孔层 42 形成在隔离片 40 的与负极片 20 相对的表面上的情况，但不限于此，还可以形成在隔离片的与正极片相对的表面（或隔离片的两面）上。

[0093] 另外，只要采用如下构造，即具有满足这里公开的优选的最大高低差 δ 的值的凹凸面的多孔层设在隔离片的表面上的构造即可，对所构建的锂二次电池的形状（外形、尺寸）没有特别限制。外包装可以为由层合膜等构成的薄片型，电池外装盒可以为圆筒形状或长方体形状的电池、或还可以为小型的纽扣形状。

[0094] 此外，这里公开的任一种锂二次电池 100，都具有与作为搭载在车辆上的电池相适的性能（例如能够得到高输出），尤其具有耐高速充放电的良好的耐久性。因此，根据本发明，如图 6 所示，能够提供具有这里公开的任一种锂二次电池 100 的车辆 1。尤其，能够提供一种车辆 1（例如汽车），其具有该锂二次电池 100 作为动力源（典型地，混合动力车或电动车辆的动力源）。

[0095] 另外，作为这里公开的技术的优选的使用对象可以列举出，被想成能够在包含 50A 以上（例如 50A～250A）进而 100A 以上（例如 100A～200A）的高速放电的充放电循环下使用的锂二次电池 100；理论容量为 1Ah 以上（进而 3Ah 以上）的大容量型且被想成能够在包含 10C 以上（例如 10C～50C）进而 20C 以上（例如 20C～40C）的高速放电的充放电循环下使用的锂二次电池等。

[0096] 工业上的可利用性

[0097] 根据本发明的构造，能够提供耐高速充放电的耐久性提高了的非水电解液二次电池。

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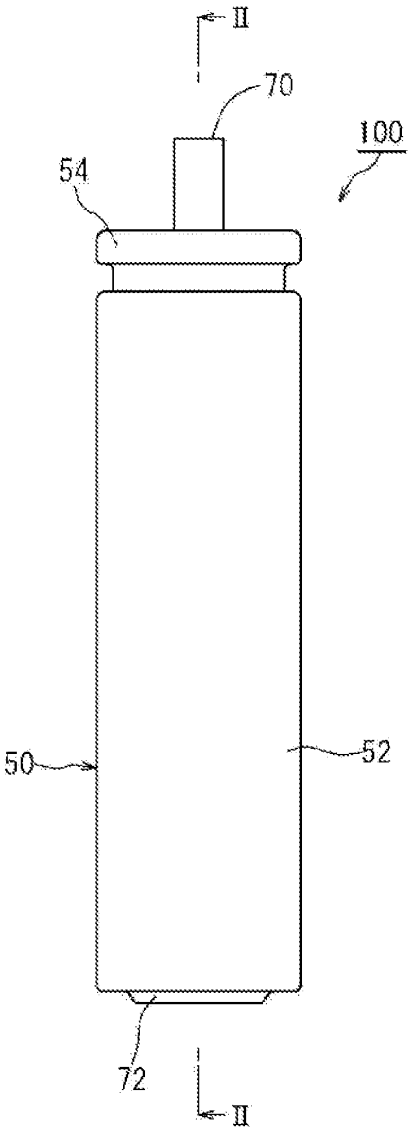


图 1

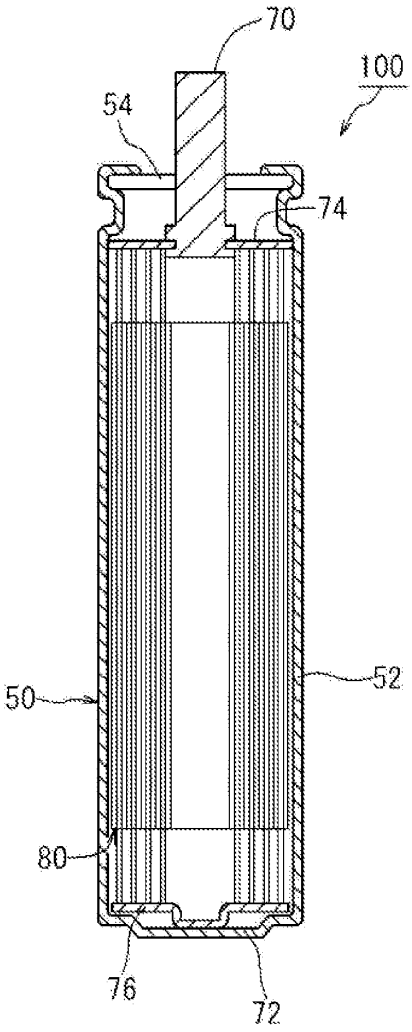


图 2

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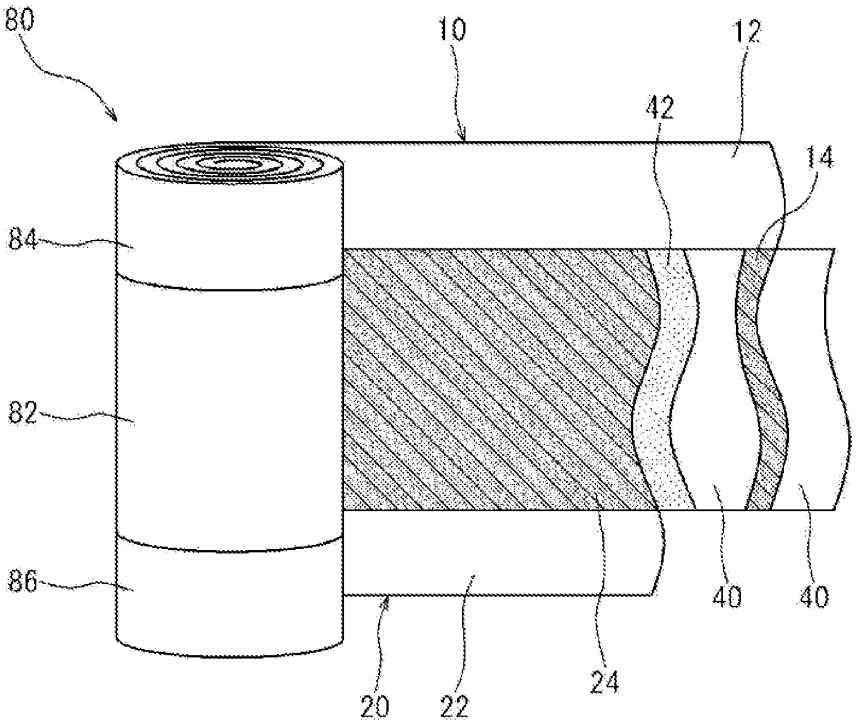


图 3

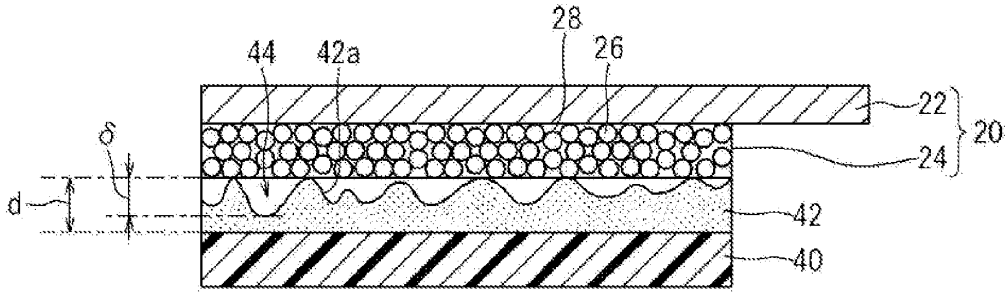


图 4

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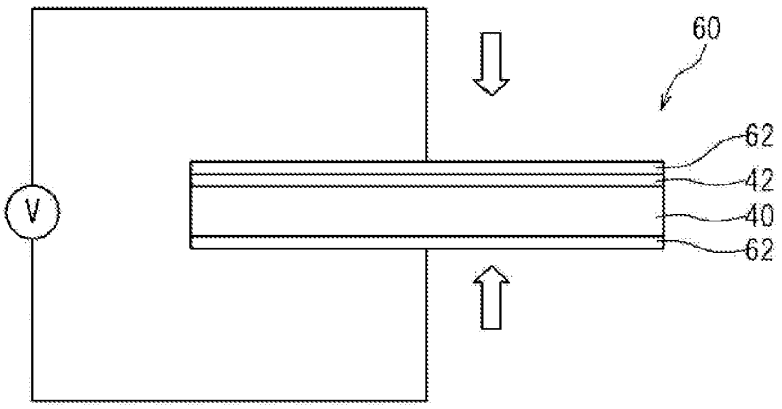


图 5

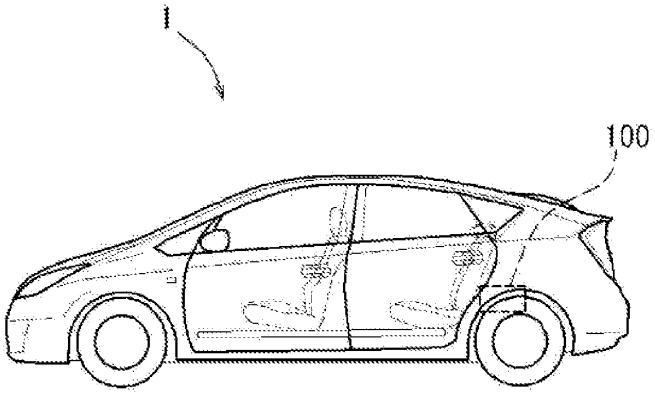


图 6

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Espacenet

CN103474602A Pore-forming ceramic isolating membrane of lithium ion battery and preparation method thereof

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CPC Y02E60/10 (EP);

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Pore-forming ceramic isolating membrane of lithium ion battery and preparation method thereof

Abstract

The invention discloses a pore-forming ceramic isolating membrane of a lithium ion battery. The pore-forming ceramic isolating membrane comprises an isolating membrane base material, wherein a porous ceramic coating is coated on single surface or double surfaces of the isolating membrane base material; the porous ceramic coating is formed by coating a sizing agent which contains nanometer ceramic powder, a binding agent as well as a pore-forming solvent on the isolating membrane base material, wherein dosage of the nanometer ceramic powder, the binding agent, a stabilizing agent and the pore-forming solvent in the sizing agent is respectively as follows in parts by weight: 88-93 parts of the nanometer ceramic powder, 4-6.5 parts of binding agent powder, 1-1.5 parts of the stabilizing agent, and 2-4 parts of the pore-forming solvent. According to the pore-forming ceramic isolating membrane of the lithium ion battery disclosed by the invention, an absorption rate of electrolyte is improved by improving a ceramic sizing agent, thereby facilitating transfer of lithium ions better, increasing inventory of the electrolyte in the battery and increasing hardness of the battery. Meanwhile, the problems that the ceramic layer is easy to drop on the isolating membrane and the coating thickness or the surface density is uneven are solved by the porous ceramic membrane coated by the novel sizing agent, and therefore, the safety performance of the battery is improved.

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DESCRIPTION CN103474602A

Pore-making ceramic isolation membrane for lithium ion battery and preparation method thereof

[0001]

Technical field

[0002]

The present invention relates to the technical field of lithium ion batteries, in particular to a lithium ion battery pore-forming ceramic isolation membrane and a coating method thereof.

[0003]

Background technique

[0004]

The fundamental reason for the burning or even explosion of lithium batteries is the thermal loss of control inside the battery. The short circuit of the positive and negative plates is a common problem, so the separator has an important isolation effect.

The isolation film has the function of isolating electrons and conducting ions in the lithium battery. A ceramic layer is coated on the isolation film. When the isolation film is damaged by foreign matter in the battery, the short-circuit point will not be enlarged due to heat at high temperature. Melting will not cause a large-area short circuit between the electrodes, which will cause the battery to burn or even explode.

As energy storage, electric vehicles, computers and other electrical appliances have continuously increased requirements for lithium-ion batteries, the single capacity and volume energy density of lithium-ion rechargeable batteries have continued to increase. It is also increasing accordingly.

When the battery is short-circuited internally, at high temperatures, the ceramic layer of the ceramic separator can maintain the complete skeleton structure of the separator, and will not lose the role of separating the positive and negative plates due to the melting of the separator substrate, resulting in a large-area short circuit of the positive and negative plates. .

[0005]

Common ceramic isolation membranes are single-layer or multi-layer PP, PE, PP/PE composite isolation membranes manufactured by dry or wet processes and coated with a ceramic layer to improve the safety performance of the battery, but the ceramic layer often sticks during use. Insufficient connection, insufficient liquid absorption speed, etc.

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Some ceramic isolation membranes add a polymer layer between the ceramic layer and the isolation membrane substrate layer. Although the liquid retention performance is improved, the ion channels of the battery are affected, and the thickness of the ceramic layer is not enough, and the safety performance is not high.

[0006]

Summary of the invention

[0007]

In order to overcome the shortcomings of the prior art, the purpose of the present invention is to provide a lithium-ion battery pore-forming ceramic isolation film to improve the safety performance, liquid absorption performance, liquid retention performance of the lithium battery, the adhesion performance of the porous ceramic layer and the lithium ion battery ion permeability.

[0008]

Another object of the present invention is to provide a method for preparing a pore-forming ceramic isolation membrane for lithium ion batteries, and the manufactured high-safety pore-forming ceramic isolation membrane can improve the safety performance of the lithium ion battery.

[0009]

In order to achieve the above objectives, the technical solutions adopted by the present invention are as follows:

[0010]

A pore-forming ceramic isolation membrane for lithium ion batteries includes an isolation membrane substrate, the isolation membrane substrate is coated with a porous ceramic layer on one or both sides, and the porous ceramic layer is formed by containing nano ceramic powder and a pore-forming solvent. And the binder slurry is coated by a letterpress printing machine. The amount of nano-ceramic powder, pore-forming solvent and binder in the slurry are respectively: 88-93 parts by weight of nano-ceramic powder, binder Parts 4-6.5, stabilizer 1-1.5 parts, pore-forming solvent 2-4 parts.

[0011]

The present invention can also be realized through the following schemes:

[0012]

As a preferred solution of the present invention, the amounts of nano-ceramic powder, binder, stabilizer and pore-forming solvent in the slurry are 91 parts, 5.5 parts, 1 part, and 2.5 parts, respectively.

[0013]

As a preferred solution of the present invention, the coating thickness of the porous ceramic layer of the pore-forming ceramic membrane is 3-5 μm.

In the present invention, the thickness of the porous ceramic layer is controlled within the above range, which improves the liquid retention capacity of the porous ceramic membrane and also further improves the safety performance of the battery; the preferred thickness of the porous ceramic layer is for a small battery (Single-cell capacity less than 5AH, mainly used for 3C products, etc.) The single-sided coating thickness of the porous ceramic layer is required to be 3-4μm, and large batteries (a single-cell capacity above 5AH, mainly used for power batteries, electric vehicle batteries, energy storage batteries, etc.)) The single-sided coating thickness of the porous ceramic layer is required to be 5μm.

[0014]

In order to control the thickness and uniformity of the coating, so as to achieve the purpose of controlling the quality of the isolation film, as a preferred solution of the present invention, the solid content of the slurry is 25-30%, and the slurry viscosity is

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40-50mpa·s .

When the slurry viscosity and solid content are in the above range, it is beneficial to the relief coater to control the coating thickness and uniformity.

[0015]

As a preferred solution of the present invention, the nano-ceramic powder is one or two of Al 2 O 3 or BaSO 4 that has been nano-treated and mixed in any ratio.

[0016]

In the present invention, the pore-forming solvent adopts a low-boiling solvent such as ethyl acetate; this low-boiling solvent is water-soluble and oil-soluble, is uniformly dispersed in the material, and has a low density, so it is firstly removed during the drying process. After evaporating off, tiny fine openings are formed on the surface of the ceramic layer. After the pore-forming isolation membrane is made into a battery, it provides more channels for electrolyte immersion.

The binder is polyacrylate, and the stabilizer is sodium carboxymethyl cellulose.

Further, in order to improve the adhesion of the porous ceramic layer, the average molecular weight of the stabilizer sodium carboxymethyl cellulose is about 650,000 to 1 million, and the average molecular weight of the adhesive polyacrylate is 300 to 1.2 million.

[0017]

As a preferred solution of the present invention, the isolation film substrate is one of dry or warm porous single-layer or multi-layer PP film, PE film or PP/PE composite isolation film. The porosity is 40% to 47%.

[0018]

A coating method for pore-forming ceramic isolation membranes for lithium ion batteries, the process steps are as follows:

[0019]

1) Ceramic nano-processing: the ceramic raw materials are nano-sized, baked and sieved, and the obtained nano-ceramic powder is ready for use;

[0020]

2) Slurry preparation: After dissolving the stabilizer with water according to the above ratio and stirring, add the obtained nano ceramic powder and stir, add the binder and the pore-forming solvent in turn, and continue the stirring reaction;

[0021]

3) Coating: The oven of the heating coater, the temperature of each section of the oven is gradually increased from front to back, the slurry is injected into the trough and coated on one or both sides of the isolation film substrate, and it is dried in the oven.

[0022]

In the above method, as a preferred embodiment, the temperature of the oven in step 1) is 80-90°C, and the baking time is 24-36 hours; the stirring speed in step 2) is 700-900r/min, and the stirring reaction time is For 1.5-2h.

[0023]

In the above method, as a preferred embodiment, the temperature range of each end of the oven in step 3) is 45-50°C.

[0024]

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Compared with the prior art, the beneficial effect of the present invention is that the pore-forming ceramic isolation membrane of the lithium-ion battery of the present invention reforms the ceramic slurry, and the pore-forming ceramic layer is more conducive to the rapid absorption of the electrolyte and the improvement of lithium ions. The transfer speed increases the retention of battery electrolyte and enhances the hardness of the battery; the porous ceramic membrane coated with this new formula slurry solves the problem that the ceramic layer is easy to fall off, coating thickness or areal density on the isolation membrane. The problem of unevenness.

The invention not only improves the safety performance of the battery, but also achieves the performance that cannot be achieved by the battery made of ordinary isolation film.

[0025]

The present invention will be further described in detail below in conjunction with the drawings and specific embodiments.

[0026]

Description of the drawings

[0027]

Fig. 1 is a schematic structural diagram of an embodiment of the present invention;

[0028]

Figure 2 is a schematic structural diagram of another embodiment of the present invention;

[0029]

Figure 3 is a comparison of the appearance of the isolation membrane substrate and the pore-forming ceramic membrane of the present invention, where (a) is the isolation membrane substrate and (b) is the pore-forming ceramic isolation membrane;

[0030]

Figure 4 is an electron micrograph of the pore-forming ceramic isolation membrane of the present invention;

[0031]

Figure 5 is a schematic diagram showing the comparison of electrochromic iron puncture between the pore-forming ceramic isolation membrane of the present invention and the ordinary isolation membrane, in which (c) is the ordinary isolation membrane, and (d) is the pore-forming ceramic isolation membrane;

[0032]

Fig. 6 is a photograph comparison of the wettability of an ordinary isolation membrane and the electrolyte of the pore-forming ceramic isolation membrane of the present invention, where (e) is an ordinary isolation membrane, and (f) is a pore-forming ceramic isolation membrane.

[0033]

Detailed ways

[0034]

As shown in FIG. 1, in one embodiment, the pore-forming ceramic isolation membrane for lithium-ion batteries of the present invention includes an isolation membrane substrate 1, and the isolation membrane substrate 1 is coated with a porous ceramic membrane 2 on both sides, The porous ceramic membrane is formed by coating a slurry containing nano-ceramic powder, a pore-forming solvent and a binder, and the amounts of nano-ceramic powder, pore-forming solvent and binder in the slurry are

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respectively in parts by weight: 88-93 parts of nano ceramic powder, 4-6.5 parts of binder, 1-1.5 parts of stabilizer, 2-4 parts of pore-forming solvent.

[0035]

As shown in Fig. 2, in another embodiment, the difference from the above solution is that the isolation membrane substrate 1 according to the present invention is coated with a porous ceramic layer 2 on one side.

[0036]

The following are specific examples of the present invention for preparing the pore-forming ceramic isolation membrane for lithium ion batteries.

[0037]

Example 1

[0038]

A pore-forming ceramic isolation membrane for lithium-ion batteries is prepared by the following method:

[0039]

1) Ceramic nanometerization treatment: Nanometerize the Al 2 O 3 raw material and bake it in an oven at 85°C for 36 hours, sieving, and the obtained nanometer ceramic powder is ready for use;

[0040]

2) Slurry preparation: Take 93.75 g of sodium carboxymethyl cellulose solution with 1.6% solid content, add 300 g of deionized water, and stir for 30 min at 800 r/min; then add 144 g of nano ceramic powder from step 1) at 800 r/min Stir at the speed of 3h; add 9g of polyacrylate, add 3g of pore-forming solvent ethyl acetate, and stir at 800r/min for 1.5 ~ 2h; use trace deionized water to adjust the slurry viscosity to 47mpa·s, and the slurry solid content is 27.8%;

[0041]

3) Coating: Debug the machine and heat up the oven. The temperature of each section of the coating machine is controlled within the range of 45 ~ 50℃. The temperature of each section of the oven is gradually increased from front to back; the slurry is fed into the trough for trial coating and drying After drying, test the thickness and areal density until the adjustment meets the requirements, and then start to coat the slurry on the PP isolation film substrate.

[0042]

Example 2

[0043]

A pore-forming ceramic isolation membrane for lithium-ion batteries is prepared by the following method:

[0044]

1) Ceramic nano-treatment: after the BaSO 4 raw material is nano-treated, baked in an oven at 85°C for 24 hours, sieved, and the obtained nano-ceramic powder is ready for use;

[0045]

2) Slurry preparation: Take 125 g of sodium carboxymethyl cellulose solution with a solid content of 1.6%, add 300 g of deionized water, and stir at 800 r/min for 30 min; then add 150 g of nano ceramic powder from step 1) at 800 r/min Stir at speed

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for 3h; add 10g of polyacrylate, 4g of pore-forming solvent ethyl acetate, and stir for 1.5 ~ 2h at 800r/min; adjust the slurry viscosity to 48mpa·s with trace deionized water; the slurry solid content is 27.5 %;

[0046]

3) Coating: Debug the machine and heat up the oven. The temperature of each section of the coating machine is controlled within the range of 45 ~ 50℃. The temperature of each section of the oven is gradually increased from front to back; the slurry is fed into the trough for trial coating and drying After drying, test the thickness and areal density until the adjustment meets the requirements, and then start to coat the slurry on the PE isolation film substrate.

[0047]

Example 3

[0048]

A pore-forming ceramic isolation membrane for lithium ion batteries is prepared by the following method:

[0049]

1) Ceramic nano-treatment: mix the raw materials Al 2 O 3 and BaSO 4 in a mass ratio of 1:1, then nano-treatment, bake in an oven at 85°C for 24 to 36 hours, sieving, and the resulting nano-ceramic powder is ready for use ;

[0050]

2) Slurry preparation: Take 93.75g of carboxymethyl cellulose solution with 1.6% solid content, add 300g of deionized water, stir at 800r/min for 30min; then add 145g of nano ceramic powder in step 1), at 800r/min Stir at speed for 3h; add 9g of polyacrylate, add 3.5g of pore-forming solvent ethyl acetate, and stir for 1.5 ~ 2h at 800r/min; adjust the slurry viscosity to 46mpa·s with trace deionized water; the solid content of the slurry is 27.3%;

[0051]

3) Coating: Debug the machine and heat up the oven. The temperature of each section of the coating machine is controlled within the range of 45 ~ 50℃. The temperature of each section of the oven is gradually increased from front to back; the slurry is fed into the trough for trial coating and drying After drying, the thickness and areal density are tested until the adjustment meets the requirements, and then the slurry is coated on the PE/PP composite isolation film substrate.

[0052]

Performance testing:

[0053]

1.Electric ferrochrome puncture test: lightly touch the puncture film test with an electric soldering iron (test condition: electric soldering iron temperature 390℃), the test results are shown in Diagram 5.

[0054]

The result of Fig. 5 shows that the diameter of the ordinary isolation membrane is significantly enlarged at the contact point; the contact point of the pore-forming ceramic membrane of the present invention is not enlarged.

It shows that when heat or fire is generated by a micro-short circuit inside the cell, the pore size of the ceramic isolation membrane will not continue to increase, thereby reducing the risk of combustion.

[0055]

2.Comparison of wettability: The same electrolyte was dropped on the common ceramic membrane and the pore-forming ceramic isolation membrane of the present invention at the same time (test temperature 27°C). The test results are shown in

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Figure 6.

[0056]

The result of Fig. 6 shows that the diffusion speed of the electrolyte on the ordinary ceramic membrane is significantly higher than the diffusion speed of the electrolyte on the pore-forming ceramic isolation membrane of the present invention in the same time.

It shows that the pore-forming ceramic isolation membrane of the present invention has good liquid absorption performance and ion permeability, that is, it has good wettability.

[0057]

3.Other performance tests, test results are shown in Table 1.

[0058]

Table 1

[0059]

[0060]

[0061]

Remarks: 1.

MD means longitudinal direction (length direction); TD means transverse direction (width direction)

[0062]

2.

This standard is the result of selecting a PE substrate with a ceramic layer thickness of 4μm on one side.

Different substrates will be different.

[0063]

The foregoing embodiments are only preferred embodiments of the present invention, and cannot be used to limit the scope of protection of the present invention. Any insubstantial changes and substitutions made by those skilled in the art on the basis of the present invention belong to the present invention. The scope of protection required.

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CLAIMS CN103474602A

1.

A pore-forming ceramic isolation membrane for lithium ion batteries, comprising an isolation membrane substrate, characterized in that: the isolation membrane substrate is coated with a porous ceramic layer on one or both sides, and the porous ceramic layer is formed by containing nano ceramic powder , Pore-forming solvent and binder slurry is coated on the isolation membrane substrate, the amount of nano-ceramic powder, binder and pore-forming solvent in the slurry in parts by weight are: nano-ceramic powder 88- 93 parts, 4-6.5 parts of binder, 1-1.5 parts of stabilizer, 2-4 parts of pore-forming solvent.

2.

The pore-forming ceramic isolation membrane for lithium-ion batteries according to claim 1, wherein the amounts of nano-ceramic powder, binder, stabilizer, and pore-forming solvent in the slurry are 91 parts, 5.5 parts, and 1 parts, respectively. Servings, 2.5 servings.

3.

The pore-forming ceramic isolation membrane for lithium ion batteries according to claim 1, wherein the thickness of the coated porous ceramic layer is 3-5 μm.

4.

The pore-forming ceramic separator for lithium ion batteries according to claim 1, wherein the solid content of the slurry is 25-30%, and the viscosity of the slurry is 40-50 mpa·s.

5.

The pore-forming ceramic isolation membrane for lithium ion batteries according to any one of claims 1-3, wherein the nano-ceramic powder is one or two of Al 2 O 3 or BaSO 4 that has undergone nano-treatment Mix in any ratio.

6.

The pore-forming ceramic isolation membrane for lithium ion batteries according to claim 1, wherein the pore-forming solvent is ethyl acetate; the binder is polyacrylate, and the stabilizer is carboxymethyl cellulose. sodium.

7.

The pore-forming ceramic isolation film for lithium ion batteries according to claim 1, wherein the isolation film substrate is one of a porous single-layer or multi-layer PP film, a PE film or a PP/PE composite isolation film, The porosity of the isolation film

substrate is 40% to 47%.

8.

A method for coating a pore-forming ceramic isolation membrane for lithium-ion batteries according to any one of claims 1-7, characterized in that the process steps are as follows:

1)

Nano-ceramic treatment: the ceramic raw materials are nano-sized, baked and sieved, and the obtained nano-ceramic powder is ready for use;

2)

Slurry preparation: After the stabilizer is dissolved in water and stirred according to the above ratio, the obtained nano ceramic powder is added and stirred, the binder and the pore-forming solvent are sequentially added, and the stirring reaction is continued;

3)

Coating: Heating the oven of the relief coater, gradually increase the temperature of each section of the oven from front to back, and feed the slurry into the trough to coat on one or both sides of the isolation film substrate, and then dry it.

9.

The coating method of the pore-forming ceramic isolation film for lithium ion batteries according to claim 8, wherein the temperature of the oven in step 1) is 80-90°C, and the baking time is 24-36 hours; in step 2) The stirring speed is 700-900r/min, and the stirring reaction time is 1.5-2h.

10.

The coating method of the pore-forming ceramic isolation membrane for lithium ion batteries according to claim 8, wherein the temperature range of each end of the oven in step 3) is 45-50°C.

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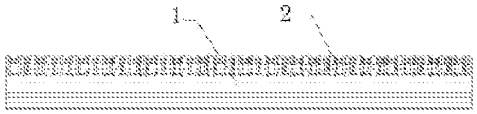
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(54)发明名称

一种锂离子电池造孔陶瓷隔离膜及其制备方法

(57)摘要

本发明公开了一种锂离子电池造孔陶瓷隔离膜,包括隔离膜基材,所述隔离膜基材单面或双面涂布有多孔陶瓷层,所述多孔陶瓷层是通过含有纳米陶瓷粉、粘结剂以及造孔溶剂的浆料涂布在隔离膜基材上而成,浆料中纳米陶瓷粉、粘结剂、稳定剂以及造孔溶剂的用量以重量份计分别为:纳米陶瓷粉 88-93 份,粘结剂份 4-6.5,稳定剂 1-1.5,造孔溶剂 2-4 份。本发明所述的锂离子电池造孔陶瓷隔离膜通过对陶瓷浆料改进,提高了电解液的吸收速度,更有利于锂离子的转移,增加了电池中电解液的保有量,增强了电池的硬度,同时,这种新的浆料涂布的多孔陶瓷膜解决了陶瓷层在隔离膜上易脱落、涂布厚度或面密度不均匀的问题,提高了电池的安全性能。



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1. 一种锂离子电池造孔陶瓷隔离膜，包括隔离膜基材，其特征在于：所述隔离膜基材单面或双面涂布有多孔陶瓷层，所述多孔陶瓷层是通过含有纳米陶瓷粉、造孔溶剂以及粘结剂的浆料涂布在隔离膜基材上而成，浆料中纳米陶瓷粉、粘结剂以及造孔溶剂的用量以重量份计分别为：纳米陶瓷粉 88-93 份，粘结剂份 4-6.5，稳定剂 1-1.5 份，造孔溶剂 2-4 份。

2. 根据权利要求 1 所述的锂离子电池造孔陶瓷隔离膜，其特征在于：所述浆料中纳米陶瓷粉、粘结剂、稳定剂、造孔溶剂的用量分别为 91 份、5.5 份、1 份、2.5 份。

3. 根据权利要求 1 所述的锂离子电池造孔陶瓷隔离膜，其特征在于：所述涂布的多孔陶瓷层厚度为 3-5μm。

4. 根据权利要求 1 所述的锂离子电池造孔陶瓷隔离膜，其特征在于：所述浆料固含量为 25-30%，浆料粘度为 40~50mpa·s。

5. 根据权利要求 1-3 任一项所述的锂离子电池造孔陶瓷隔离膜，其特征在于：所述纳米陶瓷粉为经过纳米化处理的 Al_2O_3 或 $BaSO_4$ 中的一种或两种以任意比混合。

6. 根据权利要求 1 所述的锂离子电池造孔陶瓷隔离膜，其特征在于：所述造孔溶剂为乙酸乙酯；所述粘结剂为聚丙烯酸酯，所述稳定剂为羧甲基纤维素钠。

7. 根据权利要求 1 所述的锂离子电池造孔陶瓷隔离膜，其特征在于：所述隔离膜基材为多孔单层或多层 PP 膜、PE 膜或 PP/PE 复合隔离膜中的一种，隔离膜基材的孔隙率为 40%~47%。

8. 一种如权利要求 1-7 任一项所述的锂离子电池造孔陶瓷隔离膜的涂布方法，其特征在于其工艺步骤如下：

1）陶瓷纳米化处理：将陶瓷原材料纳米化后烘烤、过筛，得到的纳米陶瓷粉备用；

2）浆料配制：按照上述比例将稳定剂加水溶解并搅拌后，加入得到的纳米陶瓷粉搅拌，依次加入粘结剂和造孔溶剂，继续搅拌反应；

3）涂布：升温凸版涂布机的烘箱，烘箱各段从前到后逐步提高温度，将浆料打入料槽中涂布在隔离膜基材的单面或双面，烘干即成。

9. 根据权利要求 8 所述的锂离子电池造孔陶瓷隔离膜的涂布方法，其特征在于：步骤 1）中烘箱的温度为 80-90℃，烘烤时间为 24-36 小时；步骤 2）中搅拌速度为 700-900r/min，搅拌反应时间为 1.5-2h。

10. 根据权利要求 8 所述的锂离子电池造孔陶瓷隔离膜的涂布方法，其特征在于：步骤 3）中烘箱各端的温度范围为 45-50℃。

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一种锂离子电池造孔陶瓷隔离膜及其制备方法

技术领域

[0001] 本发明涉及锂离子电池技术领域，具体涉及一种锂离子电池造孔陶瓷隔离膜及其涂布方法。

背景技术

[0002] 锂电池的燃烧甚至爆炸的根本原因是电池内部热失控制造成的，其中正负极片的短路是常见的问题，所以隔离膜在其中具有重要的隔离作用。隔离膜在锂电池中具有隔离电子、导通离子的作用，在隔离膜上涂上一层陶瓷层，当电池中有异物造成隔离膜破损时，短路点在高温度下不会因发热而扩大熔化，不会造成电极之间大面积短路，进而引起电池的燃烧甚至爆炸。随着贮能、电动汽车和电脑等用电器对锂离子电池的要求不断提高，锂离子充电电池单只容量和体积能量密度的不断提高，内部蓄积的能量越来越大，内部短路的危险性也在随之增大。当电池内部短路时，在高温下，陶瓷隔离膜的陶瓷层可以保持隔离膜完整的骨架结构，不因隔离膜基材熔化而失去分隔正负极片的作用，产生正负极片大面积短路。

[0003] 常见陶瓷隔离膜是在用干法或湿法工艺制造的单层或多层 PP、PE、PP/PE 复合隔离膜上涂附陶瓷层提高电池的安全性能，但在使用过程中常出现陶瓷层粘接不牢、吸液速度不够快等现象。有的陶瓷隔离膜在陶瓷层和隔离膜基材层之间加入高分子层，虽然保液性能有提高，但电池的离子通道有影响，且陶瓷层的厚度不够，安全性能不高等问题。

发明内容

[0004] 为了克服现有技术的缺陷，本发明的目的在于提供一种锂离子电池造孔陶瓷隔离膜，以提高锂电池的安全性能、吸液性能、保液性能、多孔陶瓷层的粘接性能以及锂离子通透性。

[0005] 本发明的另一目的在于提供一种锂离子电池造孔陶瓷隔离膜的制备方法，制造出的高安全造孔陶瓷隔离膜，提高锂离子电池的安全性能。

[0006] 为实现上述目的，本发明所采用的技术方案如下：

[0007] 一种锂离子电池造孔陶瓷隔离膜，包括隔离膜基材，所述隔离膜基材单面或双面涂布有多孔陶瓷层，所述多孔陶瓷层是通过含有纳米陶瓷粉、造孔溶剂以及粘结剂的浆料经凸版印刷机涂布而成，浆料中纳米陶瓷粉、造孔溶剂以及粘结剂的用量以重量份计分别为：纳米陶瓷粉 88-93 份，粘结剂份 4-6.5，稳定剂 1-1.5 份，造孔溶剂 2-4 份。

[0008] 本发明还可以通过以下方案实现：

[0009] 作为本发明的一种优选的方案，所述浆料中纳米陶瓷粉、粘结剂、稳定剂造孔溶剂的用量分别为 91 份、5.5 份、1 份，2.5 份。

[0010] 作为本发明的一种优选的方案，所述造孔陶瓷膜的多孔陶瓷层的涂层厚度为 3-5μm。本发明中，将多孔陶瓷层的厚度控制在上述范围之内，在提高多孔陶瓷膜保液能力的同时，也进一步提高了电池的安全性能；优选的所述多孔陶瓷层的厚度，小型电池（单体

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容量 5AH 以内，主要用于 3C 产品等）要求多孔陶瓷层单面涂层厚度为 3~4μm，大电池（单体容量 5AH 以上，主要用于动力电池、电动汽车电池、蓄能电池等）要求多孔陶瓷层单面涂层厚度为 5μm。

[0011] 为了控制涂布的厚度和均匀度，从而达到控制隔离膜质量的目的，作为本发明的一种优选的方案，所述浆料固含量为 25~30%，浆料粘度为 40 ～ 50mpa·s。当浆料粘度和固含量在上述范围时候，有利于凸版涂布机对涂布厚度和均匀度的控制。

[0012] 作为本发明的一种优选的方案，所述纳米陶瓷粉为经过纳米化处理的 Al_2O_3 或 $BaSO_4$ 中的一种或两种以任意比混合。

[0013] 在本发明中，所述造孔溶剂采用乙酸乙酯等低沸点的溶剂；这种低沸点溶剂具有水溶性兼油溶性，在材料中分散均匀，且密度小，所以在烘干过程中首先被蒸发掉，在陶瓷层表面形成微小的细密开孔，造孔隔离膜制作成电池后，为电解液的浸入提供更多的通道。所述粘结剂为聚丙烯酸酯，所述稳定剂为羧甲基纤维素钠。进一步的为了提高多孔陶瓷层的粘结性，所述稳定剂羧甲基纤维素钠的平均分子量 65 ～ 100 万左右，粘接剂聚丙烯酸酯的平均分子量为 30 ～ 120 万。

[0014] 作为本发明的一种优选的方案，所述隔离膜基材为干法或湿法多孔单层或多层 PP 膜、PE 膜或 PP/PE 复合隔离膜中的一种，隔离膜基材的孔隙率为 40% ～ 47%。

[0015] 一种锂离子电池造孔陶瓷隔离膜的涂布方法，其工艺步骤如下：

[0016] 1）陶瓷纳米化处理：将陶瓷原材料纳米化后烘烤、过筛，得到的纳米陶瓷粉备用；

[0017] 2）浆料配制：按照上述比例将稳定剂加水溶解并搅拌后，加入得到的纳米陶瓷粉搅拌，依次加入粘结剂和造孔溶剂，继续搅拌反应；

[0018] 3）涂布：升温涂布机的烘箱，烘箱各段从前到后逐步提高温度，将浆料打入料槽中涂布在隔离膜基材的单面或双面，通过烘箱烘干即成。

[0019] 上述方法中，作为优选的实施方案，所述步骤 1）中烘箱的温度为 80-90℃，烘烤时间为 24-36 小时；步骤 2）中搅拌速度为 700-900r/min，搅拌反应时间为 1.5-2h。

[0020] 上述方法中，作为优选的实施方案，步骤 3）中烘箱各端的温度范围为 45-50℃。

[0021] 相比现有技术，本发明的有益效果在于：本发明所述的锂离子电池造孔陶瓷隔离膜通过对陶瓷浆料的改造，造孔陶瓷层更有利于电解液的快速吸收和提高锂离子的转移速度，增加了电池电解液的保有量，又增强了电池的硬度；这种新配方浆料涂布出的多孔陶瓷膜解决了陶瓷层在隔离膜上易脱落、涂布厚度或面密度不均匀的问题。本发明不仅提高了电池的安全性能，同时也达到普通隔离膜制造的电池无法达到的性能。

[0022] 下面结合附图及具体实施方式对本发明作进一步详细说明。

附图说明

[0023] 图 1 为本发明一种实施方式的结构示意图；

[0024] 图 2 为本发明另一种实施方式的结构示意图；

[0025] 图 3 为隔离膜基材与本发明的造孔陶瓷膜后的隔离膜外观对比，其中（a）为隔离膜基材，（b）为造孔陶瓷隔离膜；

[0026] 图 4 为本发明的造孔陶瓷隔离膜的电镜图；

[0027] 图 5 为本发明的造孔陶瓷隔离膜与普通隔离膜的电铬铁穿刺对比示意图其中（c）

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为普通隔离膜，(d) 为造孔陶瓷隔离膜；

[0028] 图 6 为普通隔离膜与本发明的造孔陶瓷隔离膜电解液的浸润性的照片对比，其中 (e) 为普通隔离膜，(f) 为造孔陶瓷隔离膜。

具体实施方式

[0029] 如图 1 所示，一种实施方式中，本发明所述的锂离子电池造孔陶瓷隔离膜，包括隔离膜基材 1，所述隔离膜基材 1 双面涂布有多孔陶瓷膜 2，所述多孔陶瓷膜是通过含有纳米陶瓷粉、造孔溶剂以及粘结剂的浆料涂布而成，浆料中纳米陶瓷粉、造孔溶剂以及粘结剂的用量以重量份计分别为：纳米陶瓷粉 88~93 份，粘结剂份 4~6.5，稳定剂 1~1.5 份，造孔溶剂 2~4 份。

[0030] 如图 2 所示，另一中实施方式中，与上述方案的区别在于：本发明所述的所述隔离膜基材 1 单面涂布有多孔陶瓷层 2。

[0031] 以下是本发明制备锂离子电池造孔陶瓷隔离膜的具体实施例。

[0032] 实施例 1

[0033] 一种锂离子电池造孔陶瓷隔离膜，其是通过以下方法制备而成：

[0034] 1) 陶瓷纳米化处理：将 Al_2O_3 原料纳米化后于 85℃的烤箱中烘烤 36h，过筛，得到的纳米陶瓷粉备用；

[0035] 2) 浆料配制：取固含量 1.6% 的羧甲基纤维素钠溶液 93.75g，加去离子水 300g，以 800r/min 的转速搅拌 30min；然后加入步骤 1) 的纳米陶瓷粉 144g，以 800r/min 的转速搅拌 3h；加入聚丙烯酸酯 9g，加入造孔溶剂乙酸乙酯 3g，以 800r/min 的转速搅拌 1.5 ～ 2h；用微量去离子水调节浆料黏度为 47mpa·s，浆料固含量为 27.8%；

[0036] 3) 涂布：调试机器，并升温烘箱，涂布机各段的温度控制在 45 ～ 50℃范围内，烘箱各段从前到后逐步提高温度；将浆料打入料槽中，进行试涂，烘干后进行厚度和面密度测试，直到调节达到要求后，开始将浆料涂布在 PP 隔离膜基材上。

[0037] 实施例 2

[0038] 一种锂离子电池造孔陶瓷隔离膜，其是通过以下方法制备而成：

[0039] 1) 陶瓷纳米化处理：将 $BaSO_4$ 原料纳米化处理后于 85℃的烤箱中烘烤 24h，过筛，得到的纳米陶瓷粉备用；

[0040] 2) 浆料配制：取固含量 1.6% 的羧甲基纤维素钠溶液 125g，加去离子水 300g，以 800r/min 的转速搅拌 30min；然后加入步骤 1) 的纳米陶瓷粉 150g，以 800r/min 的转速搅拌 3h；加入聚丙烯酸酯 10g，加入造孔溶剂乙酸乙酯 4g，以 800r/min 的转速搅拌 1.5 ～ 2h；用微量去离子水调节浆料黏度为 48mpa·s；浆料固含量为 27.5%；

[0041] 3) 涂布：调试机器，并升温烘箱，涂布机各段的温度控制在 45 ～ 50℃范围内，烘箱各段从前到后逐步提高温度；将浆料打入料槽中，进行试涂，烘干后进行厚度和面密度测试，直到调节达到要求后，开始将浆料涂布在 PE 隔离膜基材上。

[0042] 实施例 3

[0043] 一种锂离子电池造孔陶瓷隔离膜，其是通过以下方法制备而成：

[0044] 1) 陶瓷纳米化处理：将原料 Al_2O_3 与 $BaSO_4$ 按照质量比为 1 ∶ 1 的比例混合后纳米化处理，于 85℃的烤箱中烘烤 24 ～ 36h，过筛，得到的纳米陶瓷粉备用；

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[0045] 2）浆料配制：取固含量 1.6% 的羧甲基纤维素溶液 93.75g，加去离子水 300g，以 800r/min 的转速搅拌 30min；然后加入步骤 1）的纳米陶瓷粉 145g，以 800r/min 的转速搅拌 3h；加入聚丙烯酸酯 9g，加入造孔溶剂乙酸乙酯 3.5g，以 800r/min 的转速搅拌 1.5 ～ 2h；用微量去离子水调节浆料黏度为 46mpa·s；浆料固含量为 27.3%；

[0046] 3）涂布：调试机器，并升温烘箱，涂布机各段的温度控制在 45 ～ 50℃范围内，烘箱各段从前到后逐步提高温度；将浆料打入料槽中，进行试涂，烘干后进行厚度和面密度测试，直到调节达到要求后，开始将浆料涂布在 PE/PP 复合隔离膜基材上。

[0047] 性能检测：

[0048] 1. 电烙铁穿刺实验：用电烙铁轻触穿刺隔离膜测试（测试条件：电烙铁温度 390℃），测试结果见示意图 5。

[0049] 图 5 的结果显示普通隔离膜在接触点直径明显扩大；本发明的造孔陶瓷膜接触点没有扩大。说明当在电芯内部微短路产生热量或着火点时，陶瓷隔离膜孔径不会继续增大，从而减小了燃烧的风险。

[0050] 2. 浸润性对比：将同一种电解液同时滴在普通陶瓷膜和本发明的造孔陶瓷隔离膜上（测试温度 27℃），测试结果见图 6。

[0051] 图 6 的结果显示在相同时间内电解液在普通陶瓷膜上的扩散速度明显比电解液在本发明的造孔陶瓷隔离膜上的扩散速度。说明本发明的造孔陶瓷隔离膜具有良好的吸液性能和离子通透性能，即具有良好的浸润性。

[0052] 3. 其他性能检测，检测结果见表 1。

[0053] 表 1

[0054]

项目		单位	规格和标准值				检验方法和仪器
外观			乳白色、平整光滑、无划痕、无色斑、无针孔				目测
厚度		um	12±3	16±3	20±3	24±3	千分尺
宽度		mm	根据需求指定				卡尺或投影仪
长度		mm	根据需求指定				收卷计米器
透气度		sec/100cc	190±60	250±60	290±60	320±60	透气度测定仪
孔隙率		%	45±5	45±5	45±5	45±5	GB/T21650.1-2008
穿刺强度		gf	≥320	≥450	≥500	≥550	GB/T23318-2009
拉伸强度	MD	Kgf/cm2	≥1000	≥1125	≥1200	≥1250	GB/T1040.3-2006
	TD		≥800	≥900	≥960	≥1000	

[0055]

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热收缩 130℃/0.5H	MD	%	≤4.0	≤4.0	≤4.0	≤4.0	取 1.5-1.0mm 的隔离膜，标记好测试点，经烘烤后，比较烘烤前后长度和宽度方向上的变化率。
	TD		≤4.0	≤4.0	≤4.0	≤4.0	
面密度		g/m3	10.6±3	12.9±3	14.8±3	17±3	取样器和电子天秤
弧度		mm	≤3.5	≤3.5	≤3.5	≤3.5	取 1 米长的隔离膜平铺在 1 米长的直钢尺上，确保隔离膜的两端同时对齐直钢尺的一边并固定。然后用卡尺在隔离膜的 0.5 米处测量隔离膜到直钢尺边缘的距离。

[0056] 备注：1. MD 指纵向（长度方向）；TD 指横向（宽度方向）

[0057] 2. 此标准是选用 PE 基材单面涂布陶瓷层厚 4μm 后的结果。不同的基材会有所不同。

[0058] 上述实施方式仅为本发明的优选实施方式，不能以此来限定本发明保护的范围，本领域的技术人员在本发明的基础上所做的任何非实质性的变化及替换均属于本发明所要求保护的范围。

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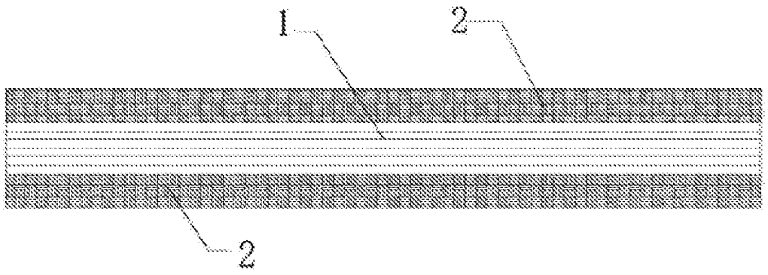


图 1

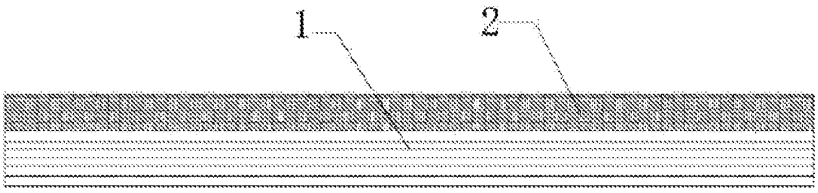


图 2

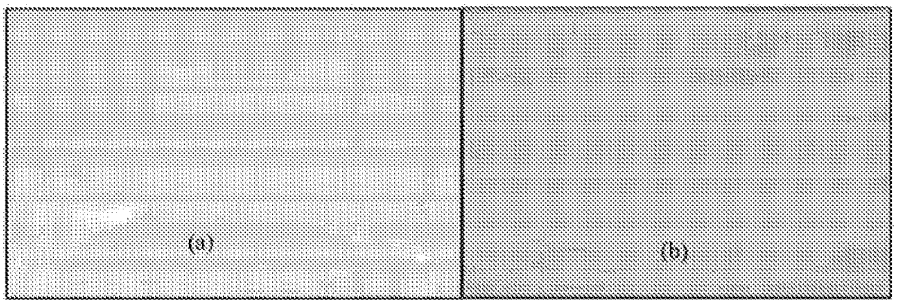


图 3

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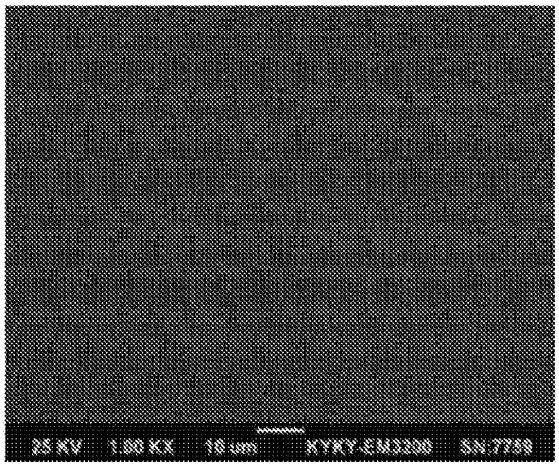


图 4



图 5



图 6

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Espacenet

CN104871341A Versatile single-layer lithium ion battery separators having nanofiber and microfiber components

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Versatile single-layer lithium ion battery separators having nanofiber and microfiber components

Abstract

An insulating (nonconductive) microporous polymeric battery separator comprised of a single layer of enmeshed microfibers and nanofibers is provided. Such a separator accords the ability to attune the porosity and pore size to any desired level through a single nonwoven fabric. Through a proper selection of materials as well as production processes, the resultant battery separator exhibits isotropic strengths, lows shrinkage, high wettability levels, and pore sizes related directly to layer thickness. The overall production method is highly efficient and yields a combination of polymeric nanofibers within a polymeric microfiber matrix and/or onto such a substrate through high shear processing that is cost effective as well. The separator, a battery including such a separator, the method of manufacturing such a separator, and the method of utilizing such a separator within a battery device, are all encompassed within this invention.

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Technical field

The present invention relates to an insulating (non-conductive) microporous polymer battery separator comprising a single layer of intertwined microfibers and nanofibers. Such a membrane can adjust the porosity and pore size to any desired level by using a single nonwoven. By appropriate selection of materials and manufacturing processes, the resulting battery separator exhibits isotropic strength, low shrinkage, high levels of wettability, and pore size directly related to layer thickness. The overall manufacturing process is highly efficient and the polymer nanofibers can be combined into a polymeric microfiber matrix and/or such a substrate by cost effective high shear processing. A separator, a battery containing the separator, a method of manufacturing the separator, and a method of using the separator in a battery device are all included in the present invention. Background technique

The battery has been used as a power generator at a remote location for many years. It produces a power circuit by controlling the movement of ions between the electrodes (anode and cathode) to provide a power source that can be used to exhaust excess ions in one electrode without potentially generating electricity. In recent years, rechargeable batteries have been created to provide longer life for such long-distance energy sources, although such batteries need to be connected to other power sources for a period of time. In summary, the battery's ability to reuse has developed even greater application potential, especially for cell phones and notebook computers, and even for cars that run on electricity only.

Such batteries typically include at least 5 different components. The outer casing (or container) covers the components in a safe and reliable manner to prevent leakage to the outside and to prevent internal exposure to the environment. Inside the casing are an anode and a cathode which are effectively separated by a membrane; and an electrolyte solution (low viscosity liquid) which transports ions between the anode and the cathode through the membrane. In the present and for the foreseeable future, rechargeable batteries will be used in a very small and portable device, with strong power generation capability to remain effective for a long time between charging intervals, and also for very large types in automobiles. Battery, such as a large electrode (at least in the surface area) that is inaccessible to each other, and a large amount of ions that must pass through the membrane continuously and constantly to complete the necessary circuitry, all of which contribute to providing operational levels Sufficient power for a car engine. For this reason, the ability and versatility of battery separators in the future must meet certain requirements, which has not been realized in today's industry.

In general, since the advent of closed cells, battery separators have been used to provide the necessary protection between the electrodes that are not desired to be contacted and to allow efficient transport of the electrolyte within the battery cells. Typically, such materials have a film structure that is sufficiently thin to reduce the weight and volume of the battery device while giving the necessary properties mentioned above. This diaphragm must also have other features to perform the proper battery function. These functions include chemical stability, proper porosity of the ionic species, effective pore size for electrolyte transport, proper permeability, effective mechanical strength, and ability to maintain dimensional and functional stability when exposed to thermal insulation (and when temperature The ability to cut off when raised to an abnormally high level).

In more detail, the diaphragm material must have sufficient strength and structure to handle a variety of different situations. First, the diaphragm cannot be torn or puncture during the stress of the battery assembly. In this way, the overall mechanical strength of the diaphragm is extremely important, especially as a material with high tensile strength in both the machined and cross-sectional (ie, transverse) directions, allowing the manufacturer to operate the diaphragm more easily without the need for rigorous guidance to avoid critical The membrane is subjected to structural damage or loss during the step. In addition, from a chemical point of view, the membrane must withstand the oxidation and reduction environment inside the battery itself, especially when fully charged. Any failure in use, especially in terms of structural integrity, that allows an abnormally large amount of current

to pass or the electrode to be touched, will destroy the ability to generate electricity and cause the battery to fail completely. Therefore, for the same reason as described above, even if it has a higher ability to weather resistant chemical exposure, the separator must not lose dimensional stability (i.e., warpage or melting) or mechanical strength during storage, manufacture, and use.

At the same time, the diaphragm must have a substantially suitable thickness to facilitate the high energy and power density of the battery itself. In order to allow long-term circulation, uniform thickness is also important because any uneven wear on the diaphragm will become a weak link in the electrolyte path and electrode contact protection.

In addition, such membranes must exhibit suitable porosity and pore size to accommodate proper transport of ions through the membrane (as well as a suitable capacity to maintain a certain amount of liquid electrolyte during use to facilitate the ion transfer). The pores themselves should be small enough to prevent electrode components from entering and/or passing through the membrane, but should also allow for a suitable transfer rate of electrolyte ions as described above. Also, the uniformity of the aperture and the pore size distribution provide a more uniform yield over time, as well as more reliable long-term stability for the entire battery as described above, in which at least the battery separator is controlled as optimally as possible. Uniform wear to allow for a longer life cycle. In addition, it is ensured that the pores therein are properly closed upon exposure to abnormally high temperatures, which helps to prevent excessive and undesired ion transfer (i.e., fire and other hazards) after battery failure.

Also, the aperture and distribution can increase or decrease the air resistance of the diaphragm, allowing a simple measurement of the diaphragm to indicate that the battery has the ability to allow sufficient electrolyte to be present inside the battery itself. For example, the mean flow pore size can be measured according to ASTM E-1294 and can be used to help determine the barrier properties of the membrane. Thus, the stiffness of the hole itself (i.e., the ability of the hole to maintain a certain size over time and exposed to a set pressure during use) with a lower aperture also allows for effective control of electrode isolation. More importantly, perhaps such a pore size can limit dendrite formation, thereby reducing the chances of crystal formation on the anode (such as lithium crystals on the graphite anode). Forming crystals on the anode can adversely affect the battery's production over time. Electrical ability.

Further, the membrane must not impair the ability of the electrolyte to completely fill the entire cell during manufacture, storage, and use. Therefore, at these stages, the membrane must exhibit suitable capillary action and/or wettability to ensure that the electrolyte is in fact suitable for transferring ions through the membrane; if the membrane does not contribute to such a situation, the electrolyte will not properly It stays on and inside the diaphragm hole and is not susceptible to the necessary ion transport. Furthermore, it should be understood that it is generally required that the separator have this suitable wettability in order to ensure dispersion of the liquid electrolyte on the surface of the membrane and inside the cell. The non-uniformity of the electrolyte dispersion can result in the formation of dendrites within the interior of the cell and on the surface of the membrane, resulting in an increased potential that causes the cell to fail and a short circuit to occur therein.

As described above, dimensional stability is also of great concern when the separator is used in a typical lithium ion battery. It is clear that the membrane must provide a porous separator for ion diffusion throughout the life of the battery. However, in some cases, elevated temperatures from external sources or within the battery itself can cause undesirable shrinkage, warpage, or melting of the sensitive diaphragm material, any of which can adversely affect battery performance over time. As such, it is very difficult to achieve this during practical use by lowering the temperature level and/or detaching the type of battery from the elevated temperature, so the membrane itself should contain materials that are resistant to this high temperature and that are not significantly affected after exposure. Alternatively, the use of a combination of materials that are one of the fibers would be highly attractive, for example, to provide such beneficial results while still allowing the membrane to function at its optimum level.

However, as noted above, the standards currently available today do not meet this critical consideration. The general purpose of an effective battery separator is to provide all of the beneficial properties in a single sheet material. Low air resistance, very small pore size and suitable pore size distribution, dimensional stability in chemical and elevated temperature environments, suitable wettability, maximum for allowing the most battery components to be present in as small an enclosed space as possible Good thickness and effective overall tensile strength (essentially isotropic), the ability to provide these properties is necessary in order to meet the following conditions: significantly reduce the possibility of electrode contact, but with controlled electrolytes from The ability of one portion of the battery to be transferred to another (ie, to close the circuit to produce the required

power), in other words, to obtain the longest maximum battery output with the smallest battery volume. At present, these properties are not effectively provided to such an extent. For example, Celgard discloses and sells an expanded membrane battery separator having a very low pore size, which is very good in the above-described aspects; however, the corresponding air resistance of such materials is extremely high, thus limiting the overall effectiveness of such membranes. Sex. In contrast, DuPont commercialized a nanofiber nonwoven membrane separator that provides very low air resistance but has an excessively large pore size therein. In addition, the overall mechanical strength exhibited by these two materials is very limited; the Celgard diaphragm has excellent strength in the machine direction but nearly zero strength in the cross-section (transverse) direction. As mentioned above, such low cross-sectional strength requirements result in at least a very fine operation required during the manufacturing process. DuPont materials are better, but the strength is quite low in both directions, although the strength in the cross-section is higher than the Celgard material. In fact, DuPont products are close to isotropic materials (nearly the same strength in both the machine direction and the cross-section) and therefore provide a more reliable material in operation than the Celgard type. However, the tensile strength of the measured DuPont diaphragm is actually very low, so the user is also required to carefully manipulate and place such materials during the manufacturing process. Similarly, due to these tensile strength problems, the dimensional stability of such prior art battery separators is very unreliable, potentially resulting in an undesired loss of structural integrity over time when materials are present in the rechargeable battery.

Accordingly, there is still a need to provide a battery separator that simultaneously provides all of these characteristics for long term, reliable lithium battery products. As such, although such membranes exhibit low air resistance and low pore size, as well as high tensile strength, suitable chemical stability, structural integrity and dimensional stability at the overall and relative isotropic levels (especially when exposed to lift) After the temperature), although highly desirable, it has so far clearly failed to provide such a valuable separator material. In addition, a method of producing a battery separator that achieves such a desired target level of quality through an efficient manufacturing process would also be expected, particularly if such desired benefits and requirements are obtained if there are fewer changes in material selection, etc. Highly anticipated; at present, the manufacturing method to this extent has yet to be developed in the entire battery separator industry. Thus, the battery cell fabrication methods described below that are effective and very straightforward are valuable in the rechargeable battery separator industry: the method provides any number of films that exhibit a variety of end results (ie, by improving the method as needed to achieve the target) Porosity and air resistance levels), in addition, provide an appropriate level of mechanical properties, heat resistance, permeability, dimensional stability, cutting properties and melting properties; to date, such materials have not been obtained.

Summary of the invention

A unique advantage of the present invention is that it is easy to manufacture by a wet nonwoven manufacturing process. Another unique advantage is that by merely changing the proportion of the constituent fibers used in the manufacturing process and appropriately calendering the produced single-layer material, it is possible to obtain pore diameter, porosity and air resistance at any target level. A further advantage of the battery separator of the present invention is that the isotropic strength properties meet the user's long-term use and reliability in the battery manufacturing stage. The ability of the separator of the present invention to provide both low air resistance and low pore size is a further advantage of the present invention. Yet another advantage of the battery separator of the present invention is to provide a particular non-conductive (and thus insulating) cloth (or paper) that does not allow charge to be transported through the diaphragm body, but rather only allows charged ions to pass through the apertures present in their structure. . Yet another advantage is the high porosity of the material, allowing for more ion flow and allowing for the ability to maintain energy over many life cycles by allowing the electrode to be fully recharged. Other advantages include, but are not limited to, the ability to tailor certain physical properties by appropriate selection of fiber materials prior to layer formation, and the ability to first use all microfibers to produce nanofibers (fibrillated form) by high shear processing. All necessary membrane components can be formed from a single starting material.

Accordingly, the present invention is directed to a polymer battery separator comprising a nonwoven combination of microfibers and nanofibers, wherein the single layer of the separator exhibits an isotropic tensile strength, and the tensile strength in the machine direction is less than Three times the tensile strength in the cross-sectional direction. More specifically, the present invention comprises a polymer battery separator comprising a single layer nonwoven combination of microfibers and nanofibers, wherein said single layer of said separator has a bimodal distribution of fiber length, microfiber The average length is greater than five times the average length of the nanofibers and the average flow pore size is less than 2000 nanometers (2.0 μm). Optionally, the present invention comprises a polymer battery separator comprising a single layer nonwoven

combination of microfibers and nanofibers, wherein said single layer of said membrane has a bimodal distribution of fiber diameters, an average of microfibers The diameter is greater than three times the average diameter of the nanofibers and the average flow pore size is less than 2000 nanometers (2.0 μm). Further, the present invention comprises a polymer battery separator comprising a single layer nonwoven combination of microfibers and nanofibers, wherein the single layer of the separator is in a processing direction and a cross section at 160 ° C for 1 hour. The directions all have a heat shrinkage ratio of less than 10%, and the average flow pore diameter is less than 0.80 μm.

The separator of the present invention also exhibits a machine direction (MD) tensile strength of more than 90 kg/cm 2 and less than 1,000 kg/cm 2 , a cross-sectional direction (CD) tensile strength of more than 30 kg/cm 2 and less than 1,000 kg/cm 2 , and The average flow pore size is less than 0.80 μm. Further, the invention comprises a battery separator as defined above and comprising a fiber monolayer comprising nanofibers and microfibers, said nanofibers having an average maximum width of less than 1000 nm, said microfibers having a maximum width greater than 3000 nanometers, and The nanofibers and the microfibers are doped with each other such that at least a portion of the nanofibers remain in the gap between the microfibers.

Furthermore, the present invention relates to a method of forming a battery separator, wherein the battery separator has a maximum thickness of 250 μm, and wherein the battery separator comprises a combination of a microfiber component and a nanofiber component, the method The method comprises the steps of: a) providing a water solvent; b) introducing a plurality of nanofibers and a plurality of microfibers therein to form a microfiber/nanofiber dispersion in an aqueous solvent; c) mixing the micron under high shear conditions a fiber/nanofiber dispersion; d) introducing a high shear of the dispersion into a paper machine; e) producing a fabric of microfiber/nanofiber material; and f) drying the fabric. The method also contemplates further processing steps including treating the fabric by a calendering process to produce a membrane material having a thickness of up to 100 microns and a pore size of up to 2000 nm.

In this publication, the term microfiber is used to mean any polymer fiber having a measured width in the order of microns, typically having a maximum width greater than 1000 nm, greater than 3000 nm, even greater than 5000 nm or even greater than 10,000 nm, up to about 40 microns. . Similarly, the term nanofiber is used to refer to any polymer fiber having a measured width in the order of nanometers, typically having a maximum width of less than 1000 nm, possibly less than 700 nm, or even less than 500 nm or even less than 300 nm (as low as about 1 nm). Regardless of the microfiber or nanofiber material, it should be understood that the width can be understood as the diameter, but in this case, since a uniform fiber structure is generally very difficult to achieve, the diameter can be understood as the average diameter. Therefore, the maximum width is used as the primary definition, especially if the fibers themselves are non-cylindrical, for such fibers, square, rectangular, triangular or other geometrical possibilities may be considered, as long as suitable microfiber and nanofiber measurements are present. They will all be within the amplitude range of the present invention. Similarly, the term insulation is used to mean an unmeasurable degree of electrical conductivity such that the fabric structure of the present invention does not allow charge to pass through the body of the cloth, but only allows passage through an electrolytic ion path that passes through the apertures present therein.

Such a combination of microfibers and nanofibers has been studied in battery separator technology, particularly in terms of the ability to provide a single layer of nonwoven fabric of two essential components for such purposes. This combination is particularly important because it provides a bimodal distribution of nonwovens having a fiber diameter and length, wherein the microfiber component has an average length that is at least 5 times, preferably greater than, the average length of the nanofiber component. The fiber is 10 times the average length, and most preferably 20 times longer than the length of the nanofiber. Further, the average fiber diameter is also a bimodal distribution, wherein the average diameter of the microfibers is greater than 3 times the average diameter of the nanofibers, preferably greater than 5 times the average diameter of the nanofibers, and most preferably greater than the average diameter of the nanofibers. 10 times. This bimodal distribution allows the microfibers to provide a single layer of membrane with strength, elasticity, permeability, modulus, tear and puncture resistance, wet strength, processing capability, and other characteristics that are not provided by the nanofiber alone.

The microfiber component can be any suitable polymer that provides the necessary chemical resistance and heat resistance described above, as well as the ability to form microfiber structures. Also, such microfibers may be fibrillated (or treated in any other similar manner, such as by plasma exposure, etc.) during or after the formation of the fibers to increase their surface area, thereby facilitating the nonwoven manufacturing process. Desirable entanglement between a plurality of such microfibers. Thus, such polymer components may include acrylics such as polyacrylonitrile, polyolefins such as polypropylene, polyethylene, polybutylene, and others,

including copolymers, polyamides, polyvinyl alcohols, polyethylene terephthalate. Glycol ester, polybutylene terephthalate, polysulfone, polyvinyl fluoride, polyvinylidene fluoride, polyvinylidene fluoride-hexafluoropropylene, polymethylpentene, polyphenylene sulfide, polyacetyl (polyacetyl), polyurethane, aromatic polyamide, semi-aromatic polyamide, polytrimethylene terephthalate, polymethyl methacrylate, polystyrene, cellulose polymer (synthetic fiber, as a non- A limiting example), polyaramids include para-aramids and meta-aramids, as well as blends, mixtures and copolymers comprising these polymers. Polyacrylates, cellulosic polymers and polyaramids are potentially preferred. Such materials offer a range of highly desirable properties that work in combination with the properties of other polymer types to achieve major beneficial results in terms of tensile strength, high temperature protection, wettability and pore size, especially with them. The nanofiber component and when it contains a micron-like fiber matrix. Such microfibers can also be pretreated with an adhesive to achieve the desired degree of contact and dimensional stability of the overall nonwoven structure after manufacture.

In addition, microfibers can be selected based on individual fiber properties to provide a combination of materials to impart desirable properties to the entire battery separator. Thus, since polyaramids, meta-aramids, and cellulosic fibers provide superior heat resistance and certain strength benefits, these fibers are embedded separately (eg, as a wet component) or by entanglement or other methods. Be embedded. Such fibers must be of sufficient length to impart the necessary strength to the entire membrane and short enough to allow proper embedding (again, such as during a wet process). For example, the microfiber component may preferably be longer than 0.5 mm, more preferably longer than 1 mm, and most preferably longer than 2 mm.

The microfiber or nanofiber is preferably a material that melts or flows under pressure or high temperature. It is particularly advantageous to have a component that melts or flows at a lower temperature than other components. For example, polyester microfibers can flow at temperatures near the melting temperature of 260 °C. In addition, the polyacrylonitrile microfibers or nanofibers can be flowed under high pressure and high temperature. Cellulose, rayon, aramid, and other microfibers or nanofibers will not flow at these temperatures. Thus, the combination of materials comprises at least one fiber that flows at high temperatures and/or pressures and at least one fiber that does not flow at the same temperature and/or pressure, which will enable the former fiber to bond with other fibers, thereby Additional strength is imparted to the nonwoven membrane.

The nanofibers can be any similar polymer component and/or combination to withstand the same types of chemical and high temperature exposure as microfibers. Due to the size of the nanofibers, it is not necessary to subject post-manufacture of such nanofiber materials to increase the entanglement in the nonwoven surface or nonwoven gap produced. However, the nanofibers can be formed by high shear treatment of the microfiber raw material to strip the nanoscale components therefrom as materials conforming to the definition of the above nanofibers. Thus, as such, the stripped or stripped nanofibers will exhibit fibrillation appearance and properties, which may result in improved interlacing in the microfiber gaps in the manufacture of the separator (not to mention the same membrane). The potential for intertwining between individual nanofibers in and/or prior to the manufacturing process). In this case, the microfiber and nanofiber material can be derived from the same material, and the nanofiber component can be formed by removing portions of the microfiber material, which nanofibers can have different lengths and different cross sections and overall dimensions. In any case, the manufacture of nanofibers can be carried out in such a way that the components removed from the microfiber raw material are collected and used, not only with the microfibers that provide the nanofibers, but with other types of microfibers. Apply in this form. In such an embodiment of the battery separator of the present invention, any type of nanofiber can be utilized for such purposes. However, it is preferred that it may create a situation in which a particular type of fiber is utilized due to its ability to provide nanofibers that exhibit potentially beneficial properties such as high temperature stability, tensile strength, and the like.

Although it is described that the "fibrillated" nanofibers can be utilized, a tailored nanofiber component can be embedded in such a microfiber matrix material to obtain a separator having a specific pore diameter produced by a wet process as a result of the present invention. Sheet. Therefore, the manufacturing process involves introducing a nanofiber component into a dilute microfiber solution, mixing it under high shear conditions, and then drying to form a resulting sheet. The sheet can then be calendered to reduce the sheet thickness as needed and further adjusted to the optimum pore size and pore size distribution present therein. The wet process enables the manufacture of suitable flakes by using an elastic flake that suitably disperses and embeds the microfiber and nanofiber components, wherein the amount of nanofibers determines the ability to fill the gap between the microfiber components, thereby The desired pores are produced in the resulting flakes. The calendering operation can relate the thickness of the sheet to the pore size, especially due to the overall tensile strength of the sheet after wet manufacturing. Thus, such a process provides a relatively simple but succinct method to provide the ability to optimize pore size distribution and size without inadvertently tearing, warping, and/or

inadvertently pressing or handling the overall structure. Disturbs its dimensional stability. Furthermore, since a simple microfiber/nanofiber/water solution can be used for the sheet manufacturing process, a simple and simple method can be achieved, and a method of reducing or even not requiring other chemicals to achieve the desired production scheme can be realized. Such pure starting materials and overall manufacturing methods further highlight the highly unanticipated benefits including not only the methods employed for the products of the present invention, but also microfibers and nanofibers and aqueous solutions for such purposes. The simple combination also includes the required battery separator materials that have not been achieved to date, and has versatility for a variety of end uses.

Therefore, it is very important for the method and product of the present invention that the nanofiber component be combined with the microfiber in a sufficiently high shear environment to introduce the actual nonwoven fabric while introducing the actual nonwoven fabric. The nanofibers are introduced as desired on the nonwoven substrate and in the nonwoven substrate. In other words, by providing two fiber materials in the nonwoven process, the manufacturer should satisfy sufficient mixing and high shear conditions to best ensure the proper degree of intertwining between the different fiber types to form the desired Single layer fabric structure. As such, the manufacturing process potentially favors a wet non-woven process in addition to the high shear type, which is used on the surface to best ensure proper introduction and retention of the nanofibers in the microfiber gap. As the water flow in the manufacturing increases, very small nanofibers will be drawn into the gap at a higher rate than the dry entanglement method, thereby imparting the above gap filling ability. In addition, the higher the water level used for this purpose, the purity of the appropriate nanofibers intertwined in the fiber matrix (recycled water and excess fibers for further use in separate battery separator manufacturing processes) and reliability high. Thus, the resulting nonwoven structure will exhibit higher uniformity in terms of thickness, porosity, and more importantly, pore size, and, in addition, as described above, calendering performance for optimizing thickness and pore size results. More reliable stability.

A method after such a wet process comprises providing a prefibrillated microfiber of a pulpy formulation comprising, for example, from 50:1 to 10000:1 part water per fiber (again, preferably alone Water, but other solvents which can be subjected to a wet process and subsequently promoted evaporation thereof, including, for example, certain non-polar alcohols, can also be used as needed. The pre-fibrillated microfibers are treated in this manner to exhibit a certain amount of existing nanofibers (residual products are removed from the microfibers themselves during fibrillation, but without the entire mesh from the subsequent microfibers) Removed). As a result of the fibrillation process, the pre-fibrillated microfibers and nanofibers are pulp-like, so as to comprise a slurry-like preparation of the above water-based solvent having the obtained pre-fibrillated microfibers and nanofibers. The slurry formulation is then mixed with a selected amount of other microfibers and/or nanofibers (preferably also in the form of pulp or slurry), or only the initial slurry is mixed and the resulting formulation is heated to at least 60 in hot water. a temperature of °C, more preferably a temperature of at least 70, most preferably at least 80, wherein there is a very low concentration of actual fiber solids (i.e., less than 1%, as low as less than 0.1 relative to the weight of water or other water-based solvent) %). The heated dispersion will then withstand a high shear environment and then placed on a flat surface. The surface has a sufficient number of pores for solvent elution, thereby obtaining a desired single layer of wet-laid nonwoven comprising intertwined fibrillated microfibers with a gap between each microfiber. And nanofibers are present in the gap and on the surface of the larger microfibers. Thus, the amount of nanofibers added to the pre-fibrillated microfiber pulp enables a greater loading between the microfiber gaps, resulting in a lower overall average pore size, especially compared to a single pre-fibrillated pulp alone. A wet nonwoven made. In contrast, by adding microfibers to the pre-fibrillated fiber slurry, a greater average pore size of the resulting wet nonwoven single layer fabric can be achieved as compared to a separate pre-fibrillated fiber slurry. By the level of nanofiber and/or microfiber addition, it is possible to target different average pore sizes, which allows the manufacturer to achieve any desired average pore size.

After the high shear mixing step, the resulting dispersion is fed to a paper machine (any type of paper machine capable of producing lightweight sheets without damage, by way of example only, for example, a Fourdrinier paper machine, a slanted net Machine head of a paper machine (Increned Wire), a vacuum net paper machine (rotoformer), etc. The lightweight sheet can be manufactured by controlling the input of the dispersion of the fibers at the end of the head and simultaneously controlling the line speed. Regarding such a method, a mechanism that does not set open draws (i.e., does not support wet fiber fabrics) is preferred. In this case, the high water level can be mitigated by vacuum equipment, which is a common step in the paper industry, at least at the initial stage (i.e., removing surface moisture to a certain level). For a suitable sheet product, a fine gauge papermaking web is necessary, especially for a gauge of a maximum of 40 gauges, more preferably a maximum of 80 stitches. The width of the paper (dispersed sheet) can be any measurement as long as the manufacturing speed does not affect the final result and the overall tensile strength (especially in the isotropic aspect) is not

lost. For efficiency purposes, the line speed can be set in the range of 25 to 1,500 ft/min, more preferably the minimum value is set to 50, and most preferably 100.

After the paper (sheet) production step is completed, the formed sheet is introduced into a drying device. Any standard drying equipment can be utilized, including heated steam tanks or hot air stoves. This heating should exceed the temperature required for evaporation of water (or other solvent), but not so high that the flakes themselves melt or deform. Therefore, the drying temperature may depend on the material used, as well as the thickness of the sheet, because some materials can withstand higher temperatures in terms of dimensional stability than other materials, and the thicker the sheet, the more generally it can withstand higher temperatures. The temperature is resistant to warping or other effects.

Thus, the manufacturer can also control the desired performance of the battery separator of the present invention by making the thickness of the single layer structure different as needed. Such thickness characteristics can be provided by the process parameters of the original wet manufacturing process alone, or the manufacturer can subsequently calender the resulting cloth to any desired thickness. Manufacturers can further achieve greater versatility in both air resistance and average pore size measurement due to the ability to calender or change the thickness of the resulting single layer fabric. This conditioning process has not been explored in the battery separator industry. The calendering step utilizes a general-purpose apparatus, and by way of example only, a combination of a hard steel roll or a single hard steel roll and a second hard rubber roll may be employed. Also, for such a purpose, as described above, if the material can withstand such a condition without any significant loss of tensile strength or the like, a plurality of calendering steps can also be carried out.

Thus, the single layer separator obtained in the present invention may have a thickness of less than 250 microns, preferably less than 100 microns, more preferably less than 50 microns, even more preferably less than 35 microns, and most preferably less than 25 microns. As described above, in order to prevent a short circuit in the use of the battery, it is necessary to be able to prevent contact between the anode and the cathode of the battery; the thickness of the diaphragm and the aperture controlled therein provide an important way to achieve the result. However, the thickness of the battery separator may also affect the effective volume of the other component portions in the closed cell body and the amount of electrolyte solution provided therein. Therefore, the entire situation involved requires a diaphragm that is effective in multiple variables. The manufacturing method of the present invention and the single-layer battery separator produced therefrom can be advantageously manufactured easily, and can provide effective desired pore size and air resistance properties, thereby making the progress of the invention and existing battery separators currently used and sold. The situation is clearly separated.

Other methods of making nonwoven sheets capable of intertwining a combination of nanofibers and microfibers can also be used to make the battery separator of the present invention. One method is to combine different nanofibers and microfibers and combine them by the above method. Other such methods include carding, cross-lapping, hydroentangling, air laying, needle punching, meltblowing, spunbonding, or a web that will enable the formation of intertwined microfibers and enable Other methods or combinations of methods in which the nanofibers fill the gaps between the microfibers described above.

In fact, as noted above, the microfiber gap forms the "hole" itself, and the nanofibers are filled into such openings to reduce the size therein, reducing to a substantially uniform extent throughout the nonwoven structure. The extremely unanticipated benefits of the overall invention, especially in order to achieve different levels of porosity as desired, enable adjustment of the pore size in the resulting nonwoven structure by merely changing the concentration of the microfibers relative to the nanofibers. Thus, for example, at the beginning of the nonwoven manufacturing process, a ratio of 30% microfiber to 70% nanofiber will provide a pore size in the range of 700 nm to 195 nm, while a combination of 10% microfiber/90% nanofiber will provide effective A smaller pore size distribution (and a more uniform range, such as 230 nm to 130 nm). Thus, based on this unpredictable result, the end user can obtain the desired porosity by making a relatively simple change in manufacturing as described above. The resulting aperture can be measured to obtain an average flow aperture. The average flow pore size can be less than 2000 nm, even less than 1000 nm, preferably less than 700 nm, more preferably less than 500 nm.

Further, it should be noted that although the present invention includes a single layer separator comprising the microfibers and the nanofibers together, it is also possible to use a multilayered fabric structure or a layer of the battery separator cloth of the present invention and at least one layer. Other different types of cloth, and this still falls within the scope of the entire invention described herein.

The battery separator described herein clearly contributes to the improvement of primary battery and rechargeable battery technology, as well as other forms of electrolyte conductive energy storage technologies such as capacitors, supercapacitors, and special capacitors. Indeed, by controlling the aperture of such a diaphragm of the present invention, the energy loss, discharge power, and other properties of these devices can be significantly improved.

DRAWINGS

BRIEF DESCRIPTION OF THE DRAWINGS Figure 1 is an SEM micrograph of a prior art expanded membrane battery separator.

2 is an SEM micrograph of a prior art nanofiber nonwoven battery separator.

Figures 3 and 4 are SEM micrographs magnified 1000 and 2000 times a potential preferred embodiment of the microfiber/nanofiber nonwoven battery separator structure of the present invention.

Figures 5 and 6 are SEM micrographs of another potentially preferred embodiment of the microfiber/nanofiber nonwoven battery separator structure of the present invention magnified 5000 and 10,000 times.

Fig. 7 is an exploded view showing the lithium ion secondary battery of the present invention comprising the battery separator of the present invention.

Detailed ways

All of the features of the present invention and its preferred embodiments will be described in detail in conjunction with the accompanying drawings and the accompanying drawings.

Production of microfibers and nanofibers

As noted above, the microfibers can be constructed from any polymer (or blend polymer) that conforms to suitable chemical and heat resistance and battery internal conditions, as well as forming a suitable fiber structure within the range. ability. Such fibers may further have the potential to be treated by fibrillation or similar techniques to increase the surface area of the fibers themselves for facilitating entanglement during the nonwoven manufacturing process. Such fibers can be produced by existing fiber manufacturing methods such as melt spinning, wet spinning, solution spinning, melt blowing, and the like. Moreover, such fibers can be used as bicomponent fibers at the outset and can be reduced or varied in size and/or shape by further processing, such as splittable pie fibers, island fibers, and the like. Such fibers can be cut to a suitable length for further processing, which can be less than 50 mm, or less than 25 mm, or even less than 12 mm. Such fibers can also be made long to give better workability or higher strength, longer than 0.5 mm, longer than 1 mm or even longer than 2 mm. Such fibers can also be fibrillated into smaller fibers or advantageously form fibers of a wet laid nonwoven.

Nanofibers useful in the present invention can be made by several prior art techniques such as islanding, centrifugal spinning, electrospinning, film or fiber fibrillation, and the like. Both Teijin and Hills are commercially available island nanofibers (the island nanofibers of Teijin are sold as NanoFront fibers, polyethylene terephthalate fibers having a diameter of 500 to 700 nm). Both Dienes and FiberRio are commercially available equipment that uses nanowires for centrifugal spinning. Xanofi is a commercially available fiber and is manufactured using high shear liquid dispersion technology. The nanofibrous polyaramid produced by DuPont exhibits excellent high temperature resistance, as well as other particularly preferred properties.

The production of electrospun nanofibers is carried out by DuPont, E-Spin Technology, or by Elmarco on a device sold for this purpose. Nanofibers fibrillated from a film are disclosed in U.S. Patent Nos. 6,110, 588, 6, 432, 347, and 6, 432, 532, incorporated herein by reference. The fibrillation can be carried out by other fibers under high shear and grinding treatment to obtain nanofibers. Engineered Fiber Technologies sells nanofibers made from fibrillated cellulose and acrylic fibers under the trade name EFTECTM. Any such nanofibers can also be further processed by cutting and high shear slurry processing to separate the fibers, thereby enabling them to be processed into wet nonwovens. Such high shear processing may or may not occur in the presence of the desired microfibers.

Generally, the aspect ratio of nanofibers produced by fibrillation differs from the initial fabrication of nanofibers in a typical manner (e.g., islands). One such aspect ratio is fully disclosed in U.S. Patent No. 6,110,588, which is incorporated herein by reference in its entirety. Thus, in a preferred embodiment, the nanofibers have a cross-sectional ratio greater than 1.5:1, preferably greater than 3.0:1, more preferably greater than 5.0:1.

As such, acrylic, polyester and polyolefin fibers are particularly preferred for this purpose, and fibrillated acrylic fibers are most preferred. However, this only indicates a potentially preferred type of polymer for this purpose, and is not intended to limit the range of possible polymeric materials or blend polymers used for this purpose.

1 and 2 provide photomicrographs of typical structures of the above Celgard expanded film material and DuPont nanofiber nonwoven battery separator material, respectively. It is worth noting that the membrane structure of the Celgard membrane shows a similar pore size, apparently formed by film extrusion and final surface cracking in a fairly uniform form. DuPont diaphragms are strictly made of nanofibers alone because the uniformity of fiber size and diameter is significant. These nanofibers themselves act as a nonwoven structure, the overall tensile strength of the membrane in the process and cross-sectional direction is very low, albeit fairly uniform in both directions. Therefore, although such a material can be uniformly processed, if such a separator is introduced into a battery, the result is that the manufacturer must eventually face other problems due to the overall strength. In contrast, the separator of Fig. 1 shows the streaks produced by the holes in the same direction (thus extruding the film in one direction), providing extremely high tensile strength in the machine direction; unfortunately, the same material is The tensile strength in the cross-sectional direction is very low, so that battery separator materials which are very difficult and questionable are actually used in the battery manufacturing industry as described above.

The material of the invention presented in microphotographs in Figures 3 and 4 has a completely different structure than the two prior art products (and based on Example 39 below). One potentially preferred embodiment of the initial combination of microfibers and nanofibers is EFTECTM A-010-4 fibrillated polyacrylonitrile fiber having a large amount of nanofibers and residual microfibers. The resulting nanofibers present in this combination are derived from the fibrillation of the initial microfibers. Nonwoven sheets made from these materials are shown in Figures 3 and 4. As an example, these fibers can be used as a matrix material to which further microfibers or further nanofibers can be added to control the pore size and other properties of the nonwoven fabric. Alternatively, such a material can be used as the nonwoven battery separator itself. An example of such a sheet to which additional microfibers are added is shown in Figures 5 and 6. Typical properties of acrylic microfiber nanofibers are shown below.

Table 1

Acrylic microfiber/nanofiber properties

As noted above, such fibers are actually present in the pulp-like formulation to facilitate introduction into the wet laid nonwoven production schedule.

Non-woven production method

The combination of materials is dispensed to provide two components at different concentrations and then introduced into the wet manufacturing process along with the two components. Handsheets were made according to TAPPI Test Method T-205, and TAPPI Test Method T-205 is incorporated herein by reference (basically, as described above, mixed together in a very high water solvent concentration formulation and typically used High shear conditions in wet manufacturing, and described as "refining" of the fibers, ultimately placing the wet structure on a flat surface to evaporate the solvent). Several different combinations are produced to form the final nonwoven structure. In this method, only the initial amount of material incorporated into each of the sheets is adjusted so as to be adjusted so as to match the different basis weights. Materials and ratios are shown in Table 2.

Figures 5 and 6 are also structurally related to embodiment 39 below. Structural similarities (larger microfibers and smaller nanofibers) are clarified, and it has also been confirmed from these photomicrographs that there are fewer nanofibers present in these structures.

The thickness of the cloth is measured and cut to a suitable size and shape for introduction into a lithium ion rechargeable battery. However, prior to any such introduction, samples of the battery separator cloth were analyzed and tested for various properties associated with use as a battery separator. Further, the following is reported in the present patent and Celgard product literature as a comparative example: a battery separator nanofiber membrane according to U.S. Patent No. 7,112,389, which is incorporated herein by reference, and a battery separator from Celgard.

Example

Fabrication of Examples 36-51 according to TAPPI Test Method T-205 using Engineered Fiber Technology EFTECTM A-010-04 fibrillated acrylic fibers (combination of microfibers and nanofibers) (as matrix fibers) and FiberVisions T426 fibers, The FiberVisions T426 fiber was a bicomponent fiber made of polypropylene and polyethylene having a length of 2 deniers and a length of 5 mm and a diameter of about 17 micrometers (as an added fiber). The sheet was calendered between two hard steel rolls at room temperature (~25 ° C) at a length of 2200 pounds per linear inch. Table 4 gives the amounts of each fiber of the examples, the adjusted basis weight, the sheet thickness (or thickness), the apparent density, and the porosity. Adjusted basis weight, sheet thickness, apparent density, and stretchability were tested according to TAPPI T220, which is incorporated herein by reference.

Table 2

Diaphragm properties

The higher the porosity, the higher the peak power output within the target cell. In theory, with such high results, by increasing the available power of a single battery, at least the number of batteries necessary to operate the necessary power levels of a particular device, such as a hybrid car, can be reduced. This benefit is also related to effective air resistance blocking. It can be seen from the following that the porosity of the separator of the present invention can also be controlled by controlling the ratio of nanofibers to microfibers, the type of nanofibers, and post treatment by calendering or the like.

Basic analysis and testing of battery separator

The test plan is as follows:

Porosity is calculated according to the method of U.S. Patent No. 7,112,389, which is incorporated herein by reference. The results are reported in %, which relates to the volumetric portion of the membrane filled with a gas or non-solid material (when in a battery, such as an electrolyte).

Gurley air resistance was tested according to the TAPPI test method T460 incorporated herein by reference. The instrument used in this test was a Gurley Densometer, Model 4110. For testing, the sample was inserted and fixed in the gas permeability meter. The cylinder gradient rises to a 100 cc (100 ml) line and is then allowed to descend to its own weight. Record the time (in seconds) that 100 cc of air passed through the sample. The result is reported in seconds/100 cc, which is the time required to pass 100 cubic centimeters of air through the membrane.

The average flow pore size was tested in accordance with ASTM E-1294, "Standard Test Method for Pore Size Characteristics of Membrane Filters Using Automatic Fluid Porosimeters," using an automatic bubble point method according to ASTM F316 and using a capillary flow porosimeter. The test was carried out by Porous Materials, Inc., Ithaca, NY.

The permeability of the diaphragm is measured based on the time required for a fixed amount of air to pass through the standard area under lighter pressure. This process is described in ASTM D-726-58.

table 3

Tensile properties and average flow pore size

Embodiments of the present invention show a very small average aperture, indicating that the target battery can have many sub-charge cycles. In addition, the pore size varies with the ratio of nanofiber to microfiber material, indicating the ability to control the pore size. This is a key advantage not found in any prior art, so that with this technology, battery manufacturers can adjust the aperture to the needs of the end user. As a result, the diaphragm can be designed for power tools or automotive applications that have different characteristics than rechargeable watch batteries, cell phones or laptops.

The tensile properties given in the examples are isotropic, i.e., all directions are the same, and there is no difference between the processing and the cross-sectional directions. The comparative examples show tensile properties in which the machine direction (MD) and the cross-sectional direction (CD) tensile strength are remarkably different. In general, nanofiber-based battery separators are very fragile. Thus, one advantage of the present invention is tensile strength, which allows for faster processing in battery manufacturing, tighter winding of the battery, and greater durability in battery use. Such MD tensile strength is preferably greater than 25 kg/cm 2 , more preferably greater than 50 kg/cm 2 , and most preferably greater than 100 kg/cm 2 . The requirement for CD tensile strength is low, preferably greater than 10 kg/cm 2 , more preferably greater than 25 kg/cm 2 , and most preferably greater than 50 kg/cm 2 .

As noted above, calendering and an increase in the number of nanofibers relative to the microfibers will reduce the overall average pore size, and even further, indicating that the techniques of the present invention are capable of achieving certain desired measurements. Sheet production of the initial separator is carried out on a paper machine (indicating that it can be manufactured in such a simple manner), and steps such as calendering are also performed.

Paper machine production

Two materials were fabricated on a vacuum cylinder paper machine. First, for Example 52, it was made of 75% EFTec A-010-4 and 25% 0.5 denier/filament and cut into polyethylene terephthalate (PET) fibers having a length of 6 mm. Second, for Example 53, it was made of 37.5% EFTec A-010-4, 37.5% EFTec L-010-4, and 25% PET fiber cut to a length of 6 mm. The fiber material was dispersed by a high shear mixer, mixed with water at a high dilution, and then fed into a front box of a vacuum cylinder paper machine to prepare a sheet having a weight of 20 g/m 2 and dried in a hot air oven. . The resulting roll was calendered at 325 °F at 2200 pounds per linear inch to give a first sheet having a thickness of -40 microns and a second sheet having a thickness of 30 microns. The shrinkage was measured at 90 ° C, 130 ° C and 160 ° C: the 12" length of the processing and section directions were measured separately, placed in an oven and held at the measured temperature for 1 hour, and the length was measured again. The shrinkage was relative to the original length. The change in length expressed as a percentage. The properties of the flakes are shown in Table 4 below.

Table 4

Film properties

It can be seen that materials having both acrylic fiber (EFTec A-010-4) and lyocell (EFTec L-010-4) materials exhibit very good properties at high temperatures. For example, many of today's stretch film separators are made of polyethylene which melts at 135 ° C and exhibits significant shrinkage at temperatures above 110 ° C; or is made of polypropylene which melts at 160 ° C and shows above 130 ° C A clear contraction. One problem known in the industry is that large batteries, especially for electric vehicles, can shrink the membranes at the edges due to shrinkage after exposure to high temperatures, causing the electrodes to contact each other at the edges, causing a short circuit and possibly causing a catastrophic thermal runaway. This in turn leads to an explosion. High temperature stability diaphragms are safer in these environments, allowing larger batteries to be used with higher energy per battery. Preferred membrane properties may have a shrinkage of less than 10% in both directions at 130 ° C, 160 ° C or 190 ° C, preferably a shrinkage of less than 6% or most preferably a shrinkage of less than 3%. Further, a separator having a high temperature stability such as lyocell fiber, rayon, para-aramid, meta-aramid or other fibers can be used to impart a low shrinkage result when forming a sheet with other materials, as in the embodiment. Shown in 53.

Additional examples under different rolling conditions were made and tested. Construction paper on a vacuum cylinder paper machine at the Herty Foundation facility containing 27% EFTec A-010-04 acrylic nanofibers, 53% EFTec L-010-04 lyocell nanofibers and 20% 0.5 denier/filament cut into 5 mm length polyester fibers. The material was mixed in a 1000 gallon hydropulper for 40 minutes and then fed into the machine at a fiber content of about 0.25% to produce a sheet having an areal density of 15 g/m 2 . The paper was calendered under different conditions, which are listed below and shown in Examples 56-60 in Table 5 below.

Description of Examples 56-60:

56: The roller was not heated, and in addition to this, calendering was carried out using the above conditions.

57: The sheet was fed into the calender together with the second sheet of Example 56 to laminate the sheets together.

58: The sheet from 56 is fed into a calender along with a roll of carbon paper (requires wt??) and then peeled off from the carbon paper.

59: The sheet from 56 was passed through the second calender under the same conditions.

60: The laminate of 57 was peeled off to form two separate sheets.

The following two points can be seen from the following examples. First, the lamella of the two sheets gives more than twice the Gurley air resistance and a lower total porosity compared to a single layer. Second, the second calendering has the effect of increasing the porosity and lowering the graininess. Finally, the two sheets fed together with the other sheet have the effect of simultaneously increasing the graininess and increasing the porosity. In all cases where additional calendering was carried out, the tensile strength was lowered.

table 5

Calendered sheet results

Wettability test

Square Celgard 2320 was attached to Square Example 39, and a drop of 1 M LiPF6 in an EC:DMC:DEC mixture (volume ratio 1:1:1) electrolyte was placed on the surface. After 5 seconds, the electrolyte was completely absorbed into Example 39, and spectral reflection was not observed (i.e., different spectra measured at different angles produced a difference in the shiny surface formed by the droplets on the surface). In contrast, the electrolyte droplets on Celgard 2320 remained well for more than 5 seconds without producing a complete capillary action on the overall structure. This spectral reflectance of the materials of the present invention is highly desirable for lithium ion battery separators to increase the processing rate of the dispersed electrolyte and to ensure uniform dispersion of the electrolyte on and in the membrane. It is known that a non-uniform dispersion of electrolyte promotes the formation of dendrites during repeated charging and discharging, thereby becoming a defect in the battery and causing a short circuit.

Therefore, it is desirable that the liquid electrolyte exhibits a uniform spectral reflection on the surface after 5 minutes of placement (in the form of droplets), preferably less than 2 minutes, more preferably less than 1 minute. Furthermore, it is desirable to fabricate an energy storage device from two electrodes, a membrane and an electrolyte such that the membrane exhibits the same spectral reflectance measurements in the same manner.

In fact, the membrane of the present invention exhibits spectral reflectance measurements in each case for up to 5 seconds (most measurements show 2 seconds and less than this value as a result), thereby exhibiting an effective capillary action of the liquid electrolyte throughout the membrane (thus Is a uniform dispersion).

Other tests were also performed for wettability measurements, including differential scanning calorimetry and thermogravimetric analysis. Example 53 was tested by thermogravimetric analysis from room temperature to 1000 °C. The sample showed a mass loss of 1.39% at the final near 100 °C, which is consistent with the water

loss from cellulose nanofibers and microfibers. Up to about 300 ° C, the material did not degrade further, and oxidation started at 335 ° C and 400 ° C and produced a sharp drop in mass of about 60%. Example 53 was also tested by differential scanning calorimetry from room temperature to 300 °C. There is a broad exotherm around center at about 100 °C, which is consistent with the discharge of water, and there is a sharp exotherm at 266 °C, starting at 250 °C and consistent with the melting point of PET.

Example 52 was tested by thermogravimetric analysis from room temperature to 1000 °C. The sample showed very little mass loss below 300 °C, starting mass loss at 335 °C until the mass loss at 400 °C was about 40%. Example 52 was also tested by differential scanning calorimetry from room temperature to 300 °C. There was almost no fluctuation between room temperature and 266 ° C, and there was a sharp exothermic curve at 266 ° C, starting at 250 ° C, which is consistent with the melting point of PET. In short, the curve showed no fluctuations except for the melting of the PET microfibers.

Battery formation and actual battery test results

Figure 7 shows a typical battery 10 construction with a housing 12 that includes all of the other components and is securely sealed to prevent environmental contamination from entering the battery and leaking any electrolyte from the battery. The anode 14 is disposed in series with the cathode 16 with at least one battery separator 18 therebetween. Electrolyte 20 is added to the cell prior to sealing to produce the necessary ions. The diaphragm 18 assists in preventing the anode 14 from contacting the cathode 16 and allowing selected ions from the electrolyte to migrate therethrough. The normal mode of the battery follows this structural description, with different structural sizes and configurations for each internal component, depending on the size and structure of the battery itself. In this case, a button cell of a substantially circular solid component is produced to suitably test the effectiveness of such a battery inner diaphragm.

To achieve that goal, first test the electrical properties of the separator as follows: Make a symmetrical lithium foil-separator-lithium foil 2016 button cell and test the resistance, then make an asymmetric carbon electrode-diaphragm-lithium foil 2016 button battery. The test was completed at the Nanotechnology Laboratory of the School of Materials Science and Engineering at Georgia Tech. For a symmetric lithium-diaphragm-lithium 2016 button cell, a 5/8" circle was cut from the selected septum and dried in a vacuum chamber of a 70 °C argon-filled glove box for approximately 12 hours and assembled as:

(a) a symmetrical lithium foil-separator-lithium foil 2016 button battery; and

(b) Asymmetrical carbon electrode-separator-lithium foil 2016 button battery.

The electrolyte used was 1 M LiPF6 in an EC:DMC:DEC mixture (volume ratio 1:1:1). Lithium foil was rolled to a thickness of 0.45 mm and one or two layers of separator were used in this study. At the same time, the Celgard 2325 diaphragm is used for comparative testing purposes.

After 2 days of storage, a constant potential electrochemical impedance spectroscopy (EIS) measurement from a frequency range of 0.01 Hz to 100 kHz was performed on each of the assembled two-electrode Li-Separator-Li button cells.

Each cell includes the following items that contribute to the total resistance: (i) Li ion transport in the electrolyte/membrane; (ii) Li ion transport in the solid-electrolyte-mesophase (SEI) layer on each Li electrode; (iii) Electron transport in Li/battery/touch. Among the compositions of these resistors, (iii) electron transport is generally negligible, and due to the high characteristic frequency of Li ions, (i) Li ion transport in the electrolyte does not give a half period in the current frequency region.

As the most interesting (i) Li ion transport in the electrolyte/membrane, the focus is on the high frequency region of the Nyquist plot associated with it. The total resistance of the ions transported through the diaphragm is approximately the value of the real part of the total resistance Z of the high frequency, whereas the imaginary part of the complex impedance is zero. As mentioned above, the resistance of the interface and electrodes is much smaller than the ionic resistance and can therefore be ignored.

Further battery production and testing

Additional pocket batteries are manufactured as follows: Standard cell phone battery electrodes have a coating weight of approximately 2.5 mAh/cm 2 . The coating produced for the test had a coating weight of 4 mAh/cm 2

(NCA) to indicate that the capacity limit of the separator exceeded the standard because the coating weight involved rate capability. One battery (manufactured) of each diaphragm type was constructed using Celgard 2325 (hereinafter, Example 54) and Example 53 (hereinafter, Example 55). The electrodes were coated, calendered, dried, soldered at the ends, placed in a sandwich package, filled and sealed with 1 M Li salt in a standard battery solvent electrolyte. The discharge capacity of the battery was tested at C/10, C/4, C/2, and C rates, and multiple discharges were performed at each rate. The results are shown in Table 7 below, which is the first discharge after formation. Percentage of /10 capacity. The specific discharge capacity at C/10 of the battery of Example 54 was 141 mAh/g, and that of the battery of Example 55 was 145 mAh/g.

Table 6

Pocket battery measurement

It can be seen from these examples that a battery fabricated using the separator of the present invention has a higher discharge capacity at a higher rate, a small advantage at C/4, and a greater and significant advantage at rates of C/2 and C. .

It will be appreciated that various modifications may be made by those skilled in the art without departing from the scope of the invention. It is therefore intended that the present invention be limited by the scope of the appended claims

CN104871341A Versatile single-layer lithium ion battery separators having nanofiber and microfiber components

Data originating from sources other than the EPO may not be accurate, complete, or up to date.

The wording below is an initial machine translation of the original publication. To generate a version using the latest translation technology, go to the original language text and use Patent Translate.

1.A polymer battery separator comprising a single layer nonwoven combination of microfibers and nanofibers, wherein a single layer of the separator has a bimodal distribution of fiber lengths, and an average length of the microfibers is greater than five of an average length of the nanofibers Times, and the average flow pore size is less than 2000 nm or 2.0 μm.

2.The battery separator of claim 1 comprising a fiber monolayer comprising nanofibers and microfibers, said nanofibers having an average maximum width of less than 1000 nm, said microfibers having a maximum width greater than 3000 nanometers, and The nanofibers and the microfibers are doped with each other such that at least a portion of the nanofibers remain in the gap between the microfibers.

3.The battery separator according to claim 1, wherein the electrolyte droplets placed on the separator are sucked into the separator to such an extent that the spectral reflection disappears in less than 5 minutes.

4.The battery separator according to claim 1, wherein the nanofibers are the same material as the microfibers.

5.The battery separator according to claim 1, wherein the nanofibers are materials different from the microfibers.

6.The battery separator according to claim 1, wherein the nanofibers are selected from the group consisting of polyaramids, meta-aramids, cellulose fibers, polyacrylates, and any combination thereof.

7.The battery separator according to claim 1, comprising island-in-the-sea nanofibers.

8.The battery separator of claim 1 comprising island-in-the-sea microfibers.

9.The battery separator of claim 1 comprising fibrillated nanofibers.

10.The battery separator of claim 1 comprising fibrillated microfibers.

11.The battery separator of claim 1 wherein the average flow pore size is less than 800 nm.

12.The battery separator of claim 1 wherein the thickness is less than 250 microns.

13.The battery separator of claim 8 wherein the thickness is less than 100 microns.

14.An energy storage device formed from two electrodes, an electrolyte, and a separator according to claim 1, wherein the spectral reflection of the droplets of the electrolyte placed on the separator disappears in less than 5 minutes.

15.A battery separator according to claim 1 comprising at least one fiber flowing at a high temperature and/or a high pressure and at least one fiber not flowing at the same temperature and/or pressure.

16.The battery separator of claim 1 comprising microfibers having a length greater than 0.5 mm.

17.A polymer battery separator comprising a single layer nonwoven combination of microfibers and nanofibers, wherein a single layer of the separator has a bimodal distribution of fiber diameters, and an average diameter of the microfibers is greater than three of an average diameter of the nanofibers Times, and the average flow pore size is less than 0.80 μm.

18.The battery separator according to claim 17, wherein the electrolyte droplets placed on the separator are sucked into the separator to such an extent that the spectral reflection disappears in less than 5 minutes.

19.The battery separator of claim 17 comprising fibrillated nanofibers.

20.The battery separator of claim 17 comprising fibrillated microfibers.

21.The battery separator of claim 17 wherein the average flow pore size is less than 800 nm.

22.A battery separator according to claim 17, comprising at least one fiber flowing at a high temperature and/or a high pressure and at least one fiber not flowing at the same temperature and/or pressure.

23.The battery separator of claim 17 comprising microfibers having a length greater than 0.5 mm.

24.A polymer battery separator comprising a single layer nonwoven combination of microfibers and nanofibers, wherein a single layer of the separator has a heat shrinkage ratio in a machine direction and a cross section at 160 ° C for 1 hour is less than 10% and the average flow pore size is less than 0.80 μm.

25.A polymer battery separator according to claim 24, wherein said separator has a heat shrinkage ratio of less than 6% in both the machine direction and the cross-sectional direction at 240 ° C for 1 hour.

26.The battery separator according to claim 24, wherein the electrolyte droplets placed on the separator are sucked into the separator to such an extent that the spectral reflection disappears in less than 5 minutes.

27.The battery separator of claim 24 comprising fibrillated nanofibers.

28.The battery separator of claim 24 comprising fibrillated microfibers.

29.The battery separator of claim 24 wherein the average flow pore size is less than 800 nm.

30.A battery separator according to claim 24 comprising at least one fiber flowing at a high temperature and/or a high pressure and at least one fiber not flowing at the same temperature and/or pressure.

31.A battery separator according to claim 24 comprising microfibers having a length greater than 0.5 mm.

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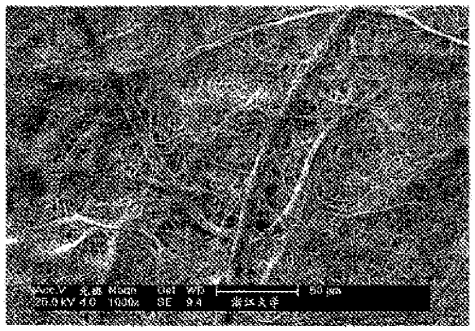
权利要求书2页 说明书18页 附图7页

(54)发明名称

具有纳米纤维和微米纤维成分的通用单层锂离子电池隔膜

(57)摘要

本发明提供一种绝缘（非导电性）微孔聚合物电池隔膜，其包含微米纤维和纳米纤维交缠而成的单层。这样的隔膜可以通过使用单一非织造布而能够将孔隙率和孔径调节为任何期望的水平。通过适当选择材料和制造工艺，所得电池隔膜展现出各向同性强度、低收缩率、高润湿性水平，以及与层厚直接相关的孔径。整体制造方法效率高，并且通过成本效率高的高剪切加工可以将聚合物纳米纤维组合到聚合物微米纤维基体中和/或这样的基底上。隔膜、含有该隔膜的电池、制造该隔膜的方法和在电池装置中利用该隔膜的方法，均包含在本发明中。



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1. 一种聚合物电池隔膜，其包含微米纤维和纳米纤维的单层非织造组合，其中，所述隔膜的单层具有纤维长度的双峰分布，微米纤维的平均长度大于纳米纤维的平均长度的五倍，并且平均流量孔径小于 2000 纳米即 2.0 μm。

2. 根据权利要求 1 所述的电池隔膜，其包含纤维单层，所述层包含纳米纤维和微米纤维，所述纳米纤维的平均最大宽度小于 1000nm，所述微米纤维的最大宽度大于 3000 纳米，并且所述纳米纤维与微米纤维相互掺杂以便至少一部分所述纳米纤维留在所述微米纤维之间的缝隙中。

3. 根据权利要求 1 所述的电池隔膜，其中，置于隔膜上的电解质液滴被吸入隔膜中，吸入的程度为光谱反射在小于 5 分钟的时间内消失。

4. 根据权利要求 1 所述的电池隔膜，其中，所述纳米纤维为与所述微米纤维相同的材料。

5. 根据权利要求 1 所述的电池隔膜，其中，所述纳米纤维为与所述微米纤维不同的材料。

6. 根据权利要求 1 所述的电池隔膜，其中，所述纳米纤维选自由以下所组成的组：聚芳酰胺、间芳酰胺、纤维素纤维、聚丙烯酸酯以及它们的任意组合。

7. 根据权利要求 1 所述的电池隔膜，其包含海岛型的纳米纤维。

8. 根据权利要求 1 所述的电池隔膜，其包含海岛型的微米纤维。

9. 根据权利要求 1 所述的电池隔膜，其包含原纤化的纳米纤维。

10. 根据权利要求 1 所述的电池隔膜，其包含原纤化的微米纤维。

11. 根据权利要求 1 所述的电池隔膜，其中，平均流量孔径小于 800nm。

12. 根据权利要求 1 所述的电池隔膜，其中，厚度小于 250 微米。

13. 根据权利要求 8 所述的电池隔膜，其中，厚度小于 100 微米。

14. 一种能量存储装置，其由两个电极、电解质和根据权利要求 1 所述的隔膜形成，其中，置放于隔膜上的所述电解质的液滴的光谱反射在小于 5 分钟的时间内消失。

15. 根据权利要求 1 所述的电池隔膜，其包含至少一种在高温和 / 或高压下流动的纤维以及至少一种在相同温度和 / 压力下不流动的纤维。

16. 根据权利要求 1 所述的电池隔膜，其包含长度大于 0.5mm 的微米纤维。

17. 一种聚合物电池隔膜，其包含微米纤维和纳米纤维的单层非织造组合，其中，所述隔膜的单层具有纤维直径的双峰分布，微米纤维的平均直径大于纳米纤维的平均直径的三倍，并且平均流量孔径小于 0.80 μm。

18. 根据权利要求 17 所述的电池隔膜，其中，置于隔膜上的电解质液滴被吸入隔膜，吸入的程度为光谱反射在小于 5 分钟的时间内消失。

19. 根据权利要求 17 所述的电池隔膜，其包含原纤化的纳米纤维。

20. 根据权利要求 17 所述的电池隔膜，其包含原纤化的微米纤维。

21. 根据权利要求 17 所述的电池隔膜，其中，平均流量孔径小于 800nm。

22. 根据权利要求 17 所述的电池隔膜，其包含至少一种在高温和 / 或高压下流动的纤维以及至少一种在相同温度和 / 压力下不流动的纤维。

23. 根据权利要求 17 所述的电池隔膜，其包含长度大于 0.5mm 的微米纤维。

24. 一种聚合物电池隔膜，其包含微米纤维和纳米纤维的单层非织造组合，其中，所述

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隔膜的单层在 160℃、1 小时的条件下在加工方向和截面方向的热收缩率均小于 10%，并且平均流量孔径小于 0.80 μm。

25. 一种根据权利要求 24 所述的聚合物电池隔膜，其中，所述隔膜在 240℃、1 小时的条件下在加工方向和截面方向的热收缩率均小于 6%。

26. 根据权利要求 24 所述的电池隔膜，其中，置于隔膜上的电解质液滴被吸入隔膜，吸入的程度为光谱反射在小于 5 分钟的时间内消失。

27. 根据权利要求 24 所述的电池隔膜，其包含原纤化的纳米纤维。

28. 根据权利要求 24 所述的电池隔膜，其包含原纤化的微米纤维。

29. 根据权利要求 24 所述的电池隔膜，其中，平均流量孔径小于 800nm。

30. 根据权利要求 24 所述的电池隔膜，其包含至少一种在高温和 / 或高压下流动的纤维以及至少一种在相同温度和 / 压力下不流动的纤维。

31. 根据权利要求 24 所述的电池隔膜，其包含长度大于 0.5mm 的微米纤维。

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具有纳米纤维和微米纤维成分的通用单层锂离子电池隔膜

技术领域

[0001] 本发明涉及绝缘（非导电性）微孔聚合物电池隔膜，其包含微米纤维和纳米纤维交缠而成的单层。这样的隔膜可以通过使用单一非织造布而能够将孔隙率和孔径调节为任何期望的水平。通过适当选择材料和制造工艺，所得电池隔膜展现出各向同性强度、低收缩率、高润湿性水平，以及与层厚直接相关的孔径。整体制造方法效率高，并且通过成本效率高的高剪切加工可以将聚合物纳米纤维组合到聚合物微米纤维基体中和/或这样的基底上。隔膜、含有该隔膜的电池、制造该隔膜的方法和在电池装置中利用该隔膜的方法，均包含在本发明中。背景技术

[0002] 电池作为在远距离地点的电能发生器已使用了许多年。其通过控制离子在电极（阳极和阴极）之间的移动产生电力电路，从而提供电源，可用至一个电极中过量的离子耗尽而不可能再产生电。近年来，已创造出充电电池来使这样的远距离能源具备更长的寿命，尽管需要将这种电池与其他电源连接一段时间。总之，这种电池的再使用能力已发展出更大的应用潜力，尤其是用于手机和笔记本电脑，甚至能够用于仅靠电运行的汽车。

[0003] 这种电池典型地包括至少5种不同组件。外壳（或容器）以安全与可靠的方式包覆各组件以防止泄露至外部以及防止内部暴露于环境。在该外壳的内部是阳极和阴极，其有效地被隔膜隔离；以及电解质溶液（低粘度液体），其通过隔膜在阳极和阴极之间传输离子。在如今以及可预见的将来，充电电池将全方位用于非常小而便携的设备，具有强大的产电能力从而在充电间隔的长时间里保持有效，还用于汽车中存在的非常大的类型的电池，这样的电池例如包括彼此不可接触的大型电极（至少在表面区域），以及必须持续且恒定地穿过膜来完成必要电路的大量离子，所有这些的产能水平有助于提供用于运转汽车发动机的足够电力。正因如此，未来电池隔膜的能力和通用性必须达到一定要求，这在当今行业还未能够实现。

[0004] 一般而言，从封闭电池的出现以来，使用电池隔膜从而在不期望接触的电极之间提供必要的保护以及允许电解质在产电电池单元内的有效传输。典型地，这种材料具有膜结构，该膜结构足够薄以减少电池装置的重量和体积，同时给予上述提到的必要性能。这种隔膜还必须具备其他特性以发挥合适的电池功能。这些功能包括化学稳定性、离子种类的合适的孔隙率、电解质传输的有效孔径、合适的透过性、有效的机械强度、以及当暴露于保温时保持尺寸和功能稳定性的能力（以及当温度升高至异常高的水平时切断的能力）。

[0005] 更详细而言，隔膜材料必须具备足够的强度和结构以应对多种不同的情况。首先，在电池组装的受力期间，隔膜不能被撕破或戳破。这样，隔膜的总体机械强度极其重要，尤其作为在加工和截面（即，横断）方向均具有高拉伸强度的材料，允许制造者更容易操作这种隔膜且无需严格的指导，以免在关键的步骤中使隔膜受到结构破坏或损失。此外，从化学观点来看，隔膜必须耐受电池自身内部的氧化和还原环境，尤其是在充满电时。使用过程中的任何失效，特别是结构完整性方面的失效，即允许异常的大量电流通过或使电极可触碰，将会毁坏产电能力而使得电池完全失效。因此，为了上述相同的理由，即使具有高于耐气候化学暴露的能力，这种隔膜还必须在存储、制造和使用过程中，不丧失尺寸稳定性（即，翘

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曲或熔化）或机械强度。

[0006] 同时，隔膜必须具备基本上合适的厚度以利于电池本身的高能量和功率密度。为了允许长期循环，均匀地厚度也十分重要，这是因为任何对隔膜不均匀的磨损将会成为电解质通路以及电极接触保护的薄弱环节。

[0007] 此外，这种隔膜必须展现出合适的孔隙率和孔径以适应离子通过该膜进行合适的传输（以及合适的容量以在使用过程中保持一定量的液体电解质来利于该离子转移）。孔本身应当足够小以防止电极成分进入和/或穿过膜，但如上所述还应当允许电解质离子的合适的转移率。还有，孔径的均匀性以及孔径分布提供更加均匀的经时产电结果，以及如上所述对于整个电池而言更加可靠的长期稳定性，在这样的系统中至少尽可能最佳控制电池隔膜的均匀磨损，以允许更长的寿命周期。此外，确保一旦暴露于异常高温时其中的孔适当关闭，这利于防止电池失效后过量和非期望的离子转移（即，防止火灾和其他灾害）。

[0008] 并且，孔径和分布可以提高或降低隔膜的空气阻力，从而允许简单测量隔膜来指示电池具有允许存在于电池本身内部的电解质充分通过的能力。例如，平均流量孔径(mean flow pore size)可根据ASTM E-1294测量，并且可使用该测量值来帮助确定隔膜的阻隔性能。因此，具有较低孔径时，孔本身的刚度（即，在使用过程中孔随时间且暴露于设定压力下保持某一大小的能力）也允许电极隔离的有效控制。更重要的是或许这样的孔径水平能够限制枝状晶形成，从而减少在阳极上形成晶体（比如在石墨阳极上的锂结晶）的几率，在阳极上形成晶体会有害地影响电池随时间的产电能力。

[0009] 进一步，在制造、存储和使用期间，隔膜一定不能削弱电解质完全填充整个电池的能力。因此，在这些阶段，隔膜必须展现出合适的毛细作用和/或润湿性以确保电解质事实上可合适地使离子转移通过膜；如果隔膜不能有助于这样的情况，则电解质将不能合适地留在隔膜孔上和内部，并且不易发生必要的离子传输。此外，应当理解通常要求隔膜具有该合适的润湿性是为了确保液态电解质在隔膜表面和电池内部的分散。电解质分散体的非均匀性可导致在电池内部和隔膜表面形成枝状晶，从而产生提高的电势而使电池失效且在其中发生短路。

[0010] 如上所述，当将该隔膜应用在典型的锂离子电池中时还十分关注尺寸稳定性。无疑隔膜在整个电池寿命期间必定提供用作离子扩散的多孔隔板。然而，在某些情况下，来自外源或电池自身内部的温度提升可使敏感的隔膜材料发生非期望的收缩、翘曲或熔化，其中任意一种均可随时间有害影响电池的性能。正因如此，在实际使用期间由于降低温度水平和/或使该类型电池从提升的温度中脱离非常难以实现，因此隔膜本身应当包含能够耐受该高温且暴露后不受明显影响的材料。可选地，使用其中一种为纤维的材料的组合将会极具吸引力，例如，可在提供这样的有益结果的同时仍使隔膜在其最适水平上发挥作用。

[0011] 然而，如上所述，现如今适合的标准不符合这种关键的考虑因素。有效电池隔膜的一般性目的在于，在单一薄片材料中提供全部的有益特性。低空气阻力、非常小的孔径和合适的孔径分布、在化学和提升的温度环境下的尺寸稳定性、合适的润湿性、用于允许最多的电池成分存在于尽可能小的封闭空间的最佳厚度以及有效的总体拉伸强度（本质上优选各向同性），提供上述这些特性的能力均是必要的，以便使材料符合如下条件：显著降低电极接触的任何可能性，但具有控制电解质从电池的一个部分传输至另一部分的能力（即，使电路闭合以产生所需电力），换言之，以最小的电池体积得到最长期的最大电池输出。目

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前，并没有有效地同时提供这些性质至这样的程度。例如，Celgard 公开且销售了一种具有非常低孔径的扩展膜电池隔膜，其在如上所述的方面非常良好；然而，这样的材料相应的空气阻力极高，因此限制了这样的隔膜的总体有效性。相反，杜邦（duPont）商业化了一种纳米纤维非织造膜隔膜，其提供非常低的空气阻力，但在其中具有过大的孔径。此外，这两种材料所展现出的总体机械强度非常有限；Celgard 隔膜在加工方向具有优异的强度，但在截面（横断）方向强度近乎为零。由于上述提及的那样，这样低的截面强度要求至少会导致在制造过程中需要非常精细的操作。杜邦材料好一些，但在两个方向上强度均相当低，尽管截面方向的强度高于 Celgard 材料。实际上，杜邦产品接近于各向同性材料（在加工方向和截面方向具有近乎相同的强度），因此相比于 Celgard 类型，提供了在操作方面更为可靠的材料。然而，所测得的杜邦隔膜的拉伸强度实际上非常低，因此还需要用户在制造过程中仔细操作和放置这样的材料。类似地，由于这些拉伸强度问题，这样的现有电池隔膜的尺寸稳定性非常不可靠，有可能导致当材料存在于充电电池中时随时间不期望地丧失它们的结构完整性。

[0012] 因此，仍需要提供一种电池隔膜，该电池隔膜同时提供全部这些用于长期、可靠的锂电池产品的特性。如此，尽管这样的隔膜展现出低空气阻力和低孔径、以及整体上和相对各向同性水平的高拉伸强度、合适的化学稳定性、结构完整性和尺寸稳定性（特别是在暴露于提升的温度后），尽管非常期望，但至今显然仍未能提供这种有价值的隔膜材料。此外，通过有效的制造工艺实现这样的期望的目标性质水平的生产电池隔膜的方法也将值得期待，特别是如果在材料选择等上改动较少就能获得这样的期望的有益效果和要求，则受到高度期待；目前，在整个电池隔膜行业中尚待开发出达到这一程度的制造方法。因此，有效且非常简单直接的下述电池隔膜制造方法在充电电池隔膜行业中是有价值的；该方法提供任意数量的展现出多种最终结果的膜（即，通过按需要改进方法以获得目标孔隙率和空气阻力水平），此外还提供适当水平的机械性质、耐热性、透过性、尺寸稳定性、切断性能和熔化性能；至今，也没有获得这样的材料。

发明内容

[0013] 本发明的独特优势在于，易于通过湿法非织造制造工艺制造。另一独特优势在于，通过仅仅改变在制造工艺中使用的成分纤维的比例并对生产的单层材料适当压延，结果能够获得任意目标水平的孔径、孔隙率和空气阻力。本发明电池隔膜的又一优势在于，各向同性的强度性能满足用户长期使用以及在电池制造阶段的可靠性。本发明隔膜同时提供低空气阻力和低孔径的能力是本发明的进一步优势。本发明电池隔膜的又另一优势在于提供特定非导电（从而绝缘）的布（或纸），其不允许电荷通过隔膜本体传输，而是仅使带电离子通过存在于其结构中的孔来传输。又另一优势是材料的高孔隙率，通过允许电极完全再充电，允许更多离子流动且提高在许多个寿命周期中保持能量的能力耐久性。其他优势包括但不限于，能够通过在形成层之前适当选择纤维材料调整某些物理特性，以及能够首先使用全部微米纤维、通过对其进行高剪切处理来产生纳米纤维（原纤化形式）从而能够由单一起始材料形成全部必要隔膜成分。

[0014] 因此，本发明涉及一种聚合物电池隔膜，其包含微米纤维和纳米纤维的非织造组合，其中，所述隔膜的所述单层展现出各向同性拉伸强度，加工方向的拉伸强度小于截面方

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向的拉伸强度的三倍。更具体而言，本发明包含一种聚合物电池隔膜，其包含微米纤维和纳米纤维的单层非织造组合，其中，所述隔膜的所述单层具有纤维长度的双峰分布，微米纤维的平均长度大于纳米纤维的平均长度的五倍，并且平均流量孔径小于 2000 纳米 (2.0 μm)。可选地，本发明包含一种聚合物电池隔膜，其包含微米纤维和纳米纤维的单层非织造组合，其中，所述隔膜的所述单层具有纤维直径的双峰分布，微米纤维的平均直径大于纳米纤维的平均直径的二倍，并且平均流量孔径小于 2000 纳米 (2.0 μm)。此外，本发明包含一种聚合物电池隔膜，其包含微米纤维和纳米纤维的单层非织造组合，其中，所述隔膜的所述单层在 160℃、1 小时的条件下在加工方向和截面方向均具有小于 10％的热收缩率，并且平均流量孔径小于 0.80 μm。

[0015] 本发明的隔膜还展现出加工方向 (MD) 拉伸强度大于 90kg/cm²且小于 1,000kg/cm²，截面方向 (CD) 拉伸强度大于 30kg/cm²且小于 1,000kg/cm²，并且平均流量孔径小于 0.80 μm。进一步，该发明包括如上定义的电池隔膜并且包括纤维单层，所述层包括纳米纤维和微米纤维，所述纳米纤维的平均最大宽度小于 1000nm，所述微米纤维的最大宽度大于 3000 纳米，并且所述纳米纤维和微米纤维相互掺杂以便至少一部分所述纳米纤维留在所述微米纤维之间的缝隙中。

[0016] 此外，本发明涉及一种形成电池隔膜的方法，其中，所述电池隔膜的最大厚度为 250 微米，并且，其中，所述电池隔膜包含微米纤维组分和纳米纤维组分的组合，所述方法包括如下步骤：a) 提供水溶剂；b) 向其中导入多个纳米纤维和多个微米纤维以在水溶剂中形成微米纤维 / 纳米纤维分散体；c) 在高剪切条件下混合所述微米纤维 / 纳米纤维分散体；d) 向造纸机中导入高剪切的所述分散体；e) 生产微米纤维 / 纳米纤维材料的织物；和 f) 干燥所述织物。该方法还可以考虑包括通过压延工艺处理该织物的进一步加工步骤，以生产厚度最多为 100 微米和孔径最大为 2000nm 的隔膜材料。

[0017] 在该公开文本中，术语微米纤维用于指任何所测宽度为微米级的聚合物纤维，通常最大宽度大于 1000nm，也可大于 3000nm，甚至大于 5000nm 或甚至可能大于 10,000nm，高至约 40 微米。同样，术语纳米纤维用于指任何所测宽度为纳米级的聚合物纤维，通常最大宽度小于 1000nm，可能小于 700nm，或甚至小于 500nm 或甚至可能小于 300nm（低至约 1nm）。无论微米纤维或纳米纤维材料，应当了解，可将宽度理解为直径，但在该情况下，由于均一的纤维结构通常非常难以实现，可将直径理解为平均直径。因此，将最大宽度用作首要定义，尤其是如果纤维自身为非圆柱形状，对于这样的纤维，可考虑正方形、长方形、三角形或其他几何形状的可能，只要存在合适的微米纤维和纳米纤维测量值，其将均处于本发明的幅值范围内。同样，术语绝缘用于指无可测程度的导电率，从而本发明的布结构不允许电荷贯穿通过布本体，而仅允许通过电解离子通路，该电解离子通路穿过存在于其中的孔。

[0018] 在电池隔膜技术中已经研究了微米纤维和纳米纤维的这样的组合，特别是在为了这样的目的提供两个基本成分的单层非织造布的能力方面。该组合尤为重要，这是因为其提供具有纤维直径和长度的双峰分布的非织造布，其中，微米纤维组分的平均长度为纳米纤维组分的平均长度的至少 5 倍，优选为大于纳米纤维的平均长度的 10 倍，最优选为长于纳米纤维长度的 20 倍。此外，平均纤维直径也为双峰分布，其中，微米纤维的平均直径大于纳米纤维的平均直径的 3 倍，优选为大于纳米纤维的平均直径的 5 倍，最优选为大于纳米纤维的平均直径的 10 倍。该双峰分布允许微米纤维向单层隔膜提供仅靠纳米纤维无法提供

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的强度、弹性、透过性、模量、耐撕破和戳破性、湿强度、加工能力和其他特性。

[0019] 微米纤维组分可以为任何合适的聚合物，其提供上述必要的化学耐性和耐热性，以及形成微米纤维结构的能力。还有，这样的微米纤维可在形成纤维过程中或形成纤维之后被原纤化（或以任何其他类似方式处理，诸如通过等离子体暴露等）以便提高其表面积，从而在非织造制造工艺中利于多个这样的微米纤维之间进行期望的缠绕。因此，这样的聚合物成分可以包括丙烯酸类诸如聚丙烯腈，聚烯烃类诸如聚丙烯、聚乙烯、聚丁烯，以及其他，包括共聚物，聚酰胺，聚乙烯醇，聚对苯二甲酸乙二醇酯，聚对苯二甲酸丁二醇酯，聚砜，聚氟乙烯，聚偏二氟乙烯，聚偏二氟乙烯－六氟丙烯，聚甲基戊烯，聚苯硫醚，聚乙酰(polyacetyl)，聚氨基甲酸酯，芳香聚酰胺，半芳香聚酰胺，聚对苯二甲酸丙二醇酯，聚甲基丙烯酸甲酯，聚苯乙烯，纤维素聚合物（人造纤维，作为一种非限制性例子），聚芳酰胺包括对芳酰胺和间芳酰胺，以及包括这些聚合物的共混物、混合物和共聚物。聚丙烯酸酯、纤维素聚合物和聚芳酰胺是潜在优选的。这样的材料提供一系列极其理想的性能，与其他聚合物类型的性能组合而起作用，从而在拉伸强度、高温保护、润湿性和孔径容量方面获得主要的有利结果，特别是含有它们作为纳米纤维成分且同时含有类似微米纤维基体时。这样的微米纤维还可使用粘合剂进行预处理以在制造后实现整个非织造结构的理想的接触度和尺寸稳定性的程度。

[0020] 此外，可根据单独的纤维性能选择微米纤维以提供材料的组合，从而将期望的特性赋予整个电池隔膜。因此，由于聚芳酰胺、间芳酰胺和纤维素纤维提供优异的耐热性和某些强度益处，因此这些纤维被单独地嵌入（例如，作为湿法组分）或通过缠绕或其他方法作为组合被嵌入。这样的纤维必须具备充分的长度以向整个隔膜给予必要的强度，并且足够短以允许适当的嵌入（再一次，诸如在湿法过程中）。例如，微米纤维组分可优选为长于0.5mm，更优选为长于1mm，最优选为长于2mm。

[0021] 微米纤维或纳米纤维优选为在压力或高温下会熔化或流动的材料。具有一种相比于其他组分在较低的温度下会熔化或流动的组分是特别有益的。例如，聚酯微米纤维在接近熔化温度260℃的温度下可以流动。此外，可使聚丙烯腈微米纤维或纳米纤维在高压和高温下流动。纤维素、人造纤维、芳酰胺以及其他微米纤维或纳米纤维将在这些温度下不会流动。因此，材料的组合包含至少一种在高温和/或高压下流动的纤维以及至少一种在相同温度和/或压力下不会流动的纤维，这将能够使前一纤维与其他纤维结合，从而对非织造隔膜赋予额外的强度。

[0022] 纳米纤维可以为任何类似的聚合物成分和/或组合，以便耐受与微米纤维相同类型的化学和高温暴露。由于纳米纤维的尺寸，无需对这样的纳米纤维材料进行制造后处理以提高在生产的非织造物表面或非织造物缝隙中的缠绕。然而，可通过微米纤维原料的高剪切处理来生成纳米纤维，以便从中剥取纳米级的组分作为符合上述纳米纤维的定义的材料。这样，同样地，该剥离或剥取的纳米纤维将表现出原纤化的外观和性能，从而可能会在隔膜的制造中发生微米纤维缝隙中的交缠的改善（更不用说在相同的隔膜制造工艺中和/或之前、改善单独纳米纤维之间的交缠的潜能）。该情况下，微米纤维和纳米纤维材料可以来自相同的材料，通过将微米纤维材料的一些部分除去来形成纳米纤维组分，该纳米纤维可能具有不同的多种长度以及不同的截面和整体尺寸。在任何情况下，纳米纤维的制造可以通过这种方式进行，其中，将从微米纤维原料除去的成分收集并使用，不仅使用提供了该

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纳米纤维的微米纤维，而是与其他类型的微米纤维一起以这样的形式应用。在本发明的电池隔膜的这样的实施方式中，任何类型的纳米纤维可以为这样的目的利用。然而，优选的是，由于具有提供展现出潜在的有益性能如高温稳定性、拉伸强度等的纳米纤维的能力，可能创造利用特定类型的纤维的情况。

[0023] 虽然描述了可以利用该“原纤化”纳米纤维，但特制的纳米纤维成分可以嵌入在这样的微米纤维基体材料中，以获得作为本发明结果的通过湿法工艺制造的具有特定的孔径的隔膜薄片。因此，该制造工艺包含，向稀湿状态的微米纤维溶液中导入纳米纤维成分，将其在高剪切条件下混合，然后干燥而形成所得薄片。然后，可以对该薄片进行压延，以便按需减少薄片厚度，并且进一步调节至在其中存在的最佳孔径和孔径分布。通过使用适当地分散并嵌入微米纤维和纳米纤维成分的弹性薄片，该湿法工艺能够进行合适的薄片制造，其中，纳米纤维的量决定将微米纤维组分之间的缝隙填充的能力，由此在所得薄片中产生所期望的孔。压延操作可以使薄片厚度与孔径相关，尤其由于湿法制造后的薄片的整体拉伸强度。由此，这样的工艺提供相对简单但简洁的方法以提供将孔径分布和尺寸最佳化的能力，不会在挤压或操作整体结构时难以避免地有害地撕破、翘曲、和／或扰乱其尺寸稳定性。此外，由于能够使用简单的微米纤维／纳米纤维／水溶液用于薄片制造工艺，使得可以实现简洁且简单的方法，还可以实现减少或甚至不需要其他化学物质以实现所期望的生产方案的方法。这样的纯起始材料和整体制造方法进一步突出了极其未预想到的益处，该益处不仅包括为了本发明的产品所采用的方法，也包括用于这样的目的的微米纤维与纳米纤维和水溶液的简单的组合，还包括亟待实现的至今为止未能获得的所需电池隔膜材料，并且具有多种最终用途的通用性。

[0024] 因此，对于本发明的方法和产品而言，非常重要的是，纳米纤维组分在充分的高剪切环境下与微米纤维组合，从而在引入实际的非织造布本身的同时，向所得微米纤维非织造衬底上和非织造衬底中按照期望地引入该纳米纤维。换言之，通过在非织造工艺中提供两种纤维材料，制造商应当满足充分的混合量和高剪切条件，以便最好地确保不同的纤维类型之间的适宜程度的交缠，从而形成所期望的单层布结构。同样地，制造方法除高剪切型之外潜在地优选湿法非织造工艺，表面上用于最好地确保在微米纤维缝隙中的纳米纤维的适宜的导入和残留位置。随着制造中的水流量增加，极小的纳米纤维将以与干式交缠法相比更高的速率被拉进该缝隙中，从而赋予上述缝隙填充能力。此外，用于该目的的水位越高，纤维基体中交缠的合适的纳米纤维的纯度（回收水和多余的纤维，对此，进一步在分开的电池隔膜制造工艺中使用）和可靠性则越高。因此，所得非织造结构将会在厚度、孔隙率方面以及更重要地在孔径方面表现出更高的均匀性，此外，如上所述，还对于为了使厚度和孔径的结果最佳化的压延表现出更可靠的稳定性。

[0025] 这样的湿法工艺后的一种方法中，包括提供纸浆状制剂的预原纤化微米纤维，其包含例如相比于每份纤维为50:1至10000:1份的水（再次，优选单独的水，但根据需要，也可以使用其他可进行湿法工艺和后续促进其蒸发的溶剂，包括，例如某些非极性醇）。将预原纤化微米纤维通过这种方式处理，从而表现出一定量的已存在的纳米纤维（残留产物在原纤化时从微米纤维本身中去除，但没有从之后的微米纤维的整个所得网目中去除）。作为原纤化工艺的结果，该预原纤化微米纤维和纳米纤维为纸浆状，以致包含具有所得预原纤化微米纤维和纳米纤维的上述水基溶剂的泥浆状制剂。然后，将该泥浆状制剂与选定量的

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其他微米纤维和/或纳米纤维混合（优选，也为纸浆或泥浆状），或仅混合初始浆料，并将所得制剂在热水中加热到至少 60℃的温度，更优选至少 70、最优选至少 80 的温度，其中具有非常低的实际纤维固体成分的浓度（即，相对于水或其他水基溶剂的重量，低于 1%，低至小于 0.1%）。然后，该经加热的分散体将承受高剪切环境，之后放置在平坦的表面上。该表面具有充分多的孔以便进行溶剂洗脱，由此得到所期望的湿法非织造布单层，其包含相互交缠的原纤化微米纤维，并在每个微米纤维之间具有缝隙，并且纳米纤维存在于该缝隙中和更大微米纤维的表面上。这样，加入到预原纤化微米纤维纸浆中的纳米纤维的量能够实现微米纤维缝隙之间更大的填充量，以使整体平均孔径低，尤其相比于仅由单独的预原纤化纸浆制作的湿法非织造物。相反，通过将微米纤维加入预原纤化纤维料浆中，可以与单独的预原纤化纤维料浆相比实现所得湿法非织造单层布的更大的平均孔径。通过纳米纤维和/或微米纤维的加入水平，能够以不同的平均孔径为目标，这使得制造商可以实现任何所期望的平均孔径水平。

[0026] 在该高剪切混合步骤之后，将所得分散体送入造纸机（能够不损坏而制作重量轻的薄片的任何类型的造纸机，仅作为例子，例如为佛氏（Fourdrinier）造纸机、斜网造纸机（Inclined Wire）、真空圆网抄纸机（rotoformer）等装置）的机头部。该重量轻的薄片可以通过在机头端部控制纤维的分散体的输入并同时控制线速度来制造。关于这样的方法，优选不设定开放式脱水（open draws）（即，不支持湿的纤维织物）的机构。该情况下，高水位可以通过真空设备（其是在造纸产业中通用的步骤）来缓解，至少在起始阶段进行（即，将表面水分去除至一定水平）。对于合适的薄片产品，细隔距的造纸网是必要的，尤其隔距为最大 40 针数（gauge）、更优选为最大 80 针数。只要制造速度不影响最终结果以及整体拉伸强度（尤其在各向同性方面）不受损失，则对纸（分散薄片）的宽度可以为任何测量值。为了效率目的，可以将线速度设为 25 至 1,500ft/min 的范围内，更优选将最小值设为 50，最优选为 100。

[0027] 该纸（薄片）制作步骤完成后，将形成的薄片导入干燥装置中。可以利用任何标准的干燥设备，包括加热的蒸汽罐或热风炉。该加热应当超出水（或其他溶剂）蒸发所需要的温度，但不能高至使薄片本身熔化或变形。因此，该干燥温度可以取决于使用的材料，以及薄片厚度，这是因为某些材料相比于其他材料可以在尺寸稳定性方面耐受更高的温度，并且薄片越厚，通常越能耐更高的温度以抵御翘曲或其他影响。

[0028] 由此，制造商也可以通过根据需要使单层结构的厚度不同，来控制本发明的电池隔膜的所期望的性能。这样的厚度特性可以单独通过最初的湿法制造方法的工艺参数而提供，或制造商可以后续压延所制得的布直至任何所期望的厚度。由于可以进行压延或改变所制得的单层布的厚度，制造商可以进一步在空气阻力和平均孔径测量这两个方面实现更大的通用性。该调节工艺在电池隔膜产业中还未曾被探索。压延步骤利用通用的装置，仅作为例子，可以采用如硬质钢辊或单根硬质钢辊和第二硬质橡胶辊的组合。同样地，为了这样的目的，如上所述，如果材料能够耐受这样的状况而不产生任何明显的拉伸强度等的损失，则也可以实施多个压延步骤。

[0029] 因此，本发明所得的单层隔膜的厚度可以为小于 250 微米，优选为小于 100 微米，更优选为小于 50 微米，甚至优选为小于 35 微米，最优选为小于 25 微米。如上所述，为了防止电池使用中的短路，需要能够防止电池的阳极和阴极之间的接触；隔膜的厚度和其中被

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控制的孔径提供为了达到该结果的重要方式。然而，电池隔膜的厚度也有可能影响到封闭电池池体中的其他成分部分的有效体积以及其中所提供的电解质溶液量。因此，所涉及的整个情况要求在多个变量方面有效的隔膜。通过本发明的制造方法和从中制得的单层电池隔膜，能够有利地易于制造，并且能够提供有效的所需孔径和空气阻力性能，从而使得该发明进展与目前使用和销售的现有电池隔膜的状况明显地区分开。

[0030] 能够使纳米纤维和微米纤维的组合交缠的其他制造非织造薄片的方法，也可以用于制作本发明的电池隔膜。一个方法是从不同的纳米纤维和微米纤维开始，通过上述方法将它们结合。其他的该方法包括梳理法、交叉铺网法、水刺法、气流法 (air laid)、针刺法、熔喷、纺粘法，或将能够使微米纤维形成交缠的网状以及能够使纳米纤维填充上述微米纤维之间的缝隙的其他方法或方法的组合。

[0031] 事实上，如上所述，微米纤维缝隙形成该“孔”本身，并且纳米纤维填充于这样的开口以减小其中的尺寸，在整个非织造结构中减少至基本上均匀的程度。作为整个发明而言极其未预想到的益处，尤其是旨在按照需要获得不同的孔隙率水平，通过仅仅改变微米纤维相对于纳米纤维的浓度而能够调节所得非织造结构中的孔径。从而，例如，在非织造制造工艺的起初阶段，30％的微米纤维对 70％的纳米纤维的比例将提供 700nm 至 195nm 范围的孔径，而 10％微米纤维 /90％纳米纤维的组合将提供有效的更小的孔径分布（以及其更均匀的范围，例如 230nm 至 130nm）。由此，根据这种不可预料的结果，终端用户可以通过如上所述在制造中进行相当简单的改变而得到所要求的孔隙率。可以对所制得的该孔径进行测量，获得平均流量孔径。该平均流量孔径可以小于 2000nm，甚至小于 1000nm，优选小于 700nm，更优选小于 500nm。

[0032] 此外，应当注意的是，虽然本发明中包含将微米纤维和纳米纤维一起包含的单层隔膜，但也可以使用多层的该布结构，或使用一层本发明的电池隔膜布和至少一层其他不同类型的布，而这仍然属于在此说明的整个发明的范围内。

[0033] 在此所述的该电池隔膜明确地有助于改善一次电池和充电电池的技术，还可以用于其他形态的电解质导电的能量储存技术如电容器、超级电容器以及特级电容器。的确，通过控制本发明的这种隔膜的孔径，可以显著地改善这些装置的能量损失、放电功率、以及其他性能。

附图说明

[0034] 图 1 是现有技术扩展膜电池隔膜的 SEM 显微照片。

[0035] 图 2 是现有技术纳米纤维非织造布电池隔膜的 SEM 显微照片。

[0036] 图 3 和图 4 是本发明微米纤维 / 纳米纤维非织造布电池隔膜结构的一个潜在优选实施方式放大 1000 和 2000 倍的 SEM 显微照片。

[0037] 图 5 和图 6 是本发明微米纤维 / 纳米纤维非织造布电池隔膜结构的另一潜在优选实施方式放大 5000 和 10000 倍的 SEM 显微照片。

[0038] 图 7 表示包含本发明电池隔膜的本发明锂离子充电电池的分解图。

具体实施方式

[0039] 将结合下文的示例性但非限制性的各附图和各实施例详细描述本发明及其优选

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实施方式的所有特性。

[0040] 微米纤维和纳米纤维的生产

[0041] 如上所述，微米纤维可由任意聚合物（或共混聚合物）来构造，该聚合物符合合适的耐化学性和耐热性以及电池内部条件，以及在所述范围内形成合适的纤维结构的能力。这样的纤维可进一步具有通过原纤化或类似技术来处理从而增大用于在非织造制造过程中利于缠绕的纤维自身表面积的潜力。这样的纤维可以由诸如熔体纺丝、湿法纺丝、溶液纺丝、熔喷等现有的纤维制造方法制造。此外，这样的纤维可在开始时作为双成分纤维且可通过进一步加工使它们的大小和 / 或形状减少或变化，诸如可分割夹层纤维 (splittable pie fibers)、海岛纤维等。这样的纤维可被切成合适的长度用于进一步加工，该长度可小于 50mm，或小于 25mm，或甚至小于 12mm。这样的纤维也可制得长以给予更好的加工性或更高的强度，其长度长于 0.5mm，长于 1mm 或甚至长于 2mm。这样的纤维也可原纤化成更小的纤维或有利地形成湿法非织造布的纤维。

[0042] 用于本发明的纳米纤维可通过几种现有技术制造，诸如海岛、离心纺丝、电纺丝、薄膜或纤维原纤化等。Teijin 和 Hills 均为市售可优选的海岛纳米纤维 (Teijin 的海岛纳米纤维销售时被称为 NanoFront 纤维，直径为 500 至 700nm 的聚对苯二甲酸乙二醇酯纤维）。Dienes 和 FiberRio 均为使用离心纺丝技术提供纳米纤维的市售设备。Xanofi 是市售纤维且使用高剪切液态分散体技术来制造。由杜邦生产的纳米纤维态的聚芳酰胺表现出优异的耐高温性，以及其他尤为优选的性能。

[0043] 电纺丝纳米纤维的生产由杜邦、E-Spin 科技来实施，或由 Elmarco 在为此目的售卖的装置上实施。美国专利第 6,110,588、6,432,347 和 6,432,532 号中公开了从膜进行原纤化的纳米纤维，这些专利整体引用于此作为参考。在高剪切、研磨处理下可由其他纤维进行原纤化得到纳米纤维。Engineered Fiber 科技以商标名 EFTEC™ 销售由原纤化的纤维素和丙烯酸纤维制造的纳米纤维。也可通过切割和高剪切浆料加工来进一步加工任何这样的纳米纤维以分离纤维，从而能够使其进行湿法非织造物加工。在所需的微米纤维存在的情况下，可发生或不发生这样的高剪切加工。

[0044] 通常，由原纤化制造的纳米纤维的横宽比不同于以典型方式（例如，海岛）初始制造作为纳米纤维的横宽比。美国专利第 6,110,588 号中完整公开了一种这样的横宽比，其整体引用于此作为参考。因此，在一个优选的实施方式中，纳米纤维的横宽比大于 1.5:1，优选大于 3.0:1，更优选大于 5.0:1。

[0045] 正因如此，丙烯酸、聚酯和聚烯烃纤维尤其优选用于该目的，可最优选原纤化的丙烯酸纤维。然而，这仅表明用于该目的的潜在优选的聚合物类型，而不用于限制用于该目的的可能的聚合物材料或共混聚合物的范围。

[0046] 图 1 和图 2 分别提供了上述 Celgard 扩展膜材料和杜邦纳米纤维非织造电池隔膜材料的典型结构的显微照片。值得注意的是，Celgard 隔膜的膜结构显示出相似的孔径，明显均以相当均匀的形式通过膜挤出和最终表面破裂而形成。杜邦隔膜严格地单独由纳米纤维制造，这是因为纤维大小和直径的均一性是明显的。这些纳米纤维本身作为非织造结构，该隔膜在加工和截面方向的总体拉伸强度是非常低的，尽管在两个方向上十分均匀。因此，虽然这样的材料可被均匀地处理，但如果将这样的隔膜导入电池，则结果制造商最终必须面对因总体强度而导致的其他难题。与此相反，图 1 隔膜在相同方向上显示出由孔产生的

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条纹（从而为在一个方向上挤出膜），提供了极其高的加工方向拉伸强度；令人遗憾的是，相同材料在截面方向上的拉伸强度非常低，从而如前所述在电池制造业中实际使用非常困难且是令人质疑的电池隔膜材料。

[0047] 图 3 和图 4 中以显微照片形式给出的本发明材料具有与这两个现有技术产品（并且基于以下实施例 39）完全不同的结构。微米纤维和纳米纤维初始组合的一个潜在优选实施方式是 EPTEC® A-010-4 原纤化的聚丙烯腈纤维，其具有大量的纳米纤维以及残留的微米纤维。存在于这一组合的所得纳米纤维来自初始微米纤维的原纤化。由这些材料制造的非织造薄片示于图 3 和图 4。作为例子，这些纤维可被用作基体材料，可向其添加进一步微米纤维或进一步的纳米纤维以控制非织造布的孔径和其他性质。或者，可将这样的材料用作非织造布电池隔膜本身。图 5 和图 6 中给出了添加附加微米纤维的这样的薄片的例子。以下示出了丙烯酸微米纤维纳米纤维的典型性质。

[0048] 表 1

[0049] 丙烯酸微米纤维 / 纳米纤维性质

[0050]

密度，g/cm^3	1.17
拉伸强度，MPa	450
模量，GPa	6.0
伸长率，%	15
典型的纤维长度，mm	4.5-6.5
加拿大标准游离度，ml	10-700
BET 表面积，m^2/g	50
回潮率，%	<2.0
表面电荷	阴离子

[0051] 如上所述，这样的纤维实际存在于纸浆样的制剂中，从而利于导入到湿法非织造布生产方案中。

[0052] 非织造生产方法

[0053] 配出材料组合以提供不同浓度的两种成分，然后在将两种成分一同导入湿法制造工艺中。根据 TAPPI 测试方法 T-205 制造手抄纸 (handsheet)，将 TAPPI 测试方法 T-205 引用于此作为参考（基本上，如上所述，一起混合在非常高水溶剂浓度配方中且为典型地用于湿法制造中的高剪切条件，并且描述为纤维“精制 (refining)”，最终将湿结构放置于平坦的表面以使溶剂蒸发）。生产几种不同组合来形成最终非织造布结构。该方法中通过调节结合至各薄片中的材料的初始量，从而仅调节以使得与不同基本重量相匹配。材料和比率示于表 2。

[0054] 图 5 和图 6 也在结构上与下文中的实施例 39 相关。阐明了结构上的相似性（较大的微米纤维和较小的纳米纤维），并且也从这些显微照片中证实在这些结构中存在的纳米纤维更少。

[0055] 测量布的厚度并切成合适的大小和形状，用于引入锂离子充电电池内。然而，在任何这样的导入之前，分析并测试电池隔膜布的样品的与适合用作电池隔膜有关的各种性质。进一步，在本专利文本和 Celgard 产品资料中报道下述作为比较例：根据美国专利 7,112,389 的电池隔膜纳米纤维膜，其引入于此作为参考；以及来自 Celgard 的电池隔膜。

[0056] 实施例

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[0057] 使用 Engineered Fiber 科技 EFTEC® A-010-04 原纤化的丙烯酸纤维（微米纤维和纳米纤维的组合）（作为基体纤维）和 FiberVisions T426 纤维、根据 TAPPI 测试方法 T-205 制造实施例 36-51，所述 FiberVisions T426 纤维为每丝 2 旦、长度切成 5mm 的由聚丙烯和聚乙烯制造的双成分纤维，并且直径为约 17 微米（作为添加纤维）。将薄片在室温下（～ 25℃）以 2200 镑 / 线性英寸长度压延于两个硬质钢辊之间。表 4 给出了实施例的各纤维的量、调节的基本重量、薄片厚（或厚度）、表观密度和孔隙率。根据 TAPPI T220 测试了调节的基本重量、薄片厚、表观密度和拉伸性，TAPPI T220 引用于此作为参考。

[0058] 表 2

[0059] 隔膜性质

[0060]

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实施例	基体纤维%	添加纤维%	每平方米基本重量	厚度	表观密度	孔隙率
			g/m²	mm	g/cm³	%
36	100	0	39.9	0.065	0.614	56.2%
37	90	10	40.2	0.067	0.600	55.6%
38	80	20	39.8	0.068	0.585	55.0%
39	70	30	39.9	0.07	0.570	54.4%
40	100	0	29.98	0.051	0.588	58.0%
41	90	10	29.89	0.053	0.564	58.2%
42	80	20	28.91	0.054	0.535	58.8%
43	70	30	30.9	0.074	0.418	66.6%
44	100	0	23.58	0.044	0.536	61.7%
45	90	10	24.8	0.046	0.539	60.1%
46	80	20	24.75	0.047	0.527	59.5%
47	70	30	24.15	0.053	0.456	63.5%
48	100	0	14.8	0.03	0.493	64.8%
49	90	10	16.6	0.036	0.461	63.8%
50	80	20	16.4	0.033	0.497	61.8%
51	70	30	16.5	0.037	0.446	64.3%

[0061] 孔隙率越高，对象电池内的峰值功率输出越高。理论上，具有这样高的结果，通过增加单个电池的可用功率，至少可减少为了运行特定设备（诸如混动汽车）的必要功率水平所必须的电池数量。这样的益处还与有效空气阻力阻挡有关。从如下可见，还可通过控制纳米纤维与微米纤维的比例、纳米纤维的类型、以及通过压延等后处理控制本发明的隔膜的孔隙率。

[0062] 电池隔膜基本分析和测试

[0063] 测试方案如下：

[0064] 根据通过引用结合至此的美国专利7,112,389中的方法来计算孔隙率。结果以%进行报告，这涉及用气体或非固态材料（当在电池中时，诸如电解质）填充的隔膜的容积部

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分。

[0065] 根据通过引用结合至此的 TAPPI 测试方法 T460 测试格利 (Gurley) 空气阻力。该测试使用的仪器是格利透气度测定仪 (Gurley Densometer)，型号 4110。为了进行测试，将样品插入并固定在该透气度测定仪内。柱面梯度 (cylinder gradient) 上升至 100cc(100ml) 线，然后允许下降至其自身重量。记录 100cc 空气通过该样本的时间 (以秒计)。以秒 /100cc 报告结果，这是使 100 立方厘米空气穿过隔膜所需的时间。

[0066] 根据 ASTM E-1294 即“使用自动流体孔隙率计的薄膜过滤器的孔径大小特性的标准测试方法”测试平均流量孔径，其中使用根据 ASTM F316 的自动泡点方法且使用毛细流动孔隙率计。由纽约州伊萨卡的 Porous Materials 有限公司实施该测试。

[0067] 隔膜的透气性是基于在较轻压力下固定量空气穿过标准面积所需要的时间来测量。在 ASTM D-726-58 中描述了这个过程。

[0068] 表 3

[0069] 拉伸性质和平均流量孔径

[0070]

实施例	MD拉伸性	CD拉伸性	平均流量孔径
	kg/cm²	kg/cm²	微米
36	94	94	0.13
37	85	85	0.13
38	67	67	0.15
39	59	59	0.20
40	88	88	0.15
41	69	69	0.18
42	51	51	0.25
43	29	29	0.62
44	74	74	0.19
45	65	65	0.23
46	56	56	0.27
47	40	40	0.69
48	52	52	
49	57	57	
50	42	42	
51	34	34	

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[0071] 本发明实施例示出非常小的平均孔径，表明能够使对象电池具有许多次充电周期。此外，孔径随着纳米纤维与微米纤维材料比例的变化而变化，这表明控制孔径的能力。这是任何现有技术中没有出现的关键优势，从而使用这个技术，电池制造商可按照终端用户的需求来调节孔径。因此，隔膜可设计用于与充电手表电池、手机或笔记本电脑具有不同特性的功率工具或汽车应用。

[0072] 实施例所给出的拉伸性质是各向同性的，即，所有方向相同，加工和截面方向之间没有不同。比较例示出加工方向 (MD) 和截面方向 (CD) 拉伸强度显著不同的拉伸性质。一般而言，基于纳米纤维的电池隔膜非常脆弱。因此，本发明的一个优势在于拉伸强度，这允许在电池制造中更快加工、电池更紧的缠绕以及在电池使用中更加耐久。这样的 MD 拉伸强度优选大于 25kg/cm^2，更优选大于 50kg/cm^2，最优选大于 100kg/cm^2。对于 CD 拉伸强度的要求较低，优选大于 10kg/cm^2，更优选大于 25kg/cm^2，最优选大于 50kg/cm^2。

[0073] 如上所述，压延和纳米纤维相对于微米纤维的数量增加将减少总体平均孔径，甚至进一步，表明本发明的技术能够实现某些期望的测量值。在造纸机上进行初始隔膜的薄片生产（表明可以这样简单的进行制造），也进行诸如压延等步骤。

[0074] 造纸机生产

[0075] 在真空圆网抄纸机上制作两种材料。第一，对于实施例 52，由 75% EFTec A-010-4 和 25% 0.5 旦 / 丝并切成长度 6mm 的聚对苯二甲酸乙二醇酯 (PET) 纤维制成。第二，对于实施例 53，由 37.5% EFTec A-010-4、37.5% EFTec L-010-4 和切成长度 6mm 的 25% PET 纤维制成。将纤维材料用高剪切混合机分散，并以高稀释度与水混合，然后送入真空圆网抄纸机前箱，制成重量为 20 克 /m^2 的薄片并在热空气烘箱中干燥。将所得的卷在 325 下以 2200 镑 / 线性英寸进行压延，得到厚度为～ 40 微米的第一薄片和 30 微米的第二薄片。在 90℃、130℃和 160℃下测量收缩率；分别测量加工和截面方向的 12″长度，放置于烘箱并在测量温度下保持 1 小时，并再次测量长度。收缩率是相对于原始长度的以百分比表达的长度的改变。薄片的性质示于下述表 4。

[0076] 表 4

[0077] 薄膜性质

[0078]

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基体薄膜性质	测量单位	实施例 42	实施例 43
厚度	μm	40	30
格利 (JIS)	秒	20	110
孔隙率	%	60%	55%
平均流量孔径	μm	0.5	0.5
TD 收缩率 @90 C / 1 小时	%	0	0
MD 收缩率 @90 C / 1 小时	%	0	0
TD 收缩率 @130 C/1 小时	%	0	0
MD 收缩率 @130 C/1 小时	%	2	1
TD 收缩率 @160 C/1 小时	%	1	0
MD 收缩率 @160 C/1 小时	%	4	2
TD 收缩率 @190 C/1 小时	%	5	0
MD 收缩率 @190 C/1 小时	%	7	2
TD 强度	Kg/cm^2	70	100
MD强度	Kg/cm^2	190	170
伸长率	%	4%	4%

[0079] 可以看到，具有丙烯酸纤维 (EFTec A-010-4) 和莱赛尔纤维 (lyocell) (EFTec L-010-4) 材料这两者的材料在高温下显示出非常良好的性质。例如，许多目前的伸展膜隔膜由聚乙烯制造，其在 135℃下熔化并在超过 110℃时显示出明显的收缩；或由聚丙烯制造，其在 160℃下熔化并在超过 130℃时显示出明显的收缩。行业中已知的一个问题是，尤其是可用于电动车辆的大型电池，由于暴露于高温后的收缩，如果隔膜收缩则会使电极在边缘彼此接触，造成短路并且可能造成灾难性的热逃逸，进而导致爆炸。具有高温稳定性的隔膜在这些环境中更加安全，允许更大的电池以每个电池更高的能量来使用。优选的隔膜性能可以在 130℃、160℃或 190℃在两个方向上具有小于 10％的收缩率，优选小于 6％的收缩率或最优选小于 3％的收缩率。此外，可以用具有高温稳定性的成分诸如莱赛尔纤维、人造纤维、对芳酰胺、间芳酰胺或其他纤维制造隔膜，从而当与其他材料形成薄片时赋予低收

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缩率的结果，如实施例 53 中所示。

[0080] 制作不同的压延条件下的附加实施例并测试。在赫蒂基础设施 (Herty Foundation facility) 的真空圆网抄纸机上构造纸，其包含 27％ EFTec A-010-04 丙烯酸纳米纤维、53％ EFTec L-010-04 莱赛尔纳米纤维和 20％ 0.5 旦 / 丝的切成 5mm 长度的聚酯纤维。将材料在 1000 加仑的水力碎浆机中混合 40 分钟，然后以约 0.25％纤维含量送入机器来制作薄片，其面密度为 15 克 /m^2。在不同条件下对该纸进行压延，其列于下文并以下表 5 中的实施例 56-60 示出。

[0081] 实施例 56-60 的说明：

[0082] 56：不对辊进行加热，除此之外，使用上述条件进行压延。

[0083] 57：将薄片与实施例 56 的第二薄片一同送入压延机，使薄片层叠在一起。

[0084] 58：将来自 56 的薄片与一卷复写纸一同送入压延机（需要 wt ?? ），然后从复写纸剥离。

[0085] 59：将来自 56 的薄片在相同条件下通过第二次压延。

[0086] 60：将 57 的层叠体剥离开，形成两个单独的薄片。

[0087] 从下述实施例可以看到下述两点。首先，与单层薄片相比，两张薄片的层叠体给出大于两倍的格利空气阻力，以及较低的总孔隙率。第二，第二次压延具有提高孔隙率和降低格利的效果。最后，与另一薄片一同送入的两张薄片具有同时提高格利和提高孔隙率的效果。进行附加压延的所有情况中拉伸强度均降低。

[0088] 表 5

[0089] 压延的薄片结果

[0090]

实施例	调节的基本重量	薄片厚	表观密度	孔隙率	MD 拉伸性	CD 拉伸性	格利空气阻力
	g/m^2	mm	g/cm^3	%	kg/cm^2	kg/cm^2	秒
56	14.7	0.031	0.474	59.6%	155	69	38
57	30.0	0.060	0.500	57.4%	136	53	105
58	15.2	0.037	0.412	64.9%	102	44	48
59	15.1	0.036	0.419	64.2%	99	40	34
60	15.0	0.036	0.415	64.6%	94	43	40

[0091] 润湿性测试

[0092] 将方形 Celgard 2320 附于方形实施例 39，并将一滴在 EC:DMC:DEC 混合物（体积比 1:1:1）电解质中的 1M LiPF6 置于表面。在 5 秒后，电解质完全被吸入实施例 39，未能观察到光谱反射（即，不同角度测量的不同光谱在表面的液滴形成的光亮面产生差异）。与此相反，在 Celgard 2320 上的电解质液滴保持远超过 5 秒而没有在整体结构上产生完全的毛细作用。本发明材料的该光谱反射结果对于锂离子电池隔膜是非常需要的，以提高分散电

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解质的加工速率，以及确保在隔膜上和内部的电解质的均匀分散。已知在重复充电和放电时电解质非均匀分散体会促进枝状晶形成，从而在电池中成为缺陷而导致短路。

[0093] 因此，液态电解质置放（以液滴形式）5 分钟后隔膜在表面展现出均匀的光谱反射是理想的，优选小于 2 分钟，更优选小于 1 分钟。此外，由两个电极、隔膜和电解质制造能量存储装置是理想的，这样，隔膜以相同的方式展现出相同的光谱反射测量值。

[0094] 事实上，本发明的隔膜展现出在各情况下的光谱反射测量最多 5 秒（大多数测量显示出 2 秒以及小于该值作为结果），从而在整个隔膜展现出液态电解质有效的毛细作用（从而为均匀的分散体）。

[0095] 还进行了其他测试用于润湿性测量，包括差示扫描量热法和热重量分析。从室温至 1000℃用热重量分析来测试实施例 53。样品在最终接近 100℃时显示出 1.39％的质量损失，这与从纤维素纳米纤维和微米纤维产生的水损失一致。直至约 300℃，材料没有进一步降解，当在 335℃和 400℃之间时氧化开始而产生约 60％的质量急剧降低。还从室温至 300℃用差示扫描量热法测试实施例 53。以约 100℃为中心存在宽的放热曲线，这与水的排出一致，并且在 266℃存在急剧的放热曲线，其在 250℃开始且与 PET 的熔点一致。

[0096] 从室温至 1000℃用热重量分析来测试实施例 52。样品在 300℃以下显示出非常小的质量损失，在 335℃开始质量损失，直至 400℃质量损失约为 40％。还从室温至 300℃用差示扫描量热法测试实施例 52。在室温和 266℃之间几乎没有波动，在 266℃存在急剧的放热曲线，其起始于 250℃，这与 PET 的熔点一致。简而言之，除了 PET 微米纤维熔化，曲线没有显示出波动。

[0097] 电池形成和实际电池测试结果

[0098] 图 7 示出了典型的带有外壳 12 的电池 10 结构，所述外壳 12 包括所有其他组件，并且安全密封以防止环境污染进入电池和从电池泄漏任何电解质。阳极 14 与阴极 16 串联设置，且在两者之间具有至少一个电池隔膜 18。在密封之前将电解质 20 加入电池以产生必要的离子。隔膜 18 辅助防止阳极 14 与阴极 16 接触，并且允许来自电解质的所选离子穿过其而迁移。电池的常规模式遵循该结构描述，对于各内部组件具有不同的结构大小和配置，这取决于电池自身的大小和结构。在这种情况下，生产基本呈圆形的固体组件的钮扣电池来合适地测试这样一种电池内隔膜的有效性。

[0099] 为了实现那个目标，首先如下测试隔膜的电性质：制作对称的锂箔－隔膜－锂箔 2016 钮扣电池并测试电阻，然后制作不对称的碳电极－隔膜－锂箔 2016 钮扣电池。在乔治亚理工大学材料科学与工程学院的纳米技术实验室完成测试。对于对称的锂－隔膜－锂 2016 钮扣电池，从所选隔膜切出 5/8″ 圆，在 70℃的充氩手套箱的真空腔室内干燥约 12 小时并组装为：

[0100] (a) 对称的锂箔－隔膜－锂箔 2016 钮扣电池；和

[0101] (b) 不对称的碳电极－隔膜－锂箔 2016 钮扣电池。

[0102] 所用电解质为 EC:DMC:DEC 混合物（体积比 1:1:1）中的 1M LiPF6。将锂箔辊轧至 0.45mm 厚度且在该研究中使用一层或两层隔膜。同时，Celgard 2325 隔膜用于比较测试目的。

[0103] 存储 2 天后，在组装的两个电极 Li－隔膜－Li 钮扣电池的每一个上执行从 0.01Hz 至 100kHz 频率范围的恒电势电化学阻抗谱 (EIS) 测量。

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[0104] 各电池包括对总电阻有贡献的下列项：(i) 电解质 / 隔膜中的 Li 离子传输；(ii) 在每一个 Li 电极上在固体 - 电解质 - 中间相 (SEI) 层中的 Li 离子传输；(iii)Li/ 电池 / 触体中的电子传输。在这些电阻的组成中，(iii) 电子传输通常可忽略，同时由于 Li 离子的高特征频率，(i) 电解质中的 Li 离子传输在当前频率区域内 Li 离子传输没有给出半周期。

[0105] 作为最感兴趣的 (i) 电解质 / 隔膜中的 Li 离子传输，关注点集中在与之关联的奈奎斯特图的高频区域上。离子穿过隔膜输送的总电阻约为高频的总电阻 Z 的实数部的值，然而复阻抗的虚部成分为零。如上所述，界面和电极的电阻远小于离子电阻，因此可被忽略。

[0106] 进一步电池生产和测试

[0107] 额外的口袋电池如下制造：标准手机电池电极具有的涂层重量为约 2.5mAh/cm^2。为测试而生产的电极的涂层重量为 4mAh/cm^2(NCA)，以表明隔膜的能力限制超过了标准情况，这是因为涂层重量涉及速率能力。用 Celgard2325(以下，实施例 54) 和实施例 53(以下，实施例 55) 构造了各隔膜类型的一个电池 (手制)。将电极涂覆、压延、干燥、连接端焊接、放入夹层封装、用标准电池溶剂电解质中的 1M Li 盐填充并密封。以 C/10、C/4、C/2 和 C 速率测试电池的放电容量，在各速率下进行多次放电，结果示于下述表 7，为相对于形成后的第一次放电即 C/10 容量的百分比。实施例 54 电池的 C/10 时的具体放电容量为 141mAh/g，实施例 55 电池为 145mAh/g。

[0108] 表 6

[0109] 口袋电池测量

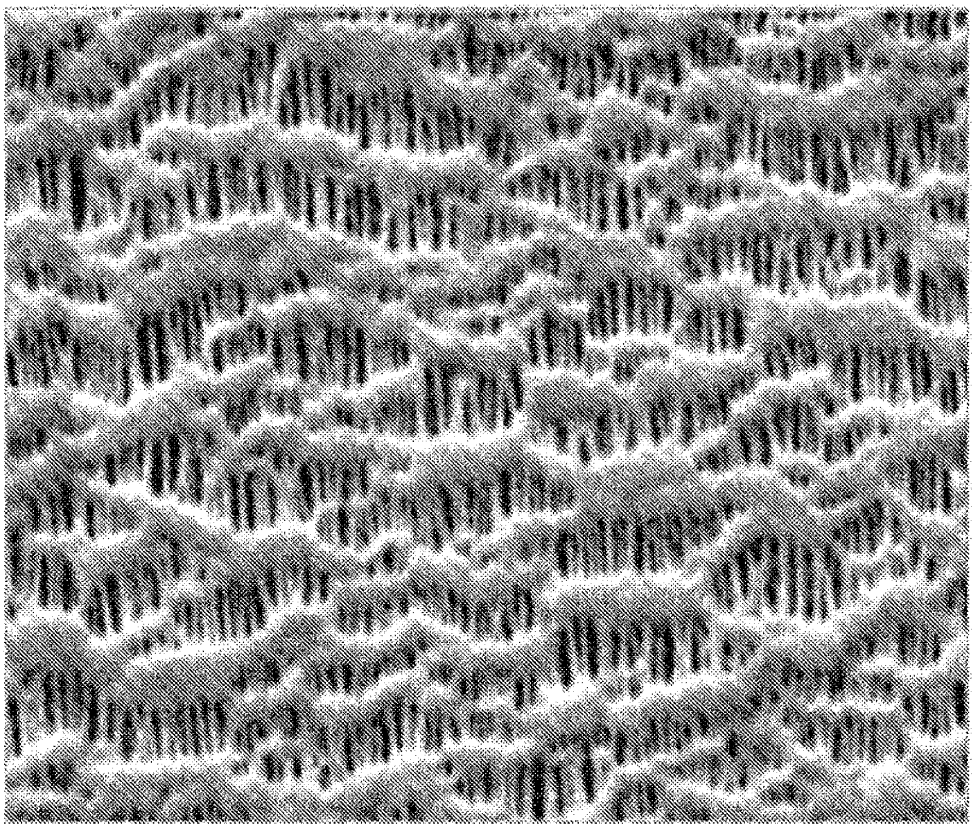
[0110]

速率	实施例 54	实施例 55
C/10	100.3%	101.3%
C/4	95.5%	98.3%
C/2	69.5%	88.7%
C	36.4%	57.1%

[0111] 从这些实施例可以看到，使用本发明隔膜制造的电池以更高的速率具有更高的放电容量，C/4 时具有小优势，速率为 C/2 和 C 时具有更大且明显的优势。

[0112] 应当理解，在不背离本发明精神的范围内，本领域普通技术人员可在本发明范围内做出各种修改。因此期望的是本发明在现有技术允许的尽可能宽的范围内由随附权利要求限定，如有需要可参考说明书。

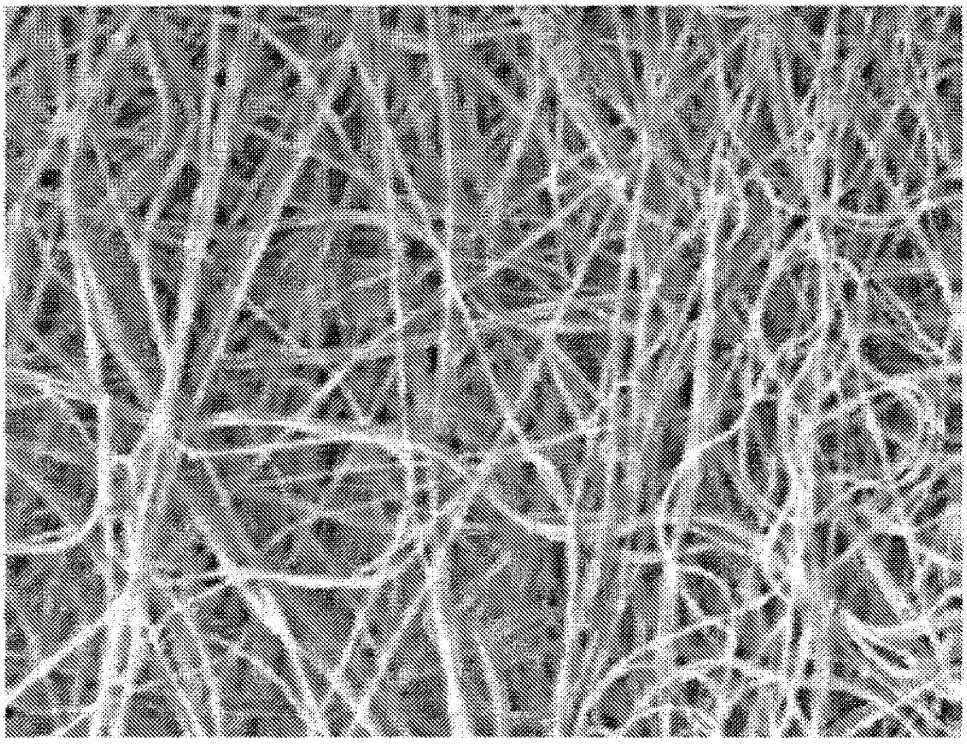
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(现有技术)

图 1

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(现有技术)

图 2

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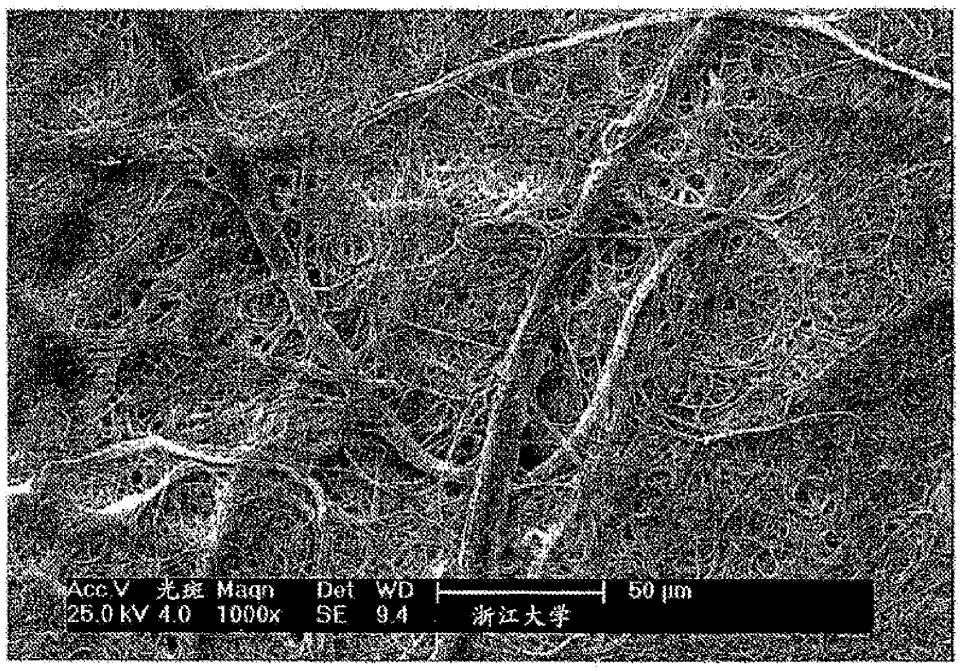


图 3

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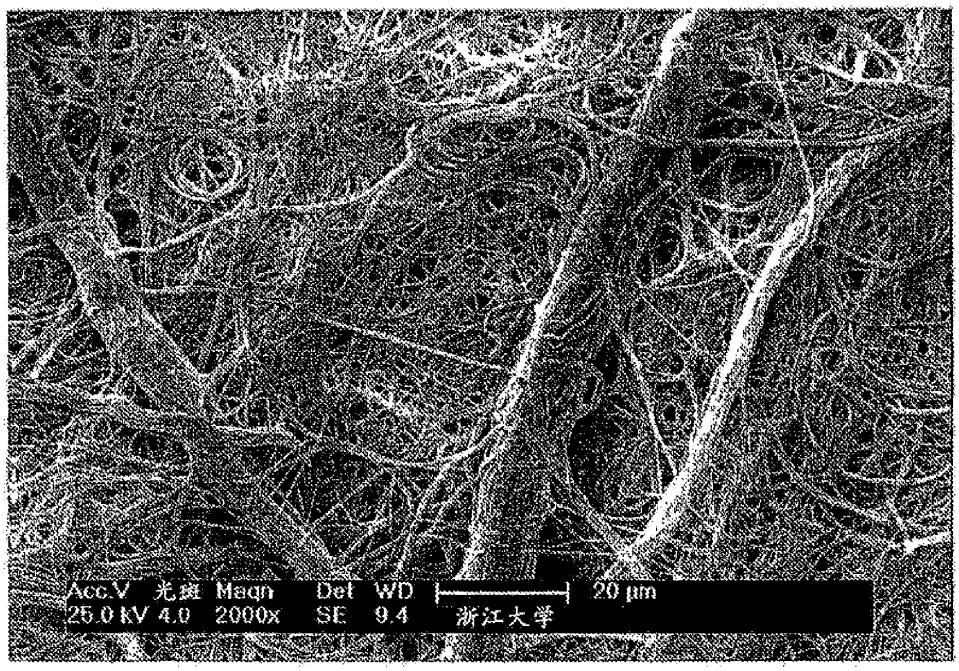


图 4

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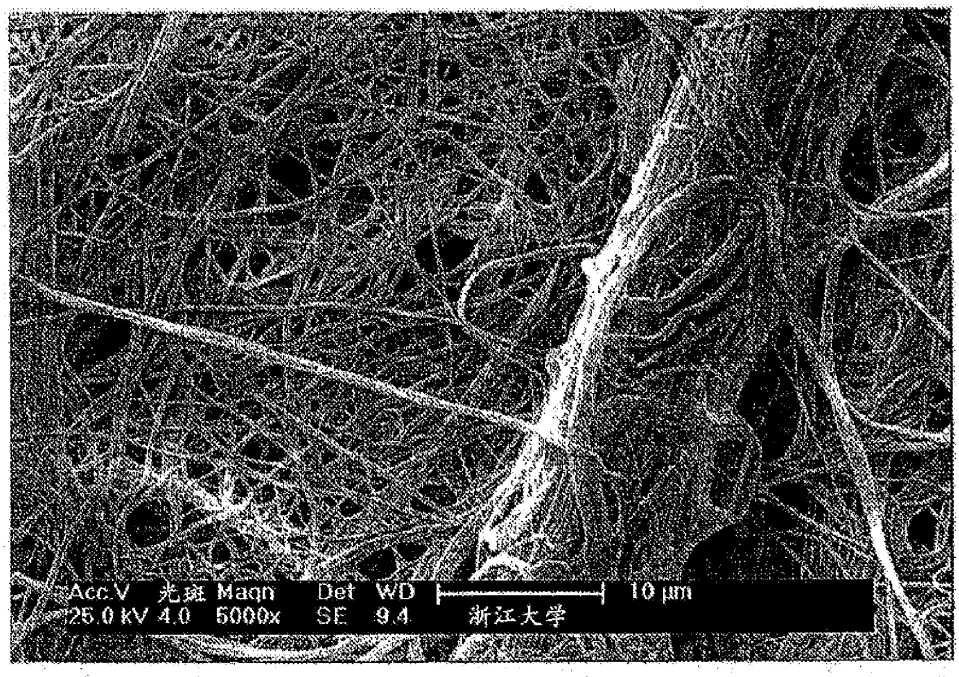


图 5

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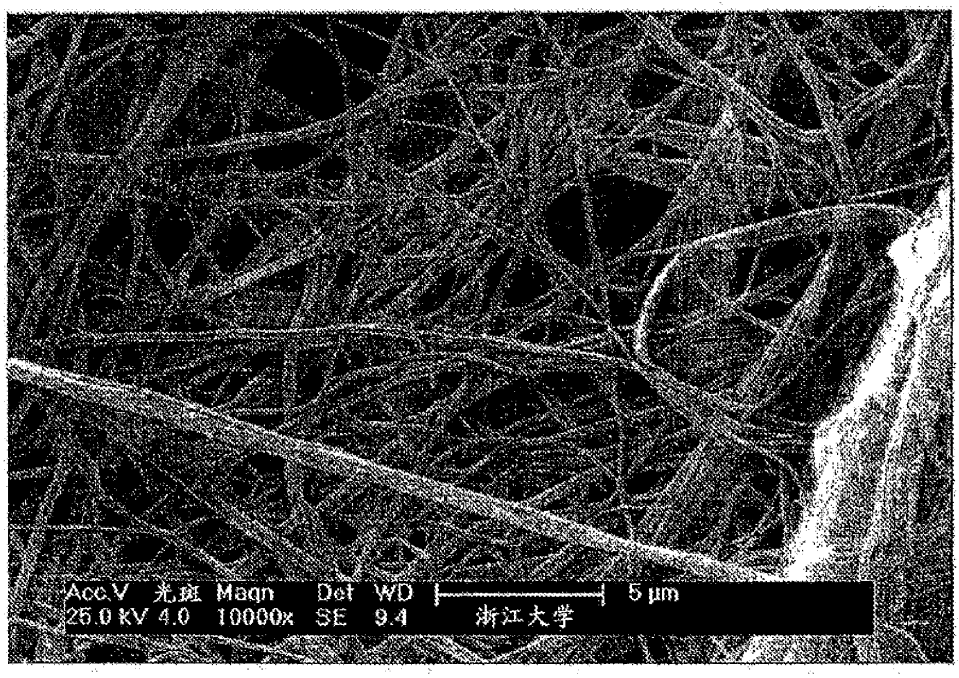


图 6

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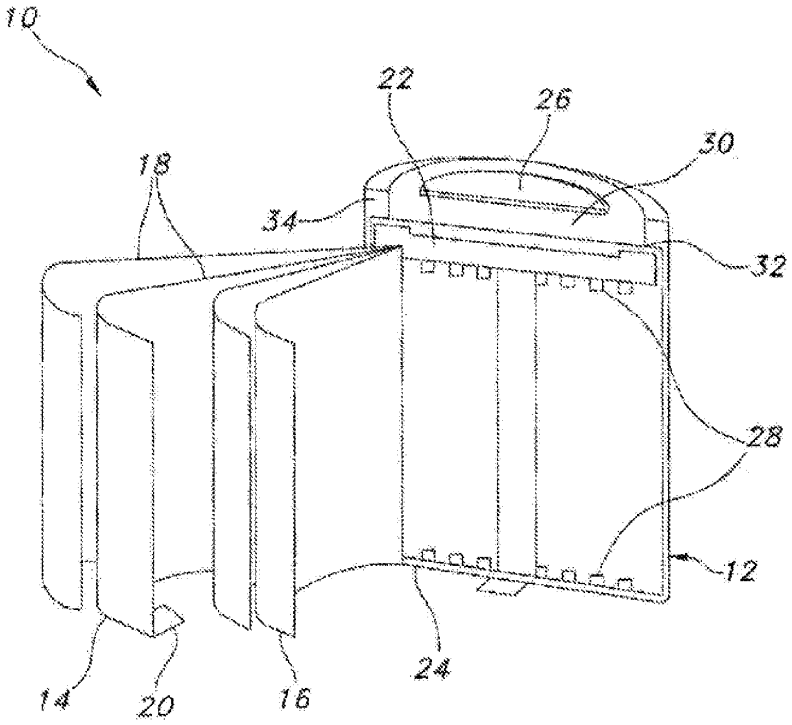


图 7

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Espacenet

CN104999745A Microporous laminated membrane and method for producing the same

Applicants: DAICEL CORP

Inventors: YO YAMATO

Classifications:

IPC ***B32B27/02; B32B27/08; B32B27/28; B32B3/24; B32B7/12;***

CPC **B01D53/228 (EP,US); B01D67/0009 (EP,US); B01D69/02 (EP,US); B01D69/10 (EP,US); B01D71/56 (EP,US); B01D71/64 (EP,US); B01D71/68 (EP,US); B32B27/12 (EP,CN,US); B32B27/28 (CN); B32B27/281 (EP,CN,US); B32B27/285 (EP,US); B32B27/286 (EP,CN,US); B32B27/34 (EP,US); B32B3/266 (CN); B32B5/022 (EP,CN,US); B32B7/12 (CN); H01G11/52 (EP,US); H01M50/403 (EP,US); H01M50/411 (EP,US); H01M50/44 (EP,US); H01M50/449 (EP,US);** B01D2053/221 (US); B01D2325/20 (EP,US); B01D2325/24 (EP,US); B01D61/147 (EP,US); B32B2262/0253 (EP,CN,US); B32B2262/0261 (EP,CN,US); B32B2307/308 (EP,US); B32B2307/538 (EP,CN,US); B32B2307/54 (EP,US); B32B2307/724 (EP,CN,US); B32B2457/00 (EP,CN,US); B32B2457/04 (CN); B32B2457/10 (EP,CN,US); B32B2457/16 (EP,CN,US); B32B2571/00 (CN); Y02E60/10 (EP); Y02E60/13 (US);

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Published as: CN104999745A;**JP2015208881A; JP6284818B2; KR20150123154A; US2015306539A1**

Microporous laminated membrane and method for producing the same

Abstract

The invention discloses a microporous laminated membrane and method for producing the same. The microporous membrane exhibits excellent air permeability with no generation of needle holes and has a high smoothness on the surface thereof, and is disposed on at least one side of the nonwoven-fabric substrate. The microporous membrane includes a multiplicity of interconnecting micropores. The micropores have an average pore diameter of from 0.01 to 10 [mu]m. The microporous membrane has an arithmetic mean surface roughness Sa of 0.5 [mu]m or less. The microporous laminated membrane has an air permeability of from 0.5 to 30 seconds. The microporous laminated membrane has a tensile strength of 4.0 N/15 mm or more. The microporous laminated membrane does not undergo interfacial peeling between the substrate and the microporous membrane as a result of a tape peel test.

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CN104999745A Microporous laminated membrane and method for producing the same

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The wording below is an initial machine translation of the original publication. To generate a version using the latest translation technology, go to the original language text and use Patent Translate.

Technical field

The present invention relates to a porous film laminate having micropores and handling strength and a method of producing the same. More specifically, the present invention relates to a porous film laminate in which a porous film having a plurality of micropores having connectivity is laminated on at least one surface of a nonwoven fabric substrate, and a method for producing the same.

Background technique

As a porous film having fine pores, for example, Patent Document 1 discloses a porous film composed of an amide imide-based polymer or an imide-based polymer. There is disclosed a porous film characterized in that the film has a thickness of 5 to 200 μm, an average pore diameter of the micropores of 0.01 to 10 μm, and a porosity of 30 to 80%, and the gas permeability indicating the connectivity of the micropores is The Gurley value is 0.2 to 29 seconds/100 cc.

Further, Patent Document 2 discloses a laminate in which a porous film is laminated on a nonwoven fabric. A porous film laminate in which a plurality of micropores having connectivity and a porous film having an average pore diameter of 0.01 to 10 μm are laminated on at least one surface of a nonwoven fabric substrate, and The base material and the porous film did not have a porous film laminate in which interfacial peeling occurred due to a tape peeling test.

Further, in Patent Document 3, a separator for drainage is disclosed as a laminate in which a nonwoven fabric is used as a base material and a porous film is formed on the surface of the nonwoven fabric. Examples of the nonwoven fabric include cellulose fibers, cellulose acetate fibers, polyester fibers, polypropylene fibers, and polyethylene fibers. As a most preferable combination, polyvinylidene fluoride is disclosed on a polyester fiber nonwoven fabric. A laminate of a porous film of ethylene (PVDF).

Further, Patent Document 4 discloses a filter for an air cleaner in which a sintered porous sheet of ultrahigh molecular weight polyethylene and a polyester nonwoven fabric are laminated. The method of manufacturing the filter includes the following stages.

1.The ultrahigh molecular weight polyethylene powder was filled in a metal mold, placed in a container, and the inside of the container was decompressed.

2.The heated steam was introduced into the vessel, and heated at 160 ° C × 6 atmosphere for 5 hours, and then slowly cooled.

3.The obtained cylindrical sintered porous body was cut into a sheet shape and then stretched to obtain a porous sheet.

4.A hot melt adhesive is applied to the porous sheet, and the polyester nonwoven fabric is bonded to the laminate.

Prior art literature

Patent literature

Patent Document 1: Japanese Patent No. 3963765

Patent Document 2: International Publication No. 2007/097249

Patent Document 3: Japanese Laid-Open Patent Publication No. 2010-221218

Patent Document 4: Japanese Laid-Open Patent Publication No. 2006-257888

Summary of the invention

Problems to be solved by the invention

However, in the case of the porous film described in Patent Document 1, since the fine pores having good connectivity are provided, the strength is extremely weak, and care must be taken in handling. Therefore, there is a problem that the use is limited. When the film is processed, a roll-to-roll operation is often used, and there is a problem that the strength of the operation cannot be ensured.

Further, in the case of the laminate described in Patent Document 2, since a porous film is formed thereon by using a nonwoven fabric as a base material, sufficient strength can be secured by the nonwoven fabric. However, since the nonwoven fabric has pores in the structure, the method of forming the porous film by casting the polymer solution into a film on the nonwoven fabric has the following problem: the polymer solution is impregnated into the pores of the nonwoven fabric, and is porous. The surface of the film becomes convex or concave, or the nonwoven fabric portion is exposed, or pinholes are generated, or the gas permeability is deteriorated. Further, there is a problem that, in general, the pores of the nonwoven fabric are significantly larger than those of the porous membrane, and are extremely uneven when viewed microscopically, and therefore, the amount of penetration of the polymer solution varies depending on the position. As a result, the thickness of the porous film also varies, and the air permeability as a characteristic thereof also varies.

In the case of the laminate described in Patent Document 3, the porous film resin layer is provided on the surface of the nonwoven fabric substrate, and a part of the porous film resin layer is embedded in the inside of the nonwoven fabric substrate. Therefore, the same problem as described above is caused. . Further, there is a problem that the degree of opening of the surface of the porous film is extremely low, or there is an uneven pore structure having a large void inside the porous film resin layer, and therefore, the gas permeability is still deviated depending on the position.

Further, in the case of the laminate described in Patent Document 4, there is a problem in that it is difficult to reduce the pore diameter and reduce the surface opening ratio by the production method. Further, the manufacturing method of the present filter has a problem that it takes a lot of work as described above. Further, there is also a problem that the porous sheet and the polyester nonwoven fabric are bonded by a hot melt adhesive, thereby impeding the gas permeability.

For this reason, a porous film laminate which is excellent in gas permeability, does not cause pinholes, has high surface smoothness, is flexible, and is excellent in workability and moldability, and a method for producing the same are required.

Accordingly, an object of the present invention is to provide a porous film laminate which is excellent in gas permeability, does not cause pinholes, has high surface smoothness, is flexible, and is operative, and a method for producing the same. And excellent in formability.

Technical solution for solving the problem

Therefore, the inventors of the present invention have conducted intensive studies in order to achieve the above object, and as a result, have found that the surface of the porous film is convex and concave, and the nonwoven fabric is partially exposed by using a general nonwoven fabric substrate. , pinholes are produced, the gas permeability is deteriorated, and it cannot withstand use. In addition, it has been found that by laminating a porous film on the surface of a nonwoven fabric base material by hot melt adhesion, it is excellent in gas permeability, does not cause pinholes, has high surface smoothness, is flexible, and is excellent in workability and moldability. The porous film laminate has completed the present invention.

That is, the present invention provides a porous film laminate in which a porous film is laminated on at least one surface of a nonwoven fabric base material, wherein

The porous membrane is provided with a plurality of micropores having connectivity, and the micropores have an average pore diameter of 0.01 to 10 μm.

The arithmetic mean surface roughness Sa of the surface of the porous film obtained by the following measurement method is 0.5 μm or less.

The value of the air permeability of the porous film laminate is 0.5 to 30 seconds.

The tensile strength of the porous film laminate is 4.0 N/15 mm or more.

The base material and the porous film did not undergo interface peeling due to the tape peeling test described below.

(tape stripping test)

A masking tape (manufactured by Teraoka Seisakusho Co., Ltd., trade name "film masking tape No. 603 (#25)", width 24 mm] was attached to the surface of the porous film of the porous film laminate, and a roller having a diameter of 30 mm and a load of 200 gf was used. After pressure bonding, T-type peeling was performed using a tensile tester at a peeling speed of 50 mm/min;

(Measurement of arithmetic mean surface roughness Sa)

The surface roughness was measured by measuring the surface shape using a non-contact surface measuring system VertScan 2.0 (manufactured by Nippon Seisakusho Co., Ltd.) using an optical interference method, and the measurement region was set to a range of 250 μm × 188 μm, and the measurement conditions were set to Objective lens = 50 times, lens barrel = 0.5 × Body, continuous zoom lens = NoRelay, filter (wave length filter) = 530white, measurement mode = Wave, field of view size = 640 × 480.

The arithmetic mean surface roughness Sa is preferably 0.4 μm or less.

The arithmetic mean surface roughness Sa is preferably 0.3 μm or less.

The arithmetic mean surface roughness Sa is preferably 0.2 μm or less.

The value of the gas permeability is preferably from 0.5 to 20 seconds.

The value of the gas permeability is preferably from 0.5 to 10 seconds.

The value of the air permeability is preferably 0.5 to 5 seconds.

The polymer solution is a mixed solution containing 8 to 25% by weight of a polymer component, 5 to 50% by weight of a water-soluble polymer, 0 to 10% by weight of water, and 30 to 82% by weight of a water-soluble polar solvent.

The porous film contains at least one selected from the group consisting of a polyimide resin, a polyamideimide resin, a polyetherimide resin, and a polyethersulfone resin.

The nonwoven fabric base material is a polyolefin-based nonwoven fabric, a polyamide-based nonwoven fabric, or a multilayer nonwoven fabric in which a part of the nonwoven fabric is a polyolefin-based nonwoven fabric or a polyamide-based nonwoven fabric.

The average open porosity (porosity) of the inside of the porous film is preferably from 30 to 80%.

The thickness of the base material is preferably from 10 to 500 μm.

The shape change rate of the porous film laminate in the high-temperature placement test described below was 5% or less:

(high temperature placement experiment)

The shape of the laminate integrated with the porous film was adjusted to a substantially rectangular shape of about 5 cm × 10 cm, and the lengths a1 and b1 of the substantially rectangular vertical sides were measured, and

the temperature was adjusted to 140 ° C in a thermostatic chamber. After the laminate was placed for 30 minutes, the laminate was taken out, and after cooling to room temperature, the lengths a2 and b2 of the substantially rectangular vertical sides were measured, and the shape change ratio was calculated using the following formula.

The shape change rate (%) is determined from a1 and a2 = {|a2-a1|/a1} × 100

Similarly, the shape change rate (%) obtained from b1 and b2 is the average value of these values as the shape change rate in the high-temperature placement experiment.

The porous film laminate is preferably used as a gas, liquid, solid filter; a separation membrane; a separator of a battery or a capacitor; or a part thereof.

The method of laminating the nonwoven fabric base material and the porous film is carried out by hot melt bonding, and the glass transition temperature of the resin constituting the porous film is determined by the melting point of the resin constituting the nonwoven fabric.

The porous film was obtained by casting a polymer solution onto a substrate and forming a film, and then introducing it into a coagulating liquid, and then drying the individual film peeled off from the substrate.

Effect of the invention

Since the porous film laminate of the present invention has a porous film having a plurality of micropores, it is excellent in flexibility and excellent in gas permeability, does not cause pinholes, has high surface smoothness, and the porous film is lining the base material. Therefore, even when it has a porosity, sufficient strength can be exhibited, and it is excellent in folding endurance and workability. According to the present invention, a porous film laminate having the above properties and a uniform film quality can be stably produced by a simple method. Since the porous film laminate obtained as described above has the above characteristics, it can be used as a gas or liquid or solid filter and separation membrane, a separator for a battery and a capacitor, or a part thereof. For example, it can be used as a liquid separation membrane, a solid separation membrane, a gas separation membrane, or a part thereof.

Specifically, a bag filter, a dust filter, an air conditioner filter, an automobile filter (air purifier, oil purifier, indoor purifying filter, external air suction filter, etc.) may be mentioned. In addition, it can be used as an electromagnetic wave control material such as a circuit board, a battery separator, an electromagnetic wave shield, or an electromagnetic wave absorber, an electrolytic capacitor, a low dielectric constant material, a cushioning material, an ink developing sheet, a test paper, an insulating material, a heat insulating material, A wide range of substrate materials such as a cell culture medium material, a radiation masking material, and an oil absorbing material are used.

DRAWINGS

Fig. 1 is an electron micrograph (SEM photograph) of the surface of a porous film produced in Production Example 1.

2 is an electron micrograph (SEM photograph) of the surface of the porous film produced in Production Example 2.

Detailed ways

The porous film laminate of the present invention will be described in detail.

[Tape peeling test]

In the porous film laminate of the present invention, the base material and the porous film are not peeled off by the tape peeling test.

The tape peeling test was carried out by attaching a masking tape [film masking tape No. 603 (#25)] manufactured by Teraoka Manufacturing Co., Ltd. having a width of 24 mm to the surface of the porous film of the porous film laminate, and using a diameter of 30 mm and 200 gf. After the load roller was pressure-bonded,

T-type peeling was performed at a peeling speed of 50 mm/min using a tensile tester. That is, the base material and the porous film were laminated with an interlaminar adhesion strength which does not cause interfacial peeling in the tape peeling test.

As described above, the porous film laminate of the present invention has a structure in which the base material and the porous film are directly laminated with a specific interlayer adhesion strength, and therefore has flexibility and excellent pore characteristics. On the other hand, it has an appropriate rigidity, so that operability is improved. Further, since the polymer component constituting the porous film can be widely selected, it has an advantage that it can be used as a material in various fields. The interlayer adhesion strength between the base material and the porous film can be adjusted by appropriately setting the physical properties of the types or interfaces constituting the raw materials of the respective layers.

[Nonwoven fabric base material]

The porous film laminate of the present invention has a structure in which a porous film is laminated on at least one surface of a nonwoven fabric substrate.

The nonwoven fabric base material may be a single layer or a multilayer composed of the same or different raw materials. The multilayer may be a laminated multilayer nonwoven fabric or a laminated film laminated at the production stage using an adhesive or the like as needed, or may be subjected to a treatment such as coating, vapor deposition or sputtering. .

The nonwoven fabric base material may be subjected to roughening treatment, easy adhesion treatment, antistatic treatment, sandblasting treatment (sand layer treatment), corona discharge treatment, plasma treatment, chemical etching treatment, water cushion treatment Surface treatment such as flame treatment, acid treatment, alkali treatment, oxidation treatment, ultraviolet irradiation treatment, and silane coupling agent treatment.

Alternatively, a plurality of the above surface treatments may be combined. For example, the substrate may be first subjected to a corona discharge treatment, a plasma treatment, a flame treatment, an acid treatment, an alkali treatment, an oxidation treatment, an ultraviolet irradiation treatment, or the like, and then subjected to a silane coupling agent treatment. Method, etc. Depending on the type of the base material, the above treatment may be intensified as compared with the separate treatment of the silane coupling agent. The silane coupling agent may be a product manufactured by Shin-Etsu Chemical Co., Ltd. or a product manufactured by Japan Energy Co., Ltd.

The thickness of the nonwoven fabric base material is, for example, 10 to 500 μm, more preferably 10 to 300 μm, still more preferably 10 to 200 μm, still more preferably 10 to 100 μm. When the thickness is too small, it is difficult to handle, and on the other hand, when the thickness is too thick, the flexibility may be lowered.

The basis weight of the nonwoven fabric base material is, for example, 2 to 250 g/m 2 , more preferably 2 to 150 g/m 2 , and still more preferably 2 to 100 g/m 2 , from the viewpoint of strength retention and flexibility. More preferably, it is 2-50 g/m□2□.

The density of the nonwoven fabric base material is, for example, 0.05 to 0.90 g/cm 3 , more preferably 0.10 to 0.80 g/cm 3 , still more preferably 0.15 to 0.70 g/cm, from the viewpoint of ensuring appropriate gas permeability. 3 .

The air permeability of the nonwoven fabric base material is preferably 30 seconds or shorter, more preferably 20 seconds or shorter, and still more preferably 10 seconds or shorter. It is to be noted that the measurement limit of the gas permeability is about 0.1 second, but the base material also includes a base material having a gas permeability of less than 0.1 second.

From the viewpoint of improving the adhesion between the nonwoven fabric base material and the porous film, it is preferable to subject the surface of the porous film substrate to the surface of the porous film side by, for example, sandblasting (Appropriate surface treatment such as sand cushion treatment, corona discharge treatment, acid treatment, alkali treatment, oxidation treatment, ultraviolet irradiation treatment, plasma treatment, chemical etching treatment, water cushion treatment, flame treatment, silane coupling agent treatment, etc. . As the silane coupling agent, the silane coupling agent exemplified above can be used. The surface treatment may be carried out in combination, and the silane coupling agent treatment and other treatments are preferably carried out in combination depending on the nonwoven fabric base material.

(nonwoven)

The nonwoven fabric refers to a concept of a sheet-like substance obtained by arranging fibers, bonding the fibers to each other by a bonding force of the adhesive or the fibers themselves, or a force of intertwining with each other, and also includes so-called paper. The nonwoven fabric can be produced by a generally known method such as a papermaking method, a meltblowing method, a spunbonding method, a needle punching method, or an electrospinning method.

The type of the resin constituting the base material of the nonwoven fabric can be selected in accordance with the melting point, chemical resistance, and the like. As the nonwoven fabric, a commercially available product can be used. For example, a polyolefin nonwoven fabric (trade name "FT-330N") manufactured by VILENE, Japan, and a polyolefin nonwoven fabric (trade name "06HOP-2" and "06HOP-4" manufactured by Hirose Paper Co., Ltd. can be obtained. "HOP-10H", "HOP-30H", "HOP-60HCF", "HOP-80H", etc. In addition, two layers of non-woven fabrics (trade name "05EP-50", "15EP-50") manufactured by Hirose Paper Co., Ltd., etc., can be obtained.

The nonwoven fabric is preferably (the glass transition temperature of the resin constituting the porous film) □ (the melting point of the resin constituting the nonwoven fabric), and is not particularly limited as long as it is the nonwoven fabric as described above. A polyolefin nonwoven fabric, a polyester nonwoven fabric, a polyamide nonwoven fabric or the like is preferably used, but two or more nonwoven fabrics and multilayer nonwoven fabrics thereof may be used. More preferably, at least one selected from the group consisting of a polyolefin nonwoven fabric and a two-layer nonwoven fabric can be used.

At present, as a generally available nonwoven fabric, a nonwoven fabric composed of a polyolefin resin (polyethylene, polypropylene) is often used, and a two-layer nonwoven fabric (for example, a polypropylene/polyester resin) is also included. Laminated product). These nonwoven fabrics are various and are inexpensive, and therefore are preferable.

Since the nonwoven fabric is used as the base material of the nonwoven fabric, there is an advantage that the porous film is laminated on the surface of the base material by a method such as thermal fusion bonding, whereby an excellent interlayer density can be obtained. The strength is laminated. Further, it has flexibility and excellent pore properties, and on the other hand, it has appropriate rigidity, so that the effect of improving workability can be obtained.

[porous membrane]

The main component of the porous film is composed of, for example, a polymer component. The polymer component is not particularly limited as long as it can form the porous film, and can be appropriately selected depending on the material constituting the porous film. Examples of the polymer component include a polyimide resin, a polyamideimide resin, a polyether sulfone resin, a polyetherimide resin, a polycarbonate resin, and a polyphenylene sulfide. Resin, liquid crystalline polyester resin, aromatic polyamide resin, polyamide resin, polybenzoxazole resin, polybenzimidazole resin, polybenzothiazole resin, polysulfone resin, fiber Plastics such as a resin or an acrylic resin. These polymer components may be used singly or in combination of two or more. Further, the copolymer of the above resin (graft polymer, block copolymer, random copolymer, etc.) may be used singly or in combination. Further, a polymer having a skeleton (polymer chain) of the above resin in the main chain or the side chain may also be used. Specific examples of such a polymer include a polysiloxane and a polyimide containing a polyimide skeleton in the main chain and containing a polysiloxane.

In addition, as a preferable example of the polymer component, those having a heat resistance, chemical resistance, and electrical properties and having a polyamideimide resin or a polyimide resin as a main component are exemplified. The polyamideimide-based resin can be usually produced by a reaction of trimellitic anhydride with a diisocyanate or a reaction of trimellitic anhydride chloride with a diamine, followed by imidization. The polyimide-based resin can be produced, for example, by obtaining a polyamic acid by a reaction of a tetracarboxylic acid component and a diamine component, and further imidating it. When the porous film is made of a polyimide-based resin, the solubility is deteriorated when the imidization is performed. Therefore, the porous film is first formed in the stage of the polyamic acid, and then imidization is carried out. Amination, chemical imidation, etc.). Other preferable examples of the polymer component include a polyetherimide resin and a polyether sulfone resin as main components.

A polytetrafluoroethylene (PTFE)-based porous film is also known as a material which is made of a resin and has heat resistance, and it can also be used in the same manner.

The thickness of the porous film is, for example, 1 to 100 μm, more preferably 1 to 50 μm, still more preferably 1 to 20 μm, still more preferably 1 to 10 μm. When the thickness is too small, it is difficult to manufacture stably, and on the other hand, when the thickness is too thick, there is a problem that gas permeability is deteriorated.

The porous membrane is provided with a plurality of micropores having connectivity, and the average pore diameter (= average pore diameter inside the membrane) of the micropores is 0.01 to 10 μm, more preferably 0.05 to 5 μm, still more preferably 0.1 to 2 μm. When the average pore diameter is outside the above range, the pore characteristics are inferior in that it is difficult to obtain a desired effect for satisfactory use. For example, when the size is too small, the gas permeability may be lowered, the cushioning performance may be lowered, the ink permeability may be lowered, and the insulation or heat insulation may be caused. When the size is too large, the filtration performance is lowered or the ink is diffused, and it is difficult to form fine wiring.

The average open porosity (porosity) inside the porous film is, for example, 30 to 80%, preferably 40 to 80%, and more preferably 45 to 80%. When the porosity is outside the above range, it is difficult to obtain desired pore characteristics satisfying the use. When the porosity is too low, the gas permeability is lowered, or the dielectric constant is increased, or the cushioning property is lowered, or the ink is not impregnated, or The heat insulating property is lowered, and even if the functional material is filled, the desired effect cannot be obtained. When the porosity is too high, there is a possibility that the strength or the folding endurance is poor.

The opening ratio (surface opening ratio) of the surface of the porous film is, for example, 48% or more (e.g., 48 to 80%), and more preferably about 60 to 80%. When the surface opening ratio is too low, the permeation performance may be insufficient. Further, even if the functional material is filled in the pores, the function may not be sufficiently exhibited. When the surface opening ratio is too high, the strength and the resistance are high. The folding property is easy to reduce.

The surface roughness (arithmetic mean surface roughness Sa) of the surface of the porous film is 0.5 μm or less, preferably 0.4 μm or less, more preferably 0.3 μm or less, and still more preferably 0.2 μm or less. When the surface roughness is too large, the smoothness may be lost. When filtering, for example, a liquid, the bubbles are easily adhered, and the portion loses the function as a filter. Further, the fine particles which are caught (or trapped) during the filtration are unevenly stuck, and the efficiency of filtration may be lowered or the filtration speed may become unstable. In addition, the surface roughness (arithmetic average surface roughness Sa) can be obtained by measuring the surface shape by a non-contact surface measuring system using an optical interference method, and based on the method described in the examples.

The porous film may be formed on at least one surface of the nonwoven fabric base material, or may be formed on both surfaces.

The porous film may be subjected to a treatment for imparting chemical resistance. As a result, chemical resistance is imparted to the porous film laminate, and in various ways of using the porous film laminate, when it comes into contact with a solvent, an acid, an alkali or the like, delamination and swelling can be avoided. It is advantageous in terms of dissolution, deterioration, and the like. The treatment for imparting chemical resistance includes physical treatment such as heat, ultraviolet rays, visible light rays, electron beams, and radiation, and chemical treatment such as coating a porous film with a chemical resistant polymer.

The porous film may be coated with a chemical resistant polymer. In such a porous film laminate, for example, a chemical-resistant film is formed on the surface of the porous film or on the surface of the micropores, and a laminate having chemical resistance can be formed. Here, the pharmaceutical product is known as a drug which dissolves, swells, shrinks, and decomposes the resin constituting the conventional porous film, and lowers the function as a porous film, and is based on the porous film and the matrix material. The type of the constituent resin is different and cannot be generalized. However, specific examples of such a drug include dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and N,N-dimethyl Acetamide (DMAc), N-methyl-2-pyrrolidone (NMP), 2-pyrrolidone, cyclohexanone, acetone, methyl acetate, ethyl acetate, ethyl lactate, acetonitrile, dichloromethane, chloroform, tetra a strong polar solvent such as ethyl chloride or tetrahydrofuran (THF); an inorganic salt such as sodium hydroxide, potassium hydroxide, calcium hydroxide, sodium carbonate or potassium carbonate; an amine such as triethylamine; and an aqueous solution in which an alkali such as

ammonium is dissolved. Or an alkali solution such as an organic solvent; an inorganic acid such as hydrogen chloride, sulfuric acid or nitric acid; an acidic solution such as an acid aqueous solution such as an organic acid having a carboxylic acid such as acetic acid or phthalic acid; or an organic solvent; and a mixture thereof.

The chemical-resistant polymer compound may have excellent resistance to a strong polar solvent, a base, an acid, or the like, and examples thereof include a phenol resin, a xylene resin, a urea resin, a melamine resin, and a benzopyrene. Heats such as amine resins, benzoxazine resins, alkyd resins, triazine resins, furan resins, unsaturated polyesters, epoxy resins, silicone resins, polyurethane resins, and polyimide resins Curable resin or photocurable resin; polyvinyl alcohol, cellulose acetate resin, polypropylene resin, fluororesin, phthalic acid resin, maleic acid resin, saturated polyester, ethylene-vinyl alcohol copolymer, A thermoplasticized resin such as chitin or chitosan. These polymer compounds may be used alone or in combination of two or more. Further, the polymer compound may be a copolymer or a graft polymer.

The porous film laminate comprising the porous film coated with the chemical-resistant polymer as described above does not completely dissolve the porous film even when it is in contact with the above-mentioned strong polar solvent, alkali, acid or the like. , or swelling, deformation, etc., or the deterioration can be controlled to the extent that it has no effect on the purpose or use. For example, in the case where the contact time between the porous film and the drug is short, it is only required to impart chemical resistance to such an extent that it does not deteriorate during the time.

In addition, since the chemical-resistant polymer compound has heat resistance at the same time, the porous film has heat resistance as compared with that before the coating with the chemical-resistant polymer compound. The possibility of reduction is small.

The functional material may be filled in the micropores constituting the porous film. Examples of the functional material include ferrite fine particles, metal fine particles (including metal-containing fine particles such as metal oxide fine particles), carbon black, carbon nanotubes, fullerenes, titanium oxide, barium titanate, and the like.

The filling condition of the functional material is not particularly limited, and it is preferable to perform the filling by the decomposition energy of submicron particles to micrometers, thereby suppressing the loss of the pore characteristics originally possessed by the porous film, and improving the ease of adjusting the functional material. Processing and handling properties such as filling amount. When the functional material is filled, when the micropores of the porous membrane are too small, it is difficult to fill the functional material, and when the micropores of the porous membrane are too large, it is difficult to control the filling of the functional material to the submicron particles to the micron unit. The average pore diameter of the micropores is preferably within the above numerical range, and the maximum pore diameter of the membrane surface is preferably 15 μm or less.

[Combination of nonwoven fabric base material and porous film]

From the viewpoint of the adhesion between the nonwoven fabric base material and the porous film, it is preferable to use a combination of the nonwoven fabric base material and the porous film to exhibit good adhesion. (Affinity) material. Specifically, the porous film contains a polyimide resin, a polyamideimide resin, a polyetherimide resin, a polytetrafluoroethylene (PTFE)-based porous film, and a polyethersulfone resin. In at least one of the nonwoven fabric base materials, a polyolefin nonwoven fabric, a polyester nonwoven fabric, a polyamide nonwoven fabric or the like is preferably used, and it is preferable to contain a two-layer nonwoven fabric selected from them, and a multilayer nonwoven fabric. At least one of the cloths.

Further, the porous film contains at least one selected from the group consisting of a polyimide resin, a polyamideimide resin, a polyetherimide resin, and a polyethersulfone resin, and the nonwoven fabric base material It is preferable to use a polyolefin nonwoven fabric, a polyester nonwoven fabric or the like, and it is more preferable to contain at least one selected from the two-layer nonwoven fabric and the multilayer nonwoven fabric.

Further, the porous film contains at least one selected from the group consisting of a polyimide resin, a polyamideimide resin, a polyetherimide resin, and a polyethersulfone resin, and the nonwoven fabric base material It is preferable to use a polyolefin nonwoven fabric, a polyester nonwoven fabric or the like, and it is more preferable to contain at least one selected from the two nonwoven fabrics.

When the porous film contains the above resin, the content thereof is, for example, 80 to 100% by weight, preferably 90 to 100% by weight, and more preferably 95 to 100% by weight based on the entire porous film.

When the nonwoven fabric base material contains the above resin or fiber, the content thereof is, for example, 60 to 100% by weight, preferably 80 to 100% by weight, and more preferably 90 to 100%, based on the entire nonwoven fabric base material. weight%.

[Porous film laminate]

The porous film laminate of the present invention has a structure in which the nonwoven fabric substrate and the porous film are integrated with excellent adhesion, and therefore has high mechanical strength. Therefore, in the case where the total thickness of the porous film laminate is, for example, less than about 100 μm, it is advantageous in that sufficient strength can be exhibited.

In a preferred embodiment of the porous film laminate of the present invention, one or both surfaces of the nonwoven fabric substrate are coated with a porous film, and a plurality of micropores having connectivity are provided, and the average pore diameter of the micropores is 0.01. A porous film laminate having a porous film of ~10 μm, the porous film having a thickness of 1 to 100 μm, a porosity of 30 to 80%, and a nonwoven fabric base material having a thickness of 10 to 500 μm. The porous film laminate as described above can be produced by appropriately setting the material, the thickness, the production conditions, and the like constituting the porous film and the substrate.

The value of the gas permeability of the porous film laminate is from 0.5 to 30 seconds, preferably from 0.5 to 20 seconds, more preferably from 0.5 to 10 seconds, still more preferably from 0.5 to 5 seconds. Since the gas permeability is in the above range, high gas permeability can be maintained, and the porous film laminate can be used for a gas or liquid filter, a battery or a separator for a battery, and the like. In addition, the value of the gas permeability of the porous film laminate can be measured by the method described in the examples using a Gurley gas permeability meter type B and JIS P8117 as a reference.

The tensile strength of the porous film laminate is 4.0 N / 15 mm or more, preferably 5.0 N / 15 mm or more, more preferably 6.0 N / 15 mm or more, and still more preferably 8.0 N / 15 mm or more. Since the tensile strength is a certain value or more, the strength and flexibility of the porous film laminate can be maintained, and the workability is good. In addition, the tensile strength of the porous film laminate can be measured by the method described in the examples using a universal tensile tester.

The shape change rate of the porous film laminate in the high-temperature placement test described below is, for example, 5% or less, preferably 4% or less, more preferably 3% or less. When the shape change rate is within the above range, the shape is maintained even at a high temperature, and the short circuit of the electrode is less likely to occur. As a result, the safety is improved, and the porous film laminate can be used for a separator for a battery or a capacitor.

(high temperature placement experiment)

The shape of the laminate integrated with the porous film was adjusted to a substantially rectangular shape of about 5 cm × 10 cm, and the lengths a1 and b1 of the substantially rectangular vertical sides were measured, and the temperature was adjusted to a temperature of 140 ° C. After the laminate was placed in the laminate for 30 minutes, the laminate was taken out, and after cooling to room temperature, the lengths a2 and b2 of the substantially rectangular vertical sides were measured, and the shape change rate was calculated using the following formula. .

The shape change rate (%) is determined from a1 and a2 = {|a2-a1|/a1} × 100

Similarly, the shape change ratio (%) was obtained from b1 and b2, and the average value of these values was taken as the shape change rate in the high-temperature placement experiment.

The porous film laminate of the present invention may have a porous film laminated on at least one surface of the base material, or may have a porous film on both surfaces of the base material. Further, the porous film may be filled with a functional material, and in the case of having a multilayer porous film, the same or different kinds of functional materials may be filled.

The porous film laminate of the present invention can be used as a filter, a separation membrane, a separator, or by directly utilizing pores of the porous membrane or functionalizing the pores of the porous membrane with a functional material. Used as part of them.

Further, in order to impart desired characteristics to the porous film laminate of the present invention, heat treatment or film formation treatment may be carried out as needed.

The porous film laminate of the present invention has the above structure, and therefore can be applied to various uses in a wide range of fields. It is particularly suitably used as a filter, a separation membrane, a separator, or as a part thereof, and can be used, for example, as a liquid separation membrane, a solid separation membrane, a gas separation membrane, or a part thereof. In addition, it can be used as a circuit board, a heat releasing material (heat sink, heat radiating plate, etc.), a battery separator, an electromagnetic wave shielding or an electromagnetic wave absorber, an electromagnetic wave control material, an electrolytic capacitor, a low dielectric constant material, a buffer material, and an ink. A wide range of substrate materials such as a developing sheet, a test paper, an insulating material, a heat insulating material, a cell culture medium material, a material for a radiation shielding layer, and an oil absorbing material are used.

Specifically, it is suitable for a bag filter, a dust collecting filter, an air conditioning filter, a filter for an automobile (air cleaner, oil cleaner, indoor clean filter, external air suction filter, etc.).

In addition, it can be used as a circuit board, a heat releasing material (heat sink, heat radiating plate, etc.), a battery separator, an electromagnetic wave shielding or an electromagnetic wave absorber, an electromagnetic wave control material, an electrolytic capacitor, a low dielectric constant material, a buffer material, and an ink. A wide range of substrate materials such as a developing sheet, a test paper, an insulating material, a heat insulating material, a cell culture medium material, a material for a radiation shielding layer, and an oil absorbing material are used.

The nonwoven fabric itself can be used in a filter, a separation membrane, and a separator. However, even if the pore diameter is the smallest, it is impossible to collect fine substances of several tens of μm or more.

The porous film laminate of the present invention can be preferably used as a filter, a separation membrane, or a separator. In order to form a porous film on the nonwoven fabric base material, the base material can ensure sufficient strength. Since the porous film has a high porosity, it can be used for a porous single film for applications requiring insufficient strength. Examples of the filter using the porous film laminate of the present invention include a filter for filtering an aqueous solution such as water or a solvent, or a filter for filtering a gas such as air; and a filter for treating waste water capable of removing foreign matter of at least submicron particles; A filter for filtration such as blood separation such as separation of red blood cells; a filter for an air conditioner such as a body of dust, pollen, mold, or cockroach separated from the air. The porous film laminate of the present invention can also be used as a base material for an oxygen-rich film used in an air conditioner.

Further, for example, it can be used as a filter for an inkjet printer. In the ink jet printer, various filters can be used depending on the purpose in order to stably eject the ink from the fine holes of the ink jet head without blocking. Various names are used depending on the manufacturer, and examples thereof include a small dish filter, an ink filling filter, a main body filter, a nozzle protection end filter (Last Chance Filter), and an ink bag (filter ink bag). , bubble suppression filter, straight-through filter, etc.

Further, for example, use as a filter used in a medical system or the like can be cited. In the medical system, liquid nitrogen or the like can be used for frozen storage of blood, storage of germ cells (sperm or egg), cultured cells, biological samples, or raw materials. Liquid nitrogen or the like used in such applications requires removal of foreign matter such as viruses. Since the virus is about 0.1 to 0.2 μm, the virus can be removed by filtering the liquid nitrogen with the porous membrane laminate of the present invention.

Further, the porous film laminate of the present invention can also be used as a test paper. The test paper can be widely used for experimental use, medical use, etc., and examples thereof include pH test paper (for example, litmus paper), water test paper (for example, ion test paper), oil test paper, moisture test paper, ozone test paper, urine test paper, blood test paper, and the like. . The ion test paper can be used to study metal ions or anions qualitatively or quantitatively. Urine test strips can be used to study urine sugar, urine protein, and occult blood in a quantitative manner. Blood test strips can be used to quantitatively study blood sugar levels and the like. The measurement methods of these test papers are simple, and therefore the use opportunities increase year by year.

Since the porous film laminate of the present invention is in close contact with the base material, sufficient strength can be ensured in operation. Further, the porous film can adsorb the indicator used in the determination, and therefore is a preferred medium. Further, since a sample such as a solvent such as water, urine or blood can be retained, it is preferably used in these applications.

The porous film laminate of the present invention can be preferably used as a separator for a battery. Battery separator Separating the positive and negative electrodes requires excellent electrolyte retention and good ion conductivity. In addition, various properties such as heat resistance, flexibility, and strength are required. According to the porous film laminate of the present invention, these characteristics can be exhibited in a balanced manner, and therefore, it is very useful as a separator for various batteries.

In order to improve the safety of the battery separator in the past fire, automotive use, or industrial use, high heat resistance is required. From this viewpoint, the porous film laminate of the present invention is also useful.

In the porous film laminate of the present invention, a water-resistant nonwoven fabric can be used as the base material, and therefore, the swelling of the nonwoven fabric base material can be prevented.

[Method for Producing Porous Film Laminate]

The porous film laminate of the present invention can be produced by laminating the porous film on at least one side of the nonwoven fabric by a method of thermal fusion bonding, for example, by polymerizing the porous film. The solution is produced by casting a solution onto a substrate and forming a film, and then contacting the coagulating liquid to make it porous, which will be described in detail below.

(Method for producing porous individual film)

The porous film can be produced by, for example, casting a polymer solution into a film shape on a film base material, contacting it with a coagulating liquid to make it porous, and then peeling it off from the film base material and performing it on the porous film. Dry to obtain a porous film. As a method of contacting and coagulating the coagulating liquid, a method of obtaining a film by a wet phase conversion method (for example, refer to JP-A-2001-145826) and a dry phase conversion method (for example, refer to International Publication) A known method such as a method of using a solvent-replacement-speed-adjusting material, and a method of using a solvent-replacement-speed-adjusting material (for example, refer to JP-A-2000-319442, JP-A-2001-67643).

The porous film can also be produced by a method for producing a resin porous film typified by a polyolefin-based porous film. When the method for producing a resin porous film is roughly classified, there are two methods of a wet method in which the porous film is formed in the extraction step and a dry method in which the porous film is formed in the stretching step. As the former method, for example, the method described in JP-A-58-59072 can be cited. Japanese Laid-Open Patent Publication No. SHO-58-59072 discloses a production method in which a plasticizer or the like is kneaded together with a resin and melt-extruded, and a plasticizer or the like is extracted and made porous in an extraction tank.

On the other hand, as the latter method, for example, a method described in JP-A-62-121737 can be cited. JP-A-62-121737 discloses a production method in which a layered crystal is formed on a melt-extruded original film, and the layered crystals are cracked and made porous by longitudinal uniaxial stretching. According to this method, unlike the wet method, the extraction step is not required, and the process can be simplified. Further, as a method for producing a biaxially-stretched porous film using a dry method, a method described in International Publication No. 2007/098339 can be mentioned. A technique of transversely stretching a porous film obtained by a known longitudinal uniaxial stretching while relaxing in the longitudinal direction by heat is disclosed in International Publication No. 2007/098339.

A polytetrafluoroethylene (PTFE)-based porous film can also be produced by the same method as the polyolefin-based porous film.

As the polymer solution to be cast, for example, a polymer component which is a material constituting the porous film, a water-soluble polymer, a water-soluble polar solvent, a mixed solution of water as needed, or the like can be used.

The polymer component which is a material constituting the porous film is preferably one which has solubility in a water-soluble polar solvent and can be formed into a film by a phase inversion method, and one of the above-mentioned exemplified materials or a mixture of two may be used. the above. Further, a monomer component (raw material) of the polymer component or an oligomer thereof, a precursor before imidization or cyclization, or the like may be used instead of the high molecular component constituting the porous film.

The addition of a water-soluble polymer or water to the cast polymer solution can effectively make the membrane structure porous into a sponge. The water-soluble polymer may, for example, be polyethylene glycol, polyvinylpyrrolidone, polyethylene oxide, polyvinyl alcohol, polyacrylic acid, polysaccharides or the like, or a derivative thereof, or a mixture thereof. Among them, polyvinylpyrrolidone is preferred in terms of suppressing the formation of voids in the inside of the film and improving the mechanical strength of the film. These water-soluble polymers may be used singly or in combination of two or more. The water-soluble polymer may have a molecular weight of 200 or more, preferably 300 or more, particularly preferably 400 or more (for example, about 400 to 200,000), and particularly preferably 1,000 or more. The void diameter can be adjusted by the addition of water. For example, when the amount of water added in the polymer solution is increased, the void diameter can be increased.

The water-soluble polymer is very effective for making the film structure into a sponge shape, and various structures can be obtained by changing the kind and amount of the water-soluble polymer. Therefore, it is highly preferred that the water-soluble polymer be used as an additive in forming a porous film for the purpose of imparting desired pore characteristics. On the other hand, the water-soluble polymer does not eventually constitute a porous film, but an unnecessary component which should be removed. In the method using the wet phase conversion method, the water-soluble polymer is easily removed by washing in a step of immersing in a coagulating liquid such as water to carry out phase inversion. On the other hand, in the dry phase conversion method, the component (unwanted component) which does not constitute the porous film is removed by heating, and the water-soluble polymer is removed by heating without using the wet phase conversion method. As described above, the manufacturing method using the wet phase conversion method is advantageous in that a porous film having desired pore characteristics can be easily produced as compared with the case of using the dry layer conversion method.

Examples of the water-soluble polar solvent include dimethyl sulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone. (NMP), 2-pyrrolidone, a mixture thereof, and the like, and a substance having solubility (a good solvent for a polymer component) is used depending on the chemical skeleton of the resin used as the polymer component.

The polymer solution to be cast preferably includes, as a material constituting the porous film, 8 to 25% by weight of the polymer component, 5 to 50% by weight of the water-soluble polymer, 0 to 10% by weight of water, and the water-soluble polar solvent 30. ~82% by weight of a mixed solution or the like. At this time, when the concentration of the polymer component is too low, the thickness of the porous film is insufficient, or it is difficult to obtain desired pore characteristics. Further, when the concentration of the polymer component is too high, the porosity tends to be small. The water-soluble polymer is added in order to make the inside of the film a homogeneous sponge-like porous structure. However, when the concentration is too low, a large void of more than 10 μm is generated inside the film, and the uniformity is lowered. In addition, when the concentration of the water-soluble polymer is too high, the solubility is deteriorated, and when it exceeds 50% by weight, problems such as weakening of the film strength tend to occur. The amount of water added can be used to adjust the void diameter, and the diameter can be increased by increasing the amount of addition.

When the polymer solution is cast into a film shape, the film is preferably held in an atmosphere having a relative humidity of 70 to 100% and a temperature of 15 to 90 ° C for 0.2 to 15 minutes, and then introduced into a non-solvent composed of a polymer component. In the coagulation solution. By placing the cast film after the above conditions, the porous film can be made homogeneous and highly connected. The reason for this is that moisture is intruded from the surface of the film to the inside by being placed under humidification conditions, and phase separation of the polymer solution is effectively promoted. Particularly preferred conditions are a relative humidity of 90 to 100%, a temperature of 30 to 80 ° C, and a relative humidity of about 100% (e.g., 95 to 100%) and a temperature of 40 to 70 °C. When the amount of water in the air is less than the above conditions, there is a case where the surface opening ratio is insufficient.

According to the method for producing a porous film, for example, a porous film having a plurality of pores having connectivity and having an average pore diameter of 0.01 to 10 μm can be easily formed. As described above, the diameter, porosity, and opening ratio of the pores of the porous membrane constituting the porous

membrane of the present invention can be determined by the type or amount of constituent components of the polymer solution, the amount of water used, the humidity of the flow delay, and the temperature. The time and the like are appropriately selected and adjusted to a desired value.

The coagulation liquid to be used in the phase-conversion method is not particularly limited as long as it is a solvent for solidifying the polymer component, and may be appropriately selected depending on the type of the polymer to be used as the polymer component. For example, the polyamideimide resin may be used. The solvent for solidifying the polyamic acid may be, for example, water; alcohol such as monohydric alcohol such as methanol or ethanol; polyhydric alcohol such as glycerin; water-soluble polymer such as polyethylene glycol; and water-soluble coagulating liquid such as a mixture thereof. .

In the method for producing a porous film, a porous film can be produced by introducing into a coagulating liquid and forming a porous film on the surface of the film base material, followed by peeling and direct drying. The drying method is not particularly limited as long as it can remove a solvent component such as a coagulating liquid, and it may be dried under heating or naturally dried at room temperature. The method of the heat treatment is not particularly limited, and may be a method of hot air treatment, hot roll treatment, or introduction into a thermostatic chamber or an oven, as long as the porous membrane can be controlled to a predetermined temperature. The heating temperature can be selected from a wide range of, for example, room temperature to 600 °C. The atmosphere during the heat treatment may be any of air, nitrogen, and an inert gas. Air is the cheapest, but it can be accompanied by an oxidation reaction. When this is avoided, nitrogen or an inert gas may be used, and nitrogen gas is preferred from the viewpoint of cost. The heating conditions are appropriately set in consideration of productivity, physical properties of the porous film, and the like. By drying, a porous film can be obtained.

The porous film obtained as described above can be further subjected to a crosslinking treatment using heat, visible light, ultraviolet rays, electron beams, radiation, or the like. By the treatment, the precursor constituting the porous film is polymerized, crosslinked, and cured to form a polymer compound. When the porous film is composed of a polymer compound, crosslinking or curing can be performed to obtain rigidity or resistance. A porous film having further improved properties such as properties. For example, a porous polyimide film can be obtained by further subjecting a porous film formed using a polyimide-based precursor to thermal imidization or chemical imidization. The porous film formed using the polyamideimide-based resin can be thermally crosslinked. It should be noted that thermal crosslinking may be carried out simultaneously with the heat treatment for drying after introduction into the coagulation liquid.

(Lamination of non-woven base material and porous film)

The lamination method of the nonwoven fabric base material and the porous film can be reasonably produced by heat fusion bonding or the like. In this case, (the glass transition temperature of the resin constituting the porous film) □ (the melting point of the resin constituting the nonwoven fabric) is preferable.

The specific manufacturing method will be described. A porous film is placed on at least one surface of the nonwoven fabric base material, and is heated from one side or both sides of the porous film by a heat source to slightly melt the surface of the nonwoven fabric base material that is in contact with the porous film, thereby obtaining a nonwoven fabric. A laminate in which a cloth base material is in close contact with a porous film. At this time, in order to protect the porous film, the nonwoven fabric base material or both from friction or the like, it is preferred to carry the protective film on one side or both sides. The heat source may be an iron, a laminating machine, a heating roll, or the like, or a laminating device, a heat sealing device, a calendering device, a roll pressing device, or the like may be used.

The reason why (the glass transition temperature of the resin constituting the porous film) □ (the melting point of the resin constituting the nonwoven fabric) is that the porous film having micropores is almost or completely unaffected by heat, and only the nonwoven fabric base material is slightly Melt. The heating may be performed by melting the nonwoven fabric and adhering it to the porous film, and heating more than necessary may cause clogging of the pores of the nonwoven fabric, which is not preferable. The heating temperature is preferably between (the glass transition temperature of the resin constituting the porous film) and (the melting point of the resin constituting the nonwoven fabric), and is preferably (the glass transition temperature of the resin constituting the porous film) □ (heating temperature) □ (the melting point of the resin constituting the nonwoven fabric). The heating temperature at this time is the temperature at which the porous film and the nonwoven fabric base material are in contact with each other. For example, a polyolefin such as polyethylene or

polypropylene has a melting point of about 130 to 165 ° C. Therefore, the heating temperature may be about 140 to 170 ° C.

In the case of a general nonwoven fabric, the air permeability measured by a Gurley gas permeability meter is 0.1 second or less of the measurement limit, and therefore, even if it is thermally deformed by a part of the heat-fusible polyolefin nonwoven fabric, it is breathable. Degree has almost no effect. However, it is not preferable to maintain it for a long time (the melting point of the resin constituting the nonwoven fabric) or more. The technical focus of controlling hot-melt bonding is heating temperature, moving speed of heat source, pressure, etc. It is important to properly control these factors.

The polymer solution is cast onto a substrate to form a film, and then introduced into a coagulating liquid. Then, a separate film peeled off from the substrate is dried, and the thus obtained porous film and nonwoven fabric substrate are thermally melt-bonded or the like. The material is laminated, and it is preferable that the glass transition temperature of the resin constituting the porous film is the melting point of the resin constituting the nonwoven fabric.

A porous film laminate in which a porous film having excellent pore characteristics and a matrix material are directly laminated can be easily obtained by the above method.

According to the method for producing a porous film laminate, a laminate having a porous film coated on one or both sides of the base material by the porous film can be easily obtained, and the porous film is provided with a plurality of connectivity The micropores have an average pore diameter of 0.01 to 10 μm.

Example

Hereinafter, the present invention will be described in more detail based on examples, but the present invention is not limited by these examples. Tape peeling test, measurement of average pore diameter, measurement of average open porosity (porosity) inside porous film, gas permeability test, high temperature placement test, measurement of arithmetic mean surface roughness Sa (surface roughness), tensile strength The measurement was carried out by the following method.

(tape stripping test)

(i) The following tape was attached to the surface of the porous film of the porous film laminate, and the tape was pressed against the bonded portion by a roll described below to press the tape.

(ii) T-peeling was performed under the conditions of 50 mm/min using the universal tensile tester described below.

(iii) Observe whether or not the interface between the porous film and the heat-resistant nonwoven fabric base material is peeled off.

Tape: manufactured by Teraoka Manufacturing Co., Ltd. (trade name "film masking tape No. 603 (#25)", 24 mm width)

Roller: 30mm diameter, 200gf load

Universal tensile testing machine: manufactured by Orientec Co., Ltd. (trade name "TENSILON RTA-500")

Further, the average pore diameter and porosity of the film in Example 1 were calculated by the following methods. These average pore diameters and porosity were obtained only by the micropores observed at the forefront of the electron micrograph, and the micropores observed inside the photograph were not targeted.

(Measurement of average pore size)

From the electron micrograph, the area of any 30 or more holes on the surface or the cross section of the laminate was measured, and the average value was defined as the average pore area S ave . Assuming that the hole is a perfect circle, the value converted from the average hole area to the hole diameter is set to the average hole diameter using the following formula. Here, π represents a pi.

Average pore size on the surface or inside [μm]=2·(S ave /π) 1/2

(Measurement of average open porosity (porosity) inside porous film)

In Comparative Example 1, since the porous film was embedded in the inside of the nonwoven fabric and integrated with the base material, it was difficult to directly measure the porosity inside the porous film. Therefore, a PET film (trade name "HS74AS": 100 μm thick) was used instead of the PET nonwoven fabric as a base material, and the stock solution was cast on the easy-adhesive surface of the PET film, and then immersed in water and solidified. Next, the porous film obtained by peeling off from the PET film and dried was measured, and the internal porosity was calculated by the following formula. When there is no base material, it is calculated directly by the following formula.

V represents the volume [cm 3] of the film, W represents the weight [g] of the porous film, and ρ represents the density [g/cm 3] of the porous film raw material. The density of the polyamideimide was 1.45 [g/cm 3], and the density of the polyetherimide was 1.27 [g/cm 3].

Porosity [%]=100-100·W/(ρ·V)

(breathability test)

The air permeability was measured using a Gurley type air permeability meter type B manufactured by TESTER SANGYO CO., LTD., based on JIS P8117. The number of seconds is measured using a digital automatic counter. The smaller the value of the gas permeability (Gee value), the higher the permeability of air, that is, the high connectivity of the micropores in the porous film. It should be noted that the air permeability of the base material and the gas permeability of the porous film laminate were evaluated by the test method unless otherwise specified.

(high temperature placement experiment)

The shape of the laminate in which the porous film was integrated was adjusted to a substantially rectangular shape of about 5 cm × 10 cm, and the distance between the two sides a and b on the vertical side was measured to evaluate the change in the shape of the sample. First, the initial distances a1 and b1 were measured. Next, the sample was placed in a thermostat adjusted to a temperature of 140 ° C and left for 30 minutes. Then, the sample was taken out, and after naturally cooling to room temperature, the distances a2 and b2 were measured. The respective rate of change of a and b was calculated using the following formula.

Rate of change of a after high temperature placement (%) = {|a2-a1|/a1} × 100

The rate of change of b was calculated in the same manner.

(Measurement of arithmetic mean surface roughness Sa (surface roughness))

The surface roughness was calculated by measuring the surface shape using a non-contact surface measuring system VertScan 2.0 (manufactured by Ryokan Corporation) using an optical interference method. The measurement area was set to a range of 250 μm × 188 μm, and the measurement conditions were an objective lens = 50 times, a lens barrel = 0.5 × Body, a continuous zoom lens = NoRelay, a filter = 530white, a measurement mode = Wave, and a field of view size = 640 × 480. The arithmetic mean surface roughness (Sa) was used as the surface roughness.

(Measurement of tensile strength)

A test piece having a size of 15 × 150 mm was taken along the MD direction (flow direction) at the time of sample preparation, and the distance between the chucks was set to 100 mm using a universal tensile tester, and the test piece was stretched at a speed of about 200 mm per minute, and the test piece was measured. Tensile Strength. The unit is expressed in N/15mm.

[Manufacturing Example 1]

Add to 100 parts by weight of a polyamideimide resin solution (trade name "VYLOMAX (HR) NN11" manufactured by Toyobo Co., Ltd.; solid content concentration: 15% by weight, solvent NMP, solution

viscosity: 20 dPa·s / 25 ° C) 35 parts by weight of polyvinylpyrrolidone (molecular weight: 55,000) was used as a raw material for film formation as a water-soluble polymer. A PET film (thickness: 100 μm: trade name "HS74AS") manufactured by Teijin DuPont Co., Ltd. was placed on a glass plate as a base material, and the easy-adhesive surface was placed thereon, and a stock solution kept at 25 ° C was cast on the PET using a film coater. On the membrane. The flow rate was carried out with a gap between the film coater and the PET film of 51 μm. After casting, it was rapidly held in a container having a humidity of about 100% and a temperature of 50 ° C for 4 minutes. Thereafter, when immersed in water and allowed to solidify and washed, the porous film was naturally peeled off from the PET film.

The porous film was obtained by natural drying at room temperature. The thickness of the porous film was about 23 μm. The porous film was observed with an electron microscope, and as a result, the average pore diameter of the pores present on the surface of the porous membrane was about 0.5 μm, the inside of the porous membrane was substantially homogeneous, and the microporosity having an average pore diameter of about 0.5 μm was present as a whole. hole. Further, the porosity inside the porous film was 70%. The air permeability of the porous film was measured, and the result was an average of 4 seconds (measured value of 3 times, 4 seconds, 4 seconds, 4 seconds). Fig. 1 shows an electron micrograph (SEM photograph) of the surface of the porous film obtained in Production Example 1.

[Manufacturing Example 2]

Polyvinylpyrrolidone (molecular weight: 55,000) was added to 100 parts by weight of a polyetherimide resin solution (manufactured by GE Plastic, Japan, trade name "ULTEM (1000)"; solid content concentration: 18% by weight, solvent NMP) A stock solution for film formation is prepared as a water-soluble polymer in parts by weight.

A PET film (thickness: 100 μm: trade name "HS74AS") manufactured by DuPont Co., Ltd., which is a base material, was placed on a glass plate, and the easy-adhesive surface was placed thereon, and the stock solution kept at 25 ° C was cast using a film coater. On the PET film. The flow delay was carried out with a gap of 51 μm between the film coater and the PET film. After casting, it was rapidly held in a container having a humidity of about 100% and a temperature of 50 ° C for 4 minutes. Thereafter, when immersed in water and solidified and washed, the porous film was naturally peeled off from the PET film. The porous film was obtained by natural drying at room temperature. The thickness of the porous film was about 24 μm. The porous film was observed with an electron microscope. As a result, the pores present on the surface of the porous film had an average pore diameter of about 1 μm, and the inside of the porous film was substantially homogeneous and had micropores having connectivity having an average pore diameter of about 1 μm as a whole. Further, the porosity inside the porous film was 73%. The air permeability of the porous film was measured, and as a result, it was an average of 4 seconds (3 times of measurement values of 3 seconds, 4 seconds, and 4 seconds). Fig. 2 shows an electron micrograph (SEM photograph) of the surface of the porous film obtained in Production Example 2.

[Example 1]

The polyamideimide-based porous film of Production Example 1 was laminated on a polyolefin nonwoven fabric manufactured by VILENE, Japan (having a thickness of about 250 μm, a basis weight of about 80 g/m 2 , a density of about 0.36 g/cm 3 , and a gas permeability of 0.1 second). : The product name "FT-330N" was placed between the PET film (manufactured by Toray Industries, thickness: 100 μm: product name "lumiler S10") and placed on a table. The temperature setting of the steam iron (product number: NI-R70) manufactured by Matsushita Electric Industrial Co., Ltd. is set to medium (about 150 ° C), and the polyamide film-based porous film is combined with the PET film at the set temperature. The side is heated. The moving speed of the steam iron was set to about 60 cm/min.

By the above method, a laminate in which a polyamideimide-based porous film and a polyolefin nonwoven fabric are integrated is obtained. The total thickness of the laminate was about 313 μm. On one side of the polyamideimide-based porous film, the glass transition temperature was about 300 ° C, so no change was observed.

The obtained laminate was subjected to a tape peeling test, and as a result, no interface peeling occurred between the nonwoven fabric and the porous film. The laminate was observed with an electron microscope, and as a result, the pores present on the surface of the porous membrane had an average pore diameter of about 0.5 μm. The air permeability of the laminate was measured and found to be 4 seconds on average (measured values of 3 times, 5 seconds, and 4 seconds), and the same values as those of the polyamideimide-based porous film

before lamination. It was not observed that the prepared laminate caused deterioration in gas permeability and there was almost no deviation.

Further, in terms of the rate of change after the high-temperature standing, both a and b were 1.0%, and almost no change in shape due to the high-temperature placement of the laminate was observed. It was confirmed that the laminate was excellent in shape stability at a high temperature.

[Embodiment 2]

The polyamideimide-based porous film of Production Example 1 was laminated on a polyolefin nonwoven fabric manufactured by VILENE, Japan (having a thickness of about 250 μm, a basis weight of about 80 g/m 2 , a density of about 0.36 g/cm 3 , and a gas permeability of 0.1 second). : The product name "FT-330N" was placed between the PI film (manufactured by Toray DuPont, thickness 25 μm: product name "Kapton (カプトン) 100H"). The temperature setting scale of the laminator (product number: LFA341D) manufactured by IRIS OHYAMA Co., Ltd. was set to 13 (about 150 ° C), and was heated from both sides together with the PI film while reaching the set temperature. The lamination speed of the laminator was about 47 cm/min.

By the above method, a laminate in which a polyamideimide-based porous film and a polyolefin nonwoven fabric are integrated is obtained. The total thickness of the laminate was about 249 μm. Since the surface of the surface of the polyolefin nonwoven fabric is thermally melted due to heating from both sides, the smoothness is increased. On one side of the polyamideimide-based porous film, the glass transition temperature was about 300 °C, and therefore, no change was observed.

The obtained laminate was subjected to a tape peeling test, and as a result, no interface peeling occurred between the nonwoven fabric and the porous film. The laminate was observed with an electron microscope, and as a result, the pores present on the surface of the porous membrane had an average pore diameter of about 0.5 μm. When the air permeability of the laminate was measured, the average value was 5 seconds (measured values of 5 seconds, 5 seconds, and 4 seconds), and the value of the polyamideimide-based porous film before lamination was almost the same, and there was almost no variation. It was not observed that the prepared laminate caused deterioration in gas permeability.

Further, in terms of the rate of change after the high-temperature standing, a and b were 1.4% and 1.5%, respectively, and almost no change in shape due to the high-temperature placement of the laminate was observed. It was confirmed that the laminate was excellent in shape stability at a high temperature.

[Example 3]

In Example 2, two layers of non-woven fabrics (one having a thickness of about 105 μm, a basis weight of about 50 g/m 2 , and a density of about 0.43 g/cm 3) made of a wide paper made of rayon paper were used. Air permeability: 0.1 second: Trade name "05EP-50") As a nonwoven fabric, a polyamideimide-based porous film was laminated on the polypropylene side of the two-layer nonwoven fabric, and Example 2 was used. In the same manner, a laminate in which a nonwoven fabric and a porous film were integrated was obtained. The total thickness of the laminate was about 135 μm. Heating was carried out from both sides, but the melting point of the polyester was about 260 ° C, so that no change was observed on the surface of one side of the polyester nonwoven fabric. On one side of the polyamideimide-based porous film, the glass transition temperature was about 300 ° C, so no change was observed.

The obtained laminate was subjected to a tape peeling test, and as a result, no interface peeling occurred between the nonwoven fabric and the porous film. The laminate was observed with an electron microscope, and as a result, the pores present on the surface of the porous membrane had an average pore diameter of about 0.5 μm. When the air permeability of the laminate was measured, the average value was 4 seconds (measured values of 3 times, 4 seconds, 4 seconds, 4 seconds), and the values of the polyamideimide-based porous film before lamination were the same, and there was no variation. It was not observed that the prepared laminate caused deterioration in gas permeability.

Further, in terms of the rate of change after the high-temperature standing, a and b were 0% and 0.5%, respectively, and almost no change in shape due to the high-temperature placement of the laminate was observed. It was confirmed that the laminate was excellent in shape stability at a high temperature.

[Example 4]

In Example 2, two layers of non-woven fabrics (one having a thickness of about 93 μm, a basis weight of about 50 g/m 2 , and a density of about 0.42 g/cm 3) made of a wide paper made of rayon paper were used. Air permeability: 0.1 second: Trade name "15EP-50") As a nonwoven fabric, a polyamideimide-based porous film was laminated on the polypropylene side of the two-layer nonwoven fabric, and Example 2 was used. In the same manner, a laminate in which a nonwoven fabric and a porous film were integrated was obtained. The total thickness of the laminate was about 131 μm. Heating was carried out from both sides, but the melting point of the polyester was about 260 ° C, and therefore no change was observed on the surface of one side of the polyester nonwoven fabric. On one side of the polyamideimide-based porous film, the glass transition temperature was about 300 ° C, and therefore, no change was observed.

The obtained laminate was subjected to a tape peeling test, and as a result, no interface peeling occurred between the nonwoven fabric and the porous film. The laminate was observed with an electron microscope, and as a result, the pores present on the surface of the porous membrane had an average pore diameter of about 0.5 μm. When the air permeability of the laminate was measured, the average value was 4 seconds (measured values of 3 times, 4 seconds, 4 seconds, 4 seconds), and the values of the polyamideimide-based porous film before lamination were the same, and there was no variation. It was not observed that the prepared laminate caused deterioration in gas permeability.

Further, in terms of the rate of change after the high-temperature standing, a and b were 0.4% and 0.5%, respectively, and almost no change in shape due to the high-temperature placement of the laminate was observed. It was confirmed that the laminate had excellent shape stability at a high temperature.

[Example 5]

In Example 2, a polyolefin nonwoven fabric (having a thickness of about 13 μm, a basis weight of about 2.6 g/m 2 , a density of about 0.20 g/cm 3 , a gas permeability of 0.1 second: trade name "06HOP-" was produced using a wide paper. 2)) A laminate of a polyamideimide-based porous film and a polyolefin nonwoven fabric was obtained in the same manner as in Example 2 except that the nonwoven fabric was used. The total thickness of the laminate was about 38 μm. Since the heating is performed from both sides, the surface of one side of the polyolefin nonwoven fabric is thermally melted, and the smoothness is increased. On one side of the polyamideimide-based porous film, the glass transition temperature was about 300 ° C, so no change was observed.

The obtained laminate was subjected to a tape peeling test, and as a result, the nonwoven fabric and the porous film did not cause interface peeling. The laminate was observed with an electron microscope, and as a result, the pores present on the surface of the porous membrane had an average pore diameter of about 0.5 μm. When the air permeability of the laminate was measured, the average value was 5 seconds (measured value of 3 times, 4 seconds, 5 seconds, and 5 seconds), and the value of the polyamideimide-based porous film before lamination was almost the same. It was not observed that the prepared laminate caused deterioration in gas permeability.

Further, in terms of the rate of change after the high-temperature standing, a and b were 1.6% and 0.7%, respectively, and the shape change caused by the laminate being placed at a high temperature was only curling. It was confirmed that the laminate had excellent shape stability at a high temperature.

[Embodiment 6]

In Example 2, a polyolefin nonwoven fabric (having a thickness of about 13 μm, a basis weight of about 2.6 g/m 2 , a density of about 0.20 g/cm 3 , a gas permeability of 0.1 second: trade name "06HOP-" was produced using a wide paper. 2)) A polyetherimide-based porous film and a polyolefin non-woven fabric were obtained in the same manner as in Example 2 except that the polyetherimide-based porous film of Production Example 2 was used as the nonwoven fabric. A laminated body of cloth. The total thickness of the laminate was about 39 μm. Since the heating is performed from both sides, the surface of one side of the polyolefin nonwoven fabric is thermally melted, and the smoothness is increased. On one side of the polyetherimide-based porous film, the glass transition temperature was about 217 ° C, so no change was observed.

The obtained laminate was subjected to a tape peeling test, and as a result, no interface peeling occurred between the nonwoven fabric and the porous film. The laminate was observed with an electron microscope, and as a result, the pores present on the surface of the porous membrane had an average pore diameter of about 1 μm. The air permeability of the laminate was measured, and as a result, it was an average of 4 seconds

(measured value of 3 times, 5 seconds, 4 seconds, and 3 seconds), and was the same as the value of the polyetherimide-based porous film before lamination. There are deviations. It was not observed that the prepared laminate caused deterioration in gas permeability.

Further, in terms of the rate of change after the high temperature standing, a and b were 0.2% and 0.6%, respectively, and the shape change caused by the laminate being placed at a high temperature was only curling. It was confirmed that the laminate had excellent shape stability at a high temperature.

[Comparative Example 1]

Add to 100 parts by weight of a polyamideimide resin solution (trade name "VYLOMAX (HR) NN11" manufactured by Toyobo Co., Ltd.; solid content concentration: 15% by weight, solvent NMP, solution viscosity: 20 dPa·s / 25 ° C) 40 parts by weight of polyvinylpyrrolidone (molecular weight: 55,000) was used as a water-soluble polymer as a stock solution for film formation. A PET nonwoven fabric (thickness: 130 μm, basis weight: about 90 g/m 2 , density of about 0.69 g/cm 3 , air permeability of 0.1 second: trade name "MF-90") of Japanese VILENE Co., Ltd. was placed on a glass plate. The stock solution held at 25 ° C was cast on the nonwoven fabric using a film coater. The flow time was carried out with a gap of 51 μm between the film coater and the nonwoven fabric. After casting, it was quickly held in a container having a humidity of about 100% and a temperature of 50 ° C for 4 minutes. Thereafter, it is immersed in water, solidified and washed, and then peeled off from the nonwoven fabric, taken out from the water, placed on a paper towel, and naturally dried at room temperature, thereby obtaining a nonwoven fabric and a porous film. Integrated laminate. The total thickness of the laminate was about 147 μm.

The obtained laminate was subjected to a tape peeling test, and as a result, no interfacial peeling occurred between the nonwoven fabric and the porous film. When the laminate was observed with an electron microscope, the porous film was adhered to the nonwoven fabric, and the pores present on the surface of the porous membrane had an average pore diameter of about 0.2 μm, and the inside of the porous membrane was substantially homogeneous and had an average pore diameter as a whole. 0.2 μm micropores with connectivity. Further, the porosity inside the porous film was 70%. The air permeability of the laminate was measured and found to be 136 seconds on average (measured values of 142 seconds, 170 seconds, and 96 seconds in three times). It was found that the gas permeability was extremely inferior to the laminate samples of Examples 1 to 6, and the variation was also extremely large.

Table 1 shows the values of the surface roughness Sa of the laminates of Examples 1 to 6 and Comparative Example 1. It was confirmed that the surface of the laminate obtained by the hot melt bonding (heat sealing) of the present invention has a very small surface roughness, but the surface of the laminate obtained by the coating of the comparative example has a relatively large surface roughness. . Further, it was confirmed that the laminate of the present invention has a smooth surface and high gas permeability, but in the comparative example, the porous film of the laminate penetrates deeply into the nonwoven fabric, thereby impeding the gas permeability.

Table 1

The results of the high temperature placement experiment are summarized in Table 2. Further, for comparison, a high-temperature placement test of a separator (thickness: about 25 μm, product model 2500) manufactured by Celgard Co., Ltd., which is a commercially available polyolefin separator, was carried out, and as a result, the separator was particularly oriented along one side after the test. Significant shrinkage occurs, which in turn produces curl. It was confirmed that the polyolefin separator has very poor shape stability at high temperatures. On the other hand, it was confirmed that the laminate of the present invention has shape stability at a high temperature.

Table 2

Table 3 shows the measurement results of the tensile strength of the laminates of Examples 1 to 6 and the porous films of Production Examples 1 and 2. The tensile strength of the laminates of Examples 1 to 6 was increased as compared with the porous films of Production Examples 1 and 2, and the workability was confirmed to be improved.

table 3

Industrial applicability

The porous film laminate of the present invention is excellent in porosity and surface smoothness, has heat resistance and flexibility, and is excellent in workability and moldability. Therefore, it can be used as a filter and separation at high temperatures. Membrane, separator, or as part of them.

CN104999745A Microporous laminated membrane and method for producing the same

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The wording below is an initial machine translation of the original publication. To generate a version using the latest translation technology, go to the original language text and use Patent Translate.

1.A porous film laminate in which a porous film is laminated on at least one side of a nonwoven fabric base material, wherein

The porous membrane is provided with a plurality of micropores having connectivity, and the micropores have an average pore diameter of 0.01 to 10 μm.

The arithmetic mean surface roughness Sa of the surface of the porous film obtained by the following measurement method is 0.5 μm or less.

The value of the air permeability of the porous film laminate is 0.5 to 30 seconds.

The tensile strength of the porous film laminate is 4.0 N/15 mm or more.

The base material and the porous film did not undergo interface peeling due to the tape peeling test described below.

(tape stripping test)

A masking tape (manufactured by Teraoka Seisakusho Co., Ltd., trade name "film masking tape No. 603 (#25)", width: 24 mm] was attached to the surface of the porous film of the porous film laminate, and a roller having a diameter of 30 mm and a load of 200 gf was used. After pressure bonding, T-type peeling was performed using a tensile tester at a peeling speed of 50 mm/min;

(Measurement of arithmetic mean surface roughness Sa)

The surface roughness was measured by measuring the surface shape using a non-contact surface measuring system VertScan 2.0 (manufactured by Nippon Seisakusho Co., Ltd.) using an optical interference method, and the measurement region was set to a range of 250 μm × 188 μm. The measurement conditions were as follows:

Objective lens = 50 times, lens barrel = 0.5 × Body, continuous zoom lens = NoRelay, filter = 530white, measurement mode = Wave, field of view size = 640 × 480.

2.The porous film laminate according to claim 1, wherein the porous film is obtained by casting a polymer solution onto a base material and forming a film, and then introducing it into a coagulating liquid, and then, from the base material. The separate film peeled off is dried.

3.The porous film laminate according to claim 1, wherein the arithmetic mean surface roughness Sa is 0.4 μm or less.

4.The porous film laminate according to claim 1, wherein the arithmetic mean surface roughness Sa is 0.3 μm or less.

5.The porous film laminate according to claim 1, wherein the arithmetic mean surface roughness Sa is 0.2 μm or less.

6.The porous film laminate according to claim 1, wherein the gas permeability is from 0.5 to 20 seconds.

7.The porous film laminate according to claim 1, wherein the gas permeability is from 0.5 to 10 seconds.

8.The porous film laminate according to claim 1, wherein the value of the gas permeability is from 0.5 to 5 seconds.

9.The porous film laminate according to claim 2, wherein the polymer solution comprises 8 to 25% by weight of a polymer component, 5 to 50% by weight of a water-soluble polymer, 0 to 10% by weight of water, and A mixed solution of 30 to 82% by weight of a water-soluble polar solvent.

10.The porous film laminate according to any one of claims 1 to 9, wherein the porous film comprises a polyimide resin, a polyamideimide resin, and a polyetherimide resin. And at least one of polyether sulfone resins.

11.The porous film laminate according to any one of claims 1 to 9, wherein the nonwoven fabric base material is a polyolefin nonwoven fabric, a polyamide nonwoven fabric, or a partial nonwoven fabric is a poly A multilayer nonwoven fabric of an olefin-based nonwoven fabric or a polyamide-based nonwoven fabric.

12.The porous film laminate according to any one of claims 1 to 9, wherein an average open porosity (porosity) of the inside of the porous film is 30 to 80%.

13.The porous film laminate according to any one of claims 1 to 9, wherein the base material has a thickness of 10 to 500 μm.

14.The porous film laminate according to any one of claims 1 to 9, wherein the shape change rate of the porous film laminate in the following high-temperature placement test is within 5%:

(high temperature placement experiment)

The shape of the laminate integrated with the porous film was adjusted to a substantially rectangular shape of about 5 cm × 10 cm, and the lengths a1 and b1 of the substantially rectangular vertical sides were measured, and the temperature was adjusted to 140 ° C in a thermostatic chamber. After the laminate was placed for 30 minutes, the laminate was taken out, and after cooling to room temperature, the lengths a2 and b2 of the substantially rectangular vertical sides were measured, and the shape change ratio was calculated using the following formula.

Shape change rate (%) obtained from a1, a2 = {|a2-a1|/a1} × 100

Similarly, the shape change rate (%) is obtained from b1 and b2.

The average value of these values was taken as the shape change rate in the high temperature placement experiment.

15.The porous film laminate according to any one of claims 1 to 9, which is used as a filter for gas, liquid or solid; a separation membrane; a separator for a battery or a capacitor; or a part thereof.

16.A method for producing a porous film laminate for obtaining the porous film laminate according to any one of claims 1 to 9, the method comprising: a method of laminating the nonwoven fabric substrate and a porous film The glass transition temperature of the resin constituting the porous film is determined by hot melt bonding the melting point of the resin constituting the nonwoven fabric.

17.The method for producing a porous film laminate according to claim 16, wherein the porous film is obtained by casting a polymer solution onto a substrate and forming a film, and then introducing the solution into a coagulating liquid, and then The separate film peeled off from the base material is dried.

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(54)发明名称

多孔膜叠层体及其制造方法

(57)摘要

本发明的目的在于，提供一种多孔膜叠层体及其制造方法，所述多孔膜叠层体透气性优异，也没有针孔的产生，表面平滑性高，具有柔软性，而且操作性及成形加工性优异。所述多孔膜叠层体是在无纺布基体材料的至少一面上叠层有多孔膜的多孔膜叠层体而形成的，其中，所述多孔膜具备具有连通性的多个微孔，该微孔的平均孔径为0.01～10μm，多孔膜表面的算术平均表面粗糙度Sa为0.5μm以下，多孔膜叠层体的透气度的值为0.5～30秒，多孔膜叠层体的拉伸强度为4.0N/15mm以上，通过胶带剥离实验，所述基体材料和所述多孔膜没有发生界面剥离。

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1. 一种多孔膜叠层体，其在无纺布基体材料的至少一面上叠层有多孔膜，其中，

所述多孔膜具备具有连通性的多个微孔，该微孔的平均孔径为 0.01 ～ 10 μm，

用下述测定方法求出的多孔膜表面的算术平均表面粗糙度 Sa 为 0.5 μm 以下，

多孔膜叠层体的透气度的值为 0.5 ～ 30 秒，

多孔膜叠层体的拉伸强度为 4.0N/15mm 以上，

所述基体材料和所述多孔膜不会由于下述胶带剥离实验而发生界面剥离，

（胶带剥离实验）

在多孔膜叠层体的多孔膜表面上粘贴遮蔽胶带［株式会社寺冈制作所制造，商品名“film masking tape No.603(#25)”，宽度 24mm］，用直径 30mm、200gf 荷重的辊压粘后，使用拉伸试验机以 50mm/ 分钟的剥离速度进行 T 型剥离；

（算术平均表面粗糙度 Sa 的测定）

使用采用了光干涉法的非接触式表面计测系统 VertScan2.0（株式会社菱化 System 制造）测定表面形状，从而算出了表面粗糙度，测定区域设为 250 μm×188 μm 的范围，测定条件如下：

物镜＝50 倍、镜筒＝0.5×Body、连续变焦镜头＝NoRelay、滤波器＝530white、测定模式＝ Wave、视野尺寸＝ 640×480。

2. 如权利要求 1 所述的多孔膜叠层体，其中，所述多孔膜如下得到：将高分子溶液流延在基体材料上并形成膜状后，导入至凝固液中，然后，对从基体材料上剥离下来的单独的膜进行干燥。

3. 如权利要求 1 所述的多孔膜叠层体，其中，所述算术平均表面粗糙度 Sa 为 0.4 μm 以下。

4. 如权利要求 1 所述的多孔膜叠层体，其中，所述算术平均表面粗糙度 Sa 为 0.3 μm 以下。

5. 如权利要求 1 所述的多孔膜叠层体，其中，所述算术平均表面粗糙度 Sa 为 0.2 μm 以下。

6. 如权利要求 1 所述的多孔膜叠层体，其中，所述透气度的值为 0.5 ～ 20 秒。

7. 如权利要求 1 所述的多孔膜叠层体，其中，所述透气度的值为 0.5 ～ 10 秒。

8. 如权利要求 1 所述的多孔膜叠层体，其中，所述透气度的值为 0.5 ～ 5 秒。

9. 如权利要求 2 中所述的多孔膜叠层体，其中，所述高分子溶液是包括高分子成分 8 ～ 25 重量%、水溶性聚合物 5 ～ 50 重量%、水 0 ～ 10 重量%、及水溶性极性溶剂 30 ～ 82 重量%的混合溶液。

10. 如权利要求 1 ～ 9 中任一项所述的多孔膜叠层体，其中，所述多孔膜包含选自聚酰亚胺类树脂、聚酰胺酰亚胺类树脂、聚醚酰亚胺类树脂、及聚醚砜类树脂中的至少一种。

11. 如权利要求 1 ～ 9 中任一项所述的多孔膜叠层体，其中，所述无纺布基体材料为聚烯烃类无纺布、聚酰胺类无纺布、或部分无纺布为聚烯烃类无纺布、聚酰胺类无纺布的多层无纺布。

12. 如权利要求 1 ～ 9 中任一项所述的多孔膜叠层体，其中，所述多孔膜的内部的平均开孔率（孔隙率）为 30 ～ 80%。

13. 如权利要求 1 ～ 9 中任一项所述的多孔膜叠层体，其中，所述基体材料的厚度为

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10 ～ 500 μm。

14. 如权利要求 1 ～ 9 中任一项所述的多孔膜叠层体，其中，下述高温放置实验中所述多孔膜叠层体的形状变化率为 5% 以内：

（高温放置实验）

将与多孔膜一体化而成的叠层体的形状调整为约 5cm×10cm 的大致长方形，对所述大致长方形的垂直两边的长度 a1、b1 进行测定，向温度调整为 140℃的恒温槽内投入所述叠层体，放置 30 分钟后，取出所述叠层体，自然冷却至室温后，对所述大致长方形的垂直两边的长度 a2、b2 进行测定，使用下式计算形状变化率，

由 a1、a2 求出的形状变化率（%）＝ {|a2-a1|/a1}×100

同样地由 b1、b2 求出形状变化率（%），

将这些值的平均值作为本高温放置实验中的形状变化率。

15. 如权利要求 1 ～ 9 中任一项所述的多孔膜叠层体，其用作气体、液体、固体的过滤器；分离膜；电池或电容器的隔板；或它们的一部分。

16. 一种多孔膜叠层体的制造方法，其用于得到权利要求 1 ～ 9 中任一项所述多孔膜叠层体，该方法包括：所述无纺布基体材料和多孔膜的叠层方法通过热熔粘进行，构成多孔膜的树脂的玻璃化转变温度＞构成无纺布的树脂的熔点。

17. 权利要求 16 所述的多孔膜叠层体的制造方法，其中，所述多孔膜如下得到：将高分子溶液流延在基体材料上并形成膜状后，导入至凝固液中，然后，对从基体材料上剥离下来的单独的膜进行干燥。

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多孔膜叠层体及其制造方法

技术领域

[0001] 本发明涉及一种具有微孔和操作强度的多孔膜叠层体以及其制造方法。更详细而言，涉及一种在无纺布基体材料的至少一面上叠层了具备具有连通性的多个微孔的多孔膜而成的多孔膜叠层体及其制造方法。

背景技术

[0002] 作为具有微细孔的多孔膜，例如在专利文献 1 中公开有由酰胺酰亚胺类聚合物或酰亚胺类聚合物构成的多孔性膜。公开有一种多孔性膜，其特征特征在于，其该膜的厚度为 5 ～ 200 μm，微孔的平均孔径为 0.01 ～ 10 μm，孔隙率为 30 ～ 80%，表示微孔的连通性的透气度以格利值计为 0.2 ～ 29 秒 /100cc。

[0003] 另外，在专利文献 2 中公开有在无纺布上叠层有多孔膜的叠层体。公开有为在无纺布基体材料的至少一面上叠层有具备具有连通性的多个微孔、且该微孔的平均孔径为 0.01 ～ 10 μm 的多孔膜而成的多孔膜叠层体，且基体材料和多孔膜没有由于胶带剥离实验而发生界面剥离的多孔膜叠层体。

[0004] 并且，在专利文献 3 中，作为以无纺布为基体材料、且在无纺布的表面具有多孔膜的叠层体，公开有排水用分离膜。作为无纺布，可列举纤维素纤维、三乙酸纤维素纤维、聚酯纤维、聚丙烯纤维、聚乙烯纤维，作为最优选的组合，公开有在聚酯纤维制无纺布上具有聚偏氟乙烯 (PVDF) 的多孔膜而成的叠层体。

[0005] 另外，在专利文献 4 中公开有一种空气清洁器用过滤器，其叠层有超高分子量聚乙烯的烧结多孔片和聚酯无纺布。该过滤器的制造方法包括以下的阶段。

[0006] 1. 将超高分子量聚乙烯粉末填充于金属模具，并放入容器中，对容器内进行减压。

[0007] 2. 向容器内导入加热水蒸气，在 160℃ ×6 气压下加热 5 小时后，缓慢冷却。

[0008] 3. 将制成的圆柱状的烧结多孔体切削成片状后，进行拉伸，得到多孔片。

[0009] 4. 在多孔片上涂布热熔粘合剂，并贴合聚酯无纺布而进行层叠。

[0010] 现有技术文献

[0011] 专利文献

[0012] 专利文献 1 :日本专利第 3963765 号

[0013] 专利文献 2 :国际公开第 2007/097249 号

[0014] 专利文献 3 :日本特开 2010-221218 号公报

[0015] 专利文献 4 :日本特开 2006-257888 号公报

发明内容

[0016] 发明要解决的问题

[0017] 但是，专利文献 1 中记载的多孔膜的情况下，由于具有连通性好的微细孔，因此强度非常弱，在操作上需要注意，因此，存在在用途受到限制的问题。在进行膜的加工时，大多采用辊对辊操作，有时存在不能确保经得起该操作的强度等问题。

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[0018] 另外，专利文献 2 中记载的叠层体的情况下，由于以无纺布作为基体材料，在其上形成多孔膜，因此，可以利用无纺布确保充分的强度。但是，由于无纺布在结构上具有孔，因此，将高分子溶液在无纺布上流延成膜状而形成多孔膜的方法存在如下问题：高分子溶液浸透于无纺布的孔内，多孔膜表面成为凸凹，或无纺布部分露出，或产生针孔，或透气性变差。而且，存在如下问题：一般而言，无纺布具有的孔与多孔膜具有的孔相比明显较大，从微观上观察时非常不均匀，因此，高分子溶液浸透量因位置不同而有偏差，结果，多孔膜的厚度也有偏差，作为其特性的透气度也有偏差。

[0019] 专利文献 3 中记载的叠层体的情况下，在无纺布基体材料的表面具有多孔膜树脂层，多孔膜树脂层的一部分嵌入无纺布基体材料的内部，因此，存在与上述同样的问题。另外，存在如下问题：多孔膜表面的开孔度非常低，或在多孔膜树脂层内部具有存在巨大空隙的不匀质孔结构，因此，透气度仍然因位置不同而有偏差。

[0020] 另外，专利文献 4 记载的叠层体的情况下，存在如下问题：难以通过制造方法来减小孔径、以及减小表面开口率。另外，本过滤器的制造方法如上所述存在非常花费工夫的问题。另外，也存在如下问题：多孔片和聚酯无纺布通过热熔粘合剂而贴合，因此阻碍透气性。

[0021] 因此，需要透气性优异、不会产生针孔、表面平滑性高、具有柔软性、而且操作性及成形加工性优异的多孔膜叠层体及其制造方法。

[0022] 因此，本发明的目的在于，提供一种多孔膜叠层体及其制造方法，所述多孔膜叠层体透气性优异，不会产生针孔，表面平滑性高，具有柔软性，而且操作性及成形加工性优异。

[0023] 用于解决问题的技术方案

[0024] 因此，本发明人为了达到上述目的进行了潜心研究，结果发现：就使用一般的无纺布基体材料通过涂布制作的多孔膜叠层体而言，多孔膜表面为凸凹、无纺布部分露出、产生针孔，透气性变差，经不起使用。另外发现，通过利用热熔粘在无纺布基体材料的表面上叠层多孔膜，可得到透气性优异、不产生针孔、表面平滑性高、具有柔软性、而且操作性及成形加工性优异的多孔膜叠层体，完成了本发明。

[0025] 即，本发明提供一种多孔膜叠层体，其在无纺布基体材料的至少一面上叠层有多孔膜，其中，

[0026] 所述多孔膜具备具有连通性的多个微孔，该微孔的平均孔径为 0.01 ～ 10 μm，

[0027] 用下述测定方法求出的多孔膜表面的算术平均表面粗糙度 Sa 为 0.5 μm 以下，

[0028] 多孔膜叠层体的透气度的值为 0.5 ～ 30 秒，

[0029] 多孔膜叠层体的拉伸强度为 4.0N/15mm 以上，

[0030] 所述基体材料和所述多孔膜不会由于下述胶带剥离实验而发生界面剥离，

[0031] （胶带剥离实验）

[0032] 在多孔膜叠层体的多孔膜表面上粘贴遮蔽胶带〔株式会社寺冈制作所制造，商品名“film masking tape No.603(#25)”、宽度 24mm〕，用直径 30mm、200gf 荷重的辊压粘后，使用拉伸试验机以 50mm/ 分钟的剥离速度进行 T 型剥离；

[0033] （算术平均表面粗糙度 Sa 的测定）

[0034] 使用采用了光干涉法的非接触式表面计测系统 VertScan2.0（株式会社菱化 System 制造）测定表面形状，从而算出了表面粗糙度，测定区域设为 250 μm×188 μm 的范

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围，测定条件设为物镜＝50倍、镜筒＝0.5×Body、连续变焦镜头＝NoRelay、滤波器（wavelength filter）＝530white、测定模式＝Wave、视野尺寸＝640×480。

[0035] 所述算术平均表面粗糙度Sa优选为0.4μm以下。

[0036] 所述算术平均表面粗糙度Sa优选为0.3μm以下。

[0037] 所述算术平均表面粗糙度Sa优选为0.2μm以下。

[0038] 所述透气度的值优选为0.5～20秒。

[0039] 所述透气度的值优选为0.5～10秒。

[0040] 所述透气度的值优选为0.5～5秒。

[0041] 所述高分子溶液是包含高分子成分8～25重量%、水溶性聚合物5～50重量%、水0～10重量%、及水溶性极性溶剂30～82重量%的混合溶液。

[0042] 所述多孔膜包含选自聚酰亚胺类树脂、聚酰胺酰亚胺类树脂、聚醚酰亚胺类树脂、及聚醚砜类树脂中的至少一种。

[0043] 所述无纺布基体材料为聚烯烃类无纺布、聚酰胺类无纺布、或部分无纺布为聚烯烃类无纺布、聚酰胺类无纺布的多层无纺布。

[0044] 所述多孔膜的内部的平均开孔率（孔隙率）优选为30～80%。

[0045] 所述基体材料的厚度优选为10～500μm。

[0046] 下述高温放置实验中所述多孔膜叠层体的形状变化率为5%以内：

[0047] （高温放置实验）

[0048] 将与多孔膜一体化而成的叠层体的形状调整为约5cm×10cm的大致长方形，对所述大致长方形的垂直两边的长度a1、b1进行测定，向温度调整为140℃的恒温槽内投入所述叠层体，放置30分钟后，取出所述叠层体，自然冷却至室温后，对所述大致长方形的垂直的两边的长度a2、b2进行测定，使用下式计算形状变化率，

[0049] 由a1、a2求出形状变化率（%）＝{|a2-a1|/a1}×100

[0050] 同样地由b1、b2求出的形状变化率（%），将这些值的平均值作为本高温放置实验中的形状变化率。

[0051] 所述多孔膜叠层体优选用作气体、液体、固体的过滤器；分离膜；电池或电容器的隔板；或它们的一部分。

[0052] 所述无纺布基体材料和多孔膜的叠层方法通过热熔粘进行，构成多孔膜的树脂的玻璃化转变温度＞构成无纺布的树脂的熔点。

[0053] 所述多孔膜如下得到：将高分子溶液流延在基体材料上并形成膜状后，导入至凝固液中，然后，对从基体材料上剥离下来的单独的膜进行干燥。

[0054] 发明的效果

[0055] 本发明的多孔膜叠层体具备具有多个微孔的多孔膜，因此，柔软性优异，同时透气性优异，不产生针孔，表面平滑性高，而且该多孔膜衬棱褶于基体材料上，因此，即使在具有空隙率的情况下，也可以发挥充分的强度，耐折性、操作性非常优异。根据本发明，可以用简易的方法稳定地制造具有上述特性、膜质匀质的多孔膜叠层体。如上所述得到的多孔膜叠层体由于具有上述特性，因此，可以用作气体或液体或固体的过滤器及分离膜、电池用及电容器的隔板、或它们的一部分。例如，可以作为液体分离膜、固体分离膜、气体分离膜、或它们的一部分来使用。

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[0056] 具体而言，可以列举：袋式过滤器、除尘过滤器、空调过滤器、汽车的过滤器（空气净化器、油净化器、室内净化过滤器、外气吸入过滤器等）等。此外，可以作为电路用基板、电池用隔板、电磁波屏蔽或电磁波吸收体等电磁波控制材料、电解电容器、低介电常数材料、缓冲材料、油墨显像片、试纸、绝缘材料、隔热材料、细胞培养基体材料、放射线遮蔽垫层用材料、吸油材料等广范围的基板材料利用。

附图说明

[0057] 图 1 是制造例 1 中制作的多孔膜表面的电子显微镜照片（SEM 照片）。

[0058] 图 2 是制造例 2 中制作的多孔膜表面的电子显微镜照片（SEM 照片）。

具体实施方式

[0059] 对本申请发明的多孔膜叠层体进行详细地说明。

[0060] ［胶带剥离实验］

[0061] 本发明的多孔膜叠层体中所述基体材料和所述多孔膜不会由于所述胶带剥离实验而发生界面剥离。

[0062] 所述胶带剥离实验如下进行：在多孔膜叠层体的多孔膜表面粘贴 24mm 宽度的株式会社寺冈制作所制造的遮蔽胶带［膜遮蔽胶带 No. 603(#25)］、用直径 30mm、200gf 荷重的辊进行了压粘后、使用拉伸试验机以 50mm/ 分钟的剥离速度进行 T 型剥离。即，所述基体材料和所述多孔膜以不会在上述胶带剥离实验中发生界面剥离的程度的层间密合强度进行了叠层。

[0063] 如上所述，本发明的多孔膜叠层体具有所述基体材料和所述多孔膜以特定的层间密合强度直接进行了叠层的结构，因此，具有柔软性和优异的空孔特性，另一方面，具有适当的刚性，从而操作性提高。而且，可以广泛地选择构成多孔膜的高分子成分，因此，具有可以作为多种领域的材料使用的优点。所述基体材料和所述多孔膜的层间密合强度可以通过适当设定构成各层原料的种类或界面的物理特性来调整。

[0064] ［无纺布基体材料］

[0065] 本发明的多孔膜叠层体具有在无纺布基体材料的至少一面上叠层有多孔膜的结构。

[0066] 所述无纺布基体材料可以为单层、也可以为由相同或不同的原料构成的多层。所述多层可以为根据需要使用粘接剂等进行叠层多层无纺布、或在制造阶段进行了叠层的叠层膜，也可以实施涂层、蒸镀、溅射等处理而得到。

[0067] 可以对所述无纺布基体材料实施粗化处理、易粘接处理、防静电处理、喷沙处理（砂垫层处理）、电晕放电处理、等离子体处理、化学蚀刻处理、水垫层处理、火焰处理、酸处理、碱处理、氧化处理、紫外线照射处理、硅烷偶联剂处理等表面处理。

[0068] 另外，也可以组合多个上述表面处理而进行。例如，可以利用对所述基体材料首先实施电晕放电处理、等离子体处理、火焰处理、酸处理、碱处理、氧化处理、紫外线照射处理等任一种处理，然后，进行硅烷偶联剂处理的方法等。根据所述基体材料的种类不同，上述方法有时与硅烷偶联剂的单独处理相比，处理得到强化。作为所述硅烷偶联剂，可以列举信越化学工业社制造或 Japan energy 社（ジャパンエナジー社）制产品。

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[0069] 所述无纺布基体材料的厚度例如为 10 ～ 500 μm，更优选为 10 ～ 300 μm，更优选为 10 ～ 200 μm，进一步更优选为 10 ～ 100 μm。厚度过薄时，难以操作，另一方面，厚度过厚时，有时柔软性降低。

[0070] 从强度保持和柔软性的观点出发，所述无纺布基体材料的单位面积重量例如为 2 ～ 250g/m^2，更优选为 2 ～ 150g/m^2，更优选为 2 ～ 100g/m^2，进一步更优选为 2 ～ 50g/m^2。

[0071] 从确保适当的透气性的观点出发，所述无纺布基体材料的密度例如为 0.05 ～ 0.90g/cm^3，更优选为 0.10 ～ 0.80g/cm^3，进一步更优选为 0.15 ～ 0.70g/cm^3。

[0072] 所述无纺布基体材料的透气度优选为 30 秒以下，更优选为 20 秒以下，进一步优选为 10 秒以下。需要说明的是，透气度的测定极限为 0.1 秒左右，但在所述基体材料中，也包括其透气度低于 0.1 秒的基体材料。

[0073] 从提高所述无纺布基体材料和所述多孔膜之间的密合性的观点出发，优选对所述无纺布基体材料的叠层所述多孔膜一侧的表面实施例如喷沙处理（砂垫层处理）、电晕放电处理、酸处理、碱处理、氧化处理、紫外线照射处理、等离子体处理、化学蚀刻处理、水垫层处理、火焰处理、硅烷偶联剂处理等适当的表面处理。作为所述硅烷偶联剂，可以使用上述中例示的硅烷偶联剂。所述表面处理可以组合实施多个，优选根据无纺布基体材料的不同，组合实施所述硅烷偶联剂处理和其它处理。

[0074] （无纺布）

[0075] 无纺布是指下述概念：使纤维排列、通过粘接剂或纤维自身的熔粘力或相互缠绕的力使纤维相互接合而得到的片状物质，也包括所谓的纸。所述无纺布可以用抄纸法、熔喷法、纺粘法、针刺法、电子纺丝法等一般已知的方法来制造。

[0076] 构成无纺布的基体材料的树脂的种类可以根据熔点或耐药品性等进行选择。作为所述无纺布，可以利用市售产品。例如，可以获得日本 VILENE 社制的聚烯烃无纺布（商品名“FT-330N”）、广濑制纸社制造的聚烯烃无纺布（商品名“06HOP-2”、“06HOP-4”、“HOP-10H”、“HOP-30H”、“HOP-60HCF”、“HOP-80H”）等。此外，可以获得广濑制纸社制造的两层无纺布（商品名“05EP-50”、“15EP-50”）等。

[0077] 作为无纺布，优选（构成多孔膜的树脂的玻璃化转变温度）＞（构成无纺布的树脂的熔点），只要是如上所述的无纺布，就没有特别限制。优选使用聚烯烃无纺布、聚酯无纺布、聚酰胺无纺布等，但也可以为它们的两层无纺布、多层无纺布。更优选可以利用选自聚烯烃无纺布、两层无纺布中的至少一种。

[0078] 目前，作为一般可获得的无纺布，大多是由聚烯烃类树脂（聚乙烯、聚丙烯）构成的无纺布，此外，也包括两层无纺布（例如聚丙烯 / 聚酯类树脂的叠层品）。这些无纺布有多种，成本也廉价，因此优选。

[0079] 由于使用所述的无纺布作为所述无纺布基体材料，因此，具有如下优点：通过利用热熔粘等方法将多孔膜叠层在该基体材料表面，由此可以以优异的层间密合强度进行叠层。另外，具有柔软性和优异的空孔特性，另一方面，具有适当的刚性，因此，可以得到提高操作性的效果。

[0080] [多孔膜]

[0081] 所述多孔膜的主要成分例如由高分子成分构成。作为所述高分子成分，只要可以形成所述多孔膜，就没有特别限定，可以根据构成所述多孔膜的材料适当进行选择。作为所

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述高分子成分，可列举例如：聚酰亚胺类树脂、聚酰胺酰亚胺类树脂、聚醚砜类树脂、聚醚酰亚胺类树脂、聚碳酸酯类树脂、聚苯硫醚类树脂、液晶性聚酯类树脂、芳香族聚酰胺类树脂、聚酰胺类树脂、聚苯并噁唑类树脂、聚苯并咪唑类树脂、聚苯并噻唑类树脂、聚砜类树脂、纤维素类树脂、丙烯酸类树脂等塑料等。这些高分子成分可以单独使用，或两种以上混合使用。另外，上述树脂的共聚物（接枝聚合体、嵌段共聚物、无规共聚物等）可以单独使用或组合使用。进一步，也可以使用主链或侧链上含有上述树脂的骨架（聚合物链）的聚合物。作为这种聚合物的具体例，可列举聚硅氧烷和主链上含有聚酰亚胺骨架且含有聚硅氧烷的聚酰亚胺等。

[0082] 其中，作为所述高分子成分的优选实例，可列举具有耐热性、耐药品性、电特性优异且以聚酰胺酰亚胺类树脂或聚酰亚胺类树脂为主要成分的物质。聚酰胺酰亚胺类树脂通常可以如下制造：利用偏苯三酸酐和二异氰酸酯的反应、或偏苯三酸酐氯化物和二胺的反应发生聚合，然后，进行酰亚胺化。聚酰亚胺类树脂可以通过例如利用四羧酸成分和二胺成分的反应得到聚酰胺酸、对其进一步进行酰亚胺化来制造。在由聚酰亚胺类树脂构成多孔膜的情况下，进行酰亚胺化时，溶解性变差，因此，大多首先在聚酰胺酸的阶段形成多孔膜后进行酰亚胺化（热酰亚胺化、化学酰亚胺化等）。作为所述高分子成分的其它优选的实例，可列举以聚醚酰亚胺类树脂、聚醚砜类树脂为主要成分的物质。

[0083] 作为树脂制成且具有耐热性的物质，也已知有聚四氟乙烯（PTFE）类多孔膜，其也可以同样地使用。

[0084] 所述多孔膜的厚度例如为1～100μm，更优选为1～50μm，更优选为1～20μm，进一步更优选为1～10μm。厚度过薄时，难以稳定地制造，另一方面，在厚度过厚时，存在透气性变差的问题。

[0085] 所述多孔膜具备具有连通性的多个微孔，该微孔的平均孔径（＝膜内部的平均孔径）为0.01～10μm，更优选为0.05～5μm，进一步优选为0.1～2μm。平均孔径在上述范围外时，在难以得到满足用途的所期望的效果方面，空孔特性差，例如尺寸过小时，有时引起透气性降低、缓冲性能降低、油墨浸透性降低、绝缘性或隔热性降低等，在尺寸过大时，有时过滤性能降低，或油墨扩散，难以形成微细的布线。

[0086] 所述多孔膜内部的平均开孔率（孔隙率）例如为30～80%，优选为40～80%，进一步优选为45～80%。在孔隙率在上述范围外时，难以得到满足用途的所期望的空孔特性，孔隙率过低时，有时透气性降低，或介电常数升高，或缓冲性能降低，或油墨不浸透，或隔热性降低，即使填充功能性材料，也不能得到所期望的效果，孔隙率过高时，有可能强度或耐折性差。

[0087] 所述多孔膜表面的开孔率（表面开孔率）例如为48%以上（例如48～80%），更优选为60～80%左右。表面开孔率过低时，产生透过性能不充分的情况，此外，即使在空孔中填充功能性材料，有时也不能充分地发挥其功能，当表面开孔率过高时，强度、耐折性容易降低。

[0088] 所述多孔膜表面的表面粗糙度（算术平均表面粗糙度Sa）为0.5μm以下，优选为0.4μm以下，更优选为0.3μm以下，进一步优选为0.2μm以下。表面粗糙度过大时，有时平滑性丧失，在过滤例如液体时，容易粘付气泡，从而该部分失去作为过滤器的功能。另外，通过在过滤时捕捉（或捕集）的微粒子不匀质地被卡住，有时过滤的效率降低，或过滤速度

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变得不稳定。需要说明的是，表面粗糙度（算术平均表面粗糙度 Sa）可以通过利用使用光干涉法的非接触式表面计测系统测定表面形状、基于实施例记载的方法求出。

[0089] 所述多孔膜在所述无纺布基体材料的至少一面上形成即可，也可以在两面形成。

[0090] 可以对所述多孔膜实施赋予耐药品性的处理。其结果，对多孔膜叠层体赋予耐药品性，在多孔膜叠层体的多种利用方式中，在与溶剂、酸、碱等接触的情况下，在可以避免层间剥离、溶胀、溶解、变质等不良情况方面是有利的。作为赋予耐药品性的处理，可列举通过热、紫外线、可见光线、电子束、放射线等物理处理；对多孔膜包覆耐药品性高分子等化学处理等。

[0091] 所述多孔膜可以由耐药品性高分子包覆。这样的多孔膜叠层体例如在多孔膜的表面或内部的微孔表面形成耐药品性的被膜，能够构成具有耐药品性的叠层体。在此，所谓药品，可列举作为使构成现有的多孔性膜的树脂溶解、溶胀、收缩、分解，且使作为多孔性膜的功能降低的物质而公知的药品，根据多孔膜及基体材料的构成树脂的种类不同而不同不能一概而论，但作为这样的药品的具体例，可列举：二甲基亚砜（DMSO）、N,N-二甲基甲酰胺（DMF）、N,N-二甲基乙酰胺（DMAc）、N-甲基-2-吡咯烷酮（NMP）、2-吡咯烷酮、环己酮、丙酮、乙酸甲酯、乙酸乙酯、乳酸乙酯、乙腈、二氯甲烷、氯仿、四氯乙烷、四氢呋喃（THF）等强极性溶剂；氢氧化钠、氢氧化钾、氢氧化钙、碳酸钠、碳酸钾等无机盐；三乙基胺等胺类；溶解有铵等碱的水溶液或有机溶剂等碱溶液；氯化氢、硫酸、硝酸等无机酸；溶解有乙酸、苯二甲酸等具有羧酸的有机酸等酸水溶液或有机溶剂等酸性溶液；及它们的混合物等。

[0092] 所述耐药品性高分子化合物可以具有对强极性溶剂、碱、酸等药品的优异耐性，可列举例如：苯酚类树脂、二甲苯类树脂、脲类树脂、三聚氰胺类树脂、苯并胍胺类树脂、苯并噁嗪类树脂、醇酸类树脂、三嗪类树脂、呋喃类树脂、不饱和聚酯、环氧类树脂、硅树脂、聚氨酯类树脂、聚酰亚胺类树脂等热固化性树脂或光固化性树脂；聚乙烯醇、乙酸纤维素类树脂、聚丙烯类树脂、氟树脂、苯二甲酸类树脂、马来酸类树脂、饱和聚酯、乙烯-乙烯醇共聚物、壳多糖、壳聚糖等热增塑性树脂等。这些高分子化合物可以使用一种，或两种以上混合使用。另外，高分子化合物可以为共聚物，也可以为接枝聚合物。

[0093] 由如上所述的耐药品性高分子包覆的多孔膜构成的多孔膜叠层体即使在与上述强极性溶剂、碱、酸等药品接触的情况下，也完全不会产生多孔膜溶解、或溶胀而变形等变质，或可以将变质控制到对使用目的或用途没有影响的程度。例如，在多孔膜和药品接触时间短的用途中，只要赋予在该时间内不会变质的程度的耐药品性即可。

[0094] 需要说明的是，所述耐药品性高分子化合物大多同时具有耐热性，因此，所述多孔膜与用所述耐药品性高分子化合物对其进行包覆之前相比，耐热性降低的可能性小。

[0095] 可以在构成所述多孔膜的微孔中填充功能性材料。作为所述功能性材料，可列举例如：铁氧体微粒子、金属微粒子（包括金属氧化物微粒子等含金属的微粒子）、炭黑、碳纳米管、富勒烯、氧化钛、钛酸钡等。

[0096] 所述功能性材料的填充条件没有特别限定，优选通过以亚微米粒子～微米单位的分解能进行填充，从而对多孔膜本来具有的空孔特性的损失进行抑制，而且可以提高易于调整功能性材料的填充量等处理性、操作性。填充功能性材料的情况下，多孔膜的微孔过小时，难以填充功能性材料，当多孔膜的微孔过大时，难以将功能性材料的填充控制在亚微米粒子～微米单位，因此，微孔的平均孔径优选在上述数值范围内，膜表面的最大孔径优选为

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15 μm 以下。

[0097] [无纺布基体材料和多孔膜的组合]

[0098] 从所述无纺布基体材料与所述多孔膜之间的密合性的观点出发，作为构成所述无纺布基体材料和所述多孔膜的成分，优选组合使用可发挥良好的密合性（亲和性）的材料。具体而言，所述多孔膜含有选自聚酰亚胺类树脂、聚酰胺酰亚胺类树脂、聚醚酰亚胺类树脂、聚四氟乙烯（PTFE）类多孔膜及聚醚砜类树脂中的至少一种，所述无纺布基体材料优选使用聚烯烃无纺布、聚酯无纺布、聚酰胺无纺布等，优选含有选自它们的两层无纺布、多层无纺布中的至少一种。

[0099] 另外，所述多孔膜含有选自聚酰亚胺类树脂、聚酰胺酰亚胺类树脂、聚醚酰亚胺类树脂及聚醚砜类树脂中的至少一种，所述无纺布基体材料优选使用聚烯烃无纺布、聚酯无纺布等，更优选含有选自这些两层无纺布、多层无纺布中的至少一种。

[0100] 另外，所述多孔膜含有选自聚酰亚胺类树脂、聚酰胺酰亚胺类树脂、聚醚酰亚胺类树脂及聚醚砜类树脂中的至少一种，所述无纺布基体材料优选使用聚烯烃无纺布、聚酯无纺布等，进一步优选含有选自这些两层无纺布中的至少一种。

[0101] 所述多孔膜含有上述树脂的情况下，其含量相对于所述多孔膜整体例如为 80 ～ 100 重量%，优选为 90 ～ 100 重量%，更优选为 95 ～ 100 重量%。

[0102] 所述无纺布基体材料含有上述树脂或纤维的情况下，其含量相对于所述无纺布基体材料整体例如为 60 ～ 100 重量%，优选为 80 ～ 100 重量%，更优选为 90 ～ 100 重量%。

[0103] [多孔膜叠层体]

[0104] 本发明的多孔膜叠层体具有所述无纺布基体材料和所述多孔膜以优异的密合性进行了一体化的结构，所以，具有较高的机械强度。因此，从在多孔膜叠层体的总厚度例如低于 100 μm 左右较薄的情况下，仍可以发挥充分的强度这一点而言是有利的。

[0105] 本发明的多孔膜叠层体的优选形态为由多孔膜对所述无纺布基体材料的一面或两面进行包覆、且具备具有连通性的多个微孔、该微孔的平均孔径为 0.01 ～ 10 μm 的具有多孔膜的多孔膜叠层体，该多孔膜的厚度为 1 ～ 100 μm，孔隙率为 30 ～ 80%，无纺布基体材料的厚度为 10 ～ 500 μm。如上所述的多孔膜叠层体可以通过对构成多孔膜及基体材料的材料或厚度、制造条件等进行适当设定来制造。

[0106] 所述多孔膜叠层体的透气度的值为 0.5 ～ 30 秒，优选为 0.5 ～ 20 秒，更优选为 0.5 ～ 10 秒，进一步更优选为 0.5 ～ 5 秒。由于透气度为上述范围，因此，可以保持较高的透气性，多孔膜叠层体可以用于气体或液体的过滤器、电池用或电容器的隔板等。需要说明的是，多孔膜叠层体的透气度的值可以使用格利式透气度测定仪 B 型、以 JIS P8117 为基准，用实施例记载的方法进行测定。

[0107] 所述多孔膜叠层体的拉伸强度为 4.0N/15mm 以上，优选为 5.0N/15mm 以上，更优选为 6.0N/15mm 以上，进一步优选为 8.0N/15mm 以上。由于拉伸强度为一定值以上，因此，可以保持多孔膜叠层体的强度和柔软性，操作性好。需要说明的是，多孔膜叠层体的拉伸强度可以使用万能拉伸试验机、用实施例记载的方法进行测定。

[0108] 下述高温放置实验中多孔膜叠层体的形状变化率例如为 5% 以内，优选为 4% 以内，更优选为 3% 以内。形状变化率为上述范围内时，即使在高温下也保持形状，不易引起电极的短路，其结果，安全性得到提高，多孔膜叠层体可以用于电池用或电容器的隔板等。

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[0109] （高温放置实验）

[0110] 将与多孔膜一体化而成的叠层体的形状调整为约 5cm×10cm 的大致长方形，对所述大致长方形的垂直的两边的长度 a1、b1 进行测定，向温度调整为 140℃的恒温槽内投入所述叠层体，放置 30 分钟后，取出所述叠层体，自然冷却至室温后，对所述大致长方形的垂直两边的长度 a2、b2 进行测定，使用下述式计算形状变化率。

[0111] 由 a1、a2 求出形状变化率（%）＝{|a2-a1|/a1}×100

[0112] 同样地由 b1、b2 求出形状变化率（%），将这些值的平均值作为本高温放置实验中的形状变化率。

[0113] 本发明的多孔膜叠层体在基体材料的至少一面上叠层多孔膜即可，也可以在基体材料的两面上具有多孔膜。另外，可以在所述多孔膜填充有功能性材料，在具有多层多孔膜的情况下，可以填充相同或不同种类的功能性材料。

[0114] 本发明的多孔膜叠层体通过直接利用所述多孔膜具有的空孔特、或利用功能性材料对所述多孔膜的空孔进行功能化，可以作为过滤器、分离膜、隔板、或作为它们的一部分使用。

[0115] 进而，为了对本发明的多孔膜叠层体赋予所期望的特性，可以根据需要实施热处理或被膜形成处理。

[0116] 本发明的多孔膜叠层体具有上述结构，因此，可以在广泛的领域中适用于多种用途。特别适合作为过滤器、分离膜、隔板、或作为它们的一部分使用，例如，可以作为液体分离膜、固体分离膜、气体分离膜、或它们的一部分使用。此外，可以作为电路用基板、放热材料（散热片、放热板等）、电池用隔板、电磁波屏蔽或电磁波吸收体等电磁波控制材料、电解电容器、低介电常数材料、缓冲材料、油墨显像片、试纸、绝缘材料、隔热材料、细胞培养基体材料、放射线遮蔽垫层用材料、吸油材料等宽范围的基板材料使用。

[0117] 具体而言，适于袋式过滤器、集尘过滤器、空调过滤器、汽车的过滤器（空气洁净器、油洁净器、室内洁净过滤器、外气吸入过滤器等）等。

[0118] 此外，可以作为电路用基板、放热材料（散热片、放热板等）、电池用隔板、电磁波屏蔽或电磁波吸收体等电磁波控制材料、电解电容器、低介电常数材料、缓冲材料、油墨显像片、试纸、绝缘材料、隔热材料、细胞培养基体材料、放射线遮蔽垫层用材料、吸油材料等宽范围的基板材料使用。

[0119] 无纺布自身也可以在过滤器、分离膜、隔板中使用，但即使其孔径为最小，也不能捕集数十 μm 以上微细的物质。

[0120] 本发明的多孔膜叠层体可以优选作为过滤器、分离膜、隔板使用。为了在无纺布基体材料上形成多孔膜，基体材料可以确保充分的强度。由于多孔性膜的孔隙率高，因此，就多孔性单独的膜而言可以用于不要求充分强度的用途。作为使用有本发明的多孔膜叠层体的过滤器，可列举例如水等水溶液或溶剂的过滤或空气等气体的过滤用过滤器；可以除去亚微米粒子以上的异物的废水处理用过滤器；红细胞的分离等血液等过滤用过滤器；从空气中分离粉尘、花粉、霉菌、螨的尸体等空调机用过滤器等。本发明的多孔膜叠层体另外也可以用作空调机中使用的氧富化膜用的基体材料。

[0121] 此外，可列举例如作为喷墨打印机用过滤器进行使用等。就喷墨打印机而言，为了使油墨从喷墨头的微细的孔不堵塞地稳定地喷出，根据目的可使用各种过滤器。根据制造

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者而使用各种名称，作为其实例，可列举：小皿过滤器、油墨填充过滤器、主体过滤器、喷头保护用末端过滤器（Last Chance Filter）、墨囊（过滤墨囊）用过滤器、气泡抑制过滤器、直通式过滤器等。

[0122] 此外，可列举例如作为在医疗系统中使用的过滤器使用等。在医疗系统中，为了血液的冻结保存、生殖细胞（精子或卵子）、培养的细胞、生物学的样品或原料的冻结保存，可使用液体氮等。在这样的用途中使用的液体氮等需要除去病毒等异物。由于病毒为约0.1～0.2μm左右，因此，通过用本发明的多孔膜叠层体对液体氮进行过滤，可以除去病毒。

[0123] 另外，本发明的多孔膜叠层体也可以作为试纸使用。试纸可以广泛的用于实验用、医疗用等，可以列举例如：pH试纸（例如石蕊试纸）、水质检查试纸（例如离子试纸）、油试纸、水分试纸、臭氧试纸、尿试纸、血液试纸等。所述离子试纸可以定性或定量地对金属离子或阴离子进行研究。尿试纸可以定量地对尿糖、尿蛋白、潜血等进行研究。血液试纸可以定量地对血糖值等进行研究。这些试纸的测定方法简易，因此，使用机会逐年增加。

[0124] 本发明的多孔膜叠层体由于多孔膜与基体材料密合，因此，操作上可以确保充分的强度。另外，多孔膜可以对判定中使用的指示剂进行吸附，因此，是优选的介质。另外，可以保持水等溶剂、尿、血液等样品，因此，优选用于这些用途中。

[0125] 本发明的多孔膜叠层体另外可以优选作为电池用隔板使用。电池用隔板分离正负极，同时，需要电解液的保持性优异、且离子导电性良好。另外，要求具有耐热性、柔软性、强度等各种特性。根据本发明的多孔膜叠层体，可以均衡地发挥这些特性，因此，作为各种电池用隔板是非常有用的。

[0126] 为了提高电池用隔板在过去的火灾或汽车用用途或工业用用途中的安全性而要求高耐热性，从该方面考虑，本发明的多孔膜叠层体也是有用的。

[0127] 就本发明的多孔膜叠层体而言，可以使用对水具有耐性的无纺布作为基体材料，因此，可以防止无纺布基体材料的溶胀。

[0128] ［多孔膜叠层体的制造方法］

[0129] 本发明的多孔膜叠层体可通过制造多孔膜后，使所述多孔膜利用热熔粘的方法叠层于所述无纺布的至少一面上来制造，所述多孔膜可以通过例如将高分子溶液流延在基体材料上并形成膜状后、并与凝固液接触从而进行多孔化的方法来制造，以下详细地进行说明。

[0130] （多孔单独的膜的制造方法）

[0131] 所述多孔膜可以通过如下方法制造：例如在膜基体材料上将高分子溶液流延成膜状、并与凝固液接触从而进行多孔化，然后，将其从膜基体材料剥离、在对其进行干燥而得到多孔膜。作为与凝固液接触并进行多孔化的方法，可以利用如下方法：例如湿式相转换法得到膜的方法（例如参照日本特开2001-145826号公报）、干式相转换法（例如参照国际公开公报WO98/25997号小册子等）及使用溶剂置换速度调整材料的方法（例如参照日本特开2000-319442号公报、日本特开2001-67643号公报）等公知的方法。

[0132] 所述多孔膜也可以通过以聚烯烃类多孔膜为代表的树脂多孔膜的制造方法来制造。对树脂多孔膜的制造方法进行大致区分时，可列举在萃取工序中进行多孔化的湿式法和在拉伸工序中进行多孔化的干式法这两种方法。作为前者方法，可列举例如日本特开昭

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58-59072 号公报中记载的方法。在日本特开昭 58-59072 号公报中公开有将增塑剂等与树脂同时混炼并熔融挤出后、在萃取槽中对增塑剂等进行萃取并进行多孔化的制造方法。

[0133] 另一方面，作为后者方法，可列举例如日本特开昭 62-121737 号公报记载的方法。在日本特开昭 62-121737 号公报中，公开有在熔融挤出的原膜上形成层状晶体，通过纵向单轴拉伸使层状晶之间开裂并进行多孔化的制造方法。通过该方法，与湿式法不同，不需要萃取工序，可以将工序简单化。另外，作为使用有干式法的双轴拉伸多孔膜的制造方法，可列举国际公开第 2007/098339 号中记载的方法。在国际公开第 2007/098339 号中公开有将通过公知的纵向单轴拉伸得到的多孔膜一边利用热沿纵向松弛、一边进行横向拉伸的技术。

[0134] 聚四氟乙烯 (PTFE) 类多孔膜也可以用与聚烯烃类多孔膜同样的方法来制造。

[0135] 作为进行流延的高分子溶液，可以使用例如包括构成多孔膜的材料即高分子成分、水溶性聚合物、水溶性极性溶剂、根据需要的水的混合溶液等。

[0136] 作为成为所述构成多孔膜的材料即高分子成分，优选在水溶性极性溶剂中具有溶解性、且可利用相转换法形成膜的物质，可以利用上述例示物质中一种或混合利用两种以上。另外，可以使用该高分子成分的单体成分（原料）或其低聚物、酰亚胺化或环化等之前的前体等来代替所述构成多孔膜的高分子成分。

[0137] 向进行流延的高分子溶液中添加水溶性聚合物或水可有效的将膜结构多孔化为海绵状。作为所述水溶性聚合物，可列举例如：聚乙二醇、聚乙烯基吡咯烷酮、聚环氧乙烷、聚乙烯醇、聚丙烯酸、多糖类等或其衍生物、以及它们的混合物等。其中，在抑制膜内部中的空隙的形成、可以提高膜的机械强度方面，优选聚乙烯基吡咯烷酮。这些水溶性聚合物可以单独使用，或组合使用两种以上。从多孔化的观点出发，所述水溶性聚合物的分子量为 200 以上即可，优选为 300 以上，特别更优选为 400 以上（例如 400 ～ 20 万左右），特别是，分子量可以为 1000 以上。通过水的添加，可以调整空隙直径，例如增加聚合物溶液中水的添加量时，可以使空隙直径增大。

[0138] 所述水溶性聚合物对将膜结构做成海绵状非常有效，通过对所述水溶性聚合物的种类和量进行变更，可以得到多种结构。因此，在赋予期望的空孔特性的目的下，非常优选所述水溶性聚合物作为形成多孔膜时的添加剂使用。另一方面，所述水溶性聚合物最终不构成多孔膜，而是应该除去的不需要的成分。在利用湿式相转换法的方法中，所述水溶性聚合物在浸渍于水等凝固液而进行相转换的工序中很容易被清洗除去。与此相对，在干式相转换法中，不构成多孔膜的成分（不需要的成分）通过加热被除去，水溶性聚合物通过加热除去没有利用湿式相转换法的情况那么容易。如上所述，与利用干式层转换法的情况相比，利用湿式相转换法的制造方法在可以容易地制造具有所期望的空孔特性的多孔膜方面是有利的。

[0139] 作为所述水溶性极性溶剂，可列举例如：二甲基亚砜、N,N- 二甲基甲酰胺、N,N- 二甲基乙酰胺 (DMAc)、N- 甲基 -2- 吡咯烷酮 (NMP)、2- 吡咯烷酮及它们的混合物等，且根据作为所述高分子成分使用的树脂的化学骨架来使用具有溶解性的物质（高分子成分的良溶剂）。

[0140] 作为进行流延的聚合物溶液，优选包括构成多孔性膜的材料即高分子成分 8 ～ 25 重量%、水溶性聚合物 5 ～ 50 重量%、水 0 ～ 10 重量%、水溶性极性溶剂 30 ～ 82 重量%

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的混合溶液等。此时，高分子成分的浓度过低时，多孔膜的厚度变得不充分，或难以得到所期望的空孔特性。另外，高分子成分的浓度过高时，存在孔隙率变小的倾向。水溶性聚合物是为了使膜内部成为匀质的海绵状的多孔结构而添加的，但浓度过低时，在膜内部产生超过 10 μm 的巨大空隙，从而均一性降低。另外，水溶性聚合物的浓度过高时，溶解性变差，此外，在其超过 50 重量%的情况下，容易产生膜强度变弱等不良情况。水的添加量可以用于空隙径的调整，可以通过增加添加量而增大直径。

[0141] 在对高分子溶液进行流延而成为膜状时，优选将该膜在相对湿度 70 ～ 100%、温度 15 ～ 90℃的氛围下保持 0.2 ～ 15 分钟后，导入由高分子成分的非溶剂构成的凝固液中。通过将流延后的膜状物置于上述条件，可以使多孔膜成为均质且连通性高的状态。作为该理由，是因为：通过置于加湿条件下，水分从膜表面向内部侵入，有效地促进高分子溶液的相分离。特别优选的条件为相对湿度 90 ～ 100%、温度 30 ～ 80℃；以及相对湿度约 100%（例如 95 ～ 100%）、温度 40 ～ 70℃。空气中的水分量比上述条件少时，有时产生表面开孔率不充分的不良情况。

[0142] 按照所述多孔膜的制造方法，例如可以容易地成形具备具有连通性的多个微孔、且该微孔的平均孔径为 0.01 ～ 10 μm 的多孔膜。如上所述，构成本发明中的多孔膜的多孔膜微孔的直径、孔隙率、开孔率可以通过对高分子溶液构成成分的种类或量、水的使用量、流延时的湿度、温度及时间等进行适当选择而调整为所期望的值。

[0143] 作为用于相转换法的凝固液，只要是使高分子成分凝固的溶剂即可，可以根据作为高分子成分使用的高分子的种类进行适当选择，例如，只要是使聚酰胺酰亚胺类树脂或聚酰胺酸凝固的溶剂即可，可以使用例如：水；甲醇、乙醇等一元醇、甘油等多元醇等醇；聚乙二醇等水溶性高分子；以及它们的混合物等水溶性凝固液等。

[0144] 在所述多孔膜的制造方法中，可以通过导入至凝固液并在膜基体材料表面成形多孔膜后进行剥离、直接进行干燥，制造多孔膜。干燥只要是可以除去凝固液等溶剂成分的方法，就没有特别限定，可以是加热下干燥，也可以为室温下的自然干燥。加热处理的方法没有特别限制，可以为热风处理、热辊处理、或投入恒温槽或烤箱等中的方法，只要是可以将多孔膜控制在规定的温度的方法即可。加热温度可以从例如室温～ 600℃左右的宽范围中选择。加热处理时的氛围可以为空气、氮、非活性气体的任一种。使用空气，为最廉价，但可以伴有氧化反应。避免该情况时，只要使用氮或非活性气体即可，从成本面方面考虑，优选氮气。加热条件考虑生产率、多孔膜的物性等而适当设定。通过干燥，可以得到多孔膜。

[0145] 对如上所述得到的多孔膜可以进一步使用热、可见光线、紫外线、电子束、放射线等实施交联处理。通过所述处理，对构成多孔膜的前体进行聚合、交联、固化等而形成高分子化合物，多孔膜由高分子化合物构成的情况下，进行交联或固化等，可以得到刚性或耐药品性等特性进一步得到提高的多孔膜。例如，通过对使用聚酰亚胺类前体成形的多孔膜进一步实施热酰亚胺化或化学酰亚胺化等，可以得到聚酰亚胺多孔膜。可以对使用聚酰胺酰亚胺类树脂成形的多孔膜实施热交联。需要说明的是，也可以在导入至凝固液之后、与用于进行干燥的加热处理同时实施热交联。

[0146] （无纺布基体材料和多孔膜的叠层）

[0147] 所述无纺布基体材料和多孔膜的叠层方法可以通过热熔粘等合理地制造。此时，优选为（构成多孔膜的树脂的玻璃化转变温度）＞（构成无纺布的树脂的熔点）。

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[0148] 对具体的制造方法进行叙述。在无纺布基体材料的至少一面上载置多孔膜，通过热源从多孔膜的一侧或两侧进行加热，使与多孔膜相接的无纺布基体材料表面稍微熔融，由此可以得到无纺布基体材料与多孔膜密合的叠层体。此时，为了保护多孔膜、无纺布基体材料或两者免受摩擦等，优选将保护膜载置于一侧或两侧。热源可以利用熨斗、层叠机、加热辊等，也可以使用层叠装置、热封装置、压延装置、辊式压制装置等。

[0149] 优选（构成多孔膜的树脂的玻璃化转变温度）＞（构成无纺布的树脂的熔点）的原因是，具有微孔的多孔膜几乎或完全不受热的影响，仅使无纺布基体材料稍微熔融。加热只要可以熔融无纺布并使其与多孔膜密合即可，超过需要的加热有可能导致无纺布的孔的闭塞，因此不优选。加热温度优选设为（构成多孔膜的树脂的玻璃化转变温度）和（构成无纺布的树脂的熔点）之间，优选为（构成多孔膜的树脂的玻璃化转变温度）＞（加热温度）≧（构成无纺布的树脂的熔点）。此时的加热温度为多孔膜和无纺布基体材料相接时的温度。例如，聚乙烯或聚丙烯等聚烯烃的熔点为 130 ～ 165℃左右，因此，加热温度为 140 ～ 170℃左右即可。

[0150] 就一般的无纺布而言，用格利式透气度计测定的透气度为测定极限的 0.1 秒以下，因此，即使通过热熔粘聚烯烃类无纺布的一部分发生热变形，也对透气度几乎没有影响。但是，不优选长时间保持在（构成无纺布的树脂的熔点）以上。控制热熔粘的技术重点是加热温度、热源的移动速度、压力等，适当地控制这些因素是重要的。

[0151] 将高分子溶液流延至基体材料上形成膜状后，导入至凝固液中，然后，干燥从基体材料上剥离的单独的膜，通过热熔粘等对由此得到的多孔膜和无纺布基体材料进行叠层，优选构成多孔膜的树脂的玻璃化转变温度＞构成无纺布的树脂的熔点。

[0152] 用上述方法可以容易地得到对具有优异的空孔特性的多孔膜和基体材料进行直接叠层的多孔膜叠层体。

[0153] 根据所述多孔膜叠层体的制造方法，可以容易地得到所述基体材料的一面或两面由所述多孔膜包覆的具有多孔膜的叠层体，所述多孔膜具备具有连通性的多个微孔、且该微孔的平均孔径为 0.01 ～ 10μm。

[0154] 实施例

[0155] 以下，基于实施例，更详细地对本发明进行说明，但本发明并不受这些实施例限定。胶带剥离实验、平均孔径的测定、多孔膜内部的平均开孔率（孔隙率）的测定、透气度试验、高温放置实验、算术平均表面粗糙度 Sa（表面粗糙度）的测定、拉伸强度的测定用以下的方法来进行。

[0156] （胶带剥离实验）

[0157] (i) 在多孔膜叠层体的多孔膜表面上粘贴下述的胶带，用下述的辊压在粘接部分并压粘胶带。

[0158] (ii) 使用下述的万能拉伸试验机，在 50mm/ 分钟的条件下进行 T 型剥离。

[0159] (iii) 观察多孔膜和耐热无纺布基体材料的界面有无剥离。

[0160] 胶带：寺冈制作所制造、（商品名“film masking tape No.603(#25)”、24mm 宽度）

[0161] 辊：直径 30mm、200gf 荷重

[0162] 万能拉伸试验机：（株）orientec 社制造、（商品名“TENSILON RTA-500”）

[0163] 另外，实施例 1 中的膜的平均孔径及孔隙率用以下的方法算出。这些平均孔径及

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孔隙率仅以在电子显微镜照片的最前面所观察到的微孔作为对象而求出，在照片内部所观察到的微孔不作为对象。

[0164] （平均孔径的测定）

[0165] 由电子显微镜照片，对叠层体的表面或剖面的任意 30 点以上的孔测定其面积，将其平均值设为平均孔面积 S_{ave}。假设孔为正圆，将使用下述式、由平均孔面积换算为孔径的值设为平均孔径。在此，π 表示圆周率。

[0166] 表面或内部的平均孔径 [μm] = $2 \cdot (S_{ave}/\pi)^{1/2}$

[0167] （多孔膜内部的平均开孔率（孔隙率）的测定）

[0168] 在比较例 1 中，多孔膜嵌入至无纺布内部，与基体材料一体化，因此，难以直接对多孔膜内部的孔隙率进行测定。因此，使用 PET 膜（帝人杜邦社制、商品名“HS74AS”：厚度 100 μm）取代 PET 无纺布作为基体材料，在 PET 膜的易粘接面上流延原液之后，浸渍于水中并使其凝固，接着，使用从 PET 膜上剥离并干燥而得到的多孔性膜进行测定，利用下述式算出内部的孔隙率。没有基体材料的情况下，直接利用下述式算出。

[0169] V 表示膜的体积 [cm^3]，W 表示多孔膜的重量 [g]，ρ 表示多孔膜原料的密度 [g/cm^3]。聚酰胺酰亚胺的密度设为 1.45[g/cm^3]，聚醚酰亚胺的密度设为 1.27[g/cm^3]。

[0170] 孔隙率 [%] = $100-100 \cdot W/(\rho \cdot V)$

[0171] （透气度试验）

[0172] 透气度使用 TESTER SANGYO CO.,LTD 制造的格利式透气度测定仪 B 型，以 JIS P8117 为基准进行测定。秒数用数字自动计数器进行测定。透气度（格利值）的值越小，空气的透过性越高，即，意指多孔膜中的微孔的连通性高。需要说明的是，只要没有特殊说明，基体材料的透气度、多孔膜叠层体的透气度均用本试验法进行评价。

[0173] （高温放置实验）

[0174] 将与多孔膜一体化而成的叠层体的形状调整为约 5cm×10cm 的大致长方形，对垂直的两边 a、b 的距离进行测定，由此对样品形状的变化进行评价。首先，对初期的距离 a1、b1 进行了测定。接着，将样品投入至温度调整为 140℃的恒温槽内，并放置 30 分钟。接着取出样品，自然冷却至室温后，测定距离 a2、b2。使用下述式对 a、b 的各自的变化率进行计算。

[0175] 高温放置后的 a 的变化率（%）= {|a2-a1|/a1}×100

[0176] 用同样的方法算出 b 的变化率。

[0177] （算术平均表面粗糙度 Sa（表面粗糙度）的测定）

[0178] 采用使用了光干涉法的非接触式表面计测系统 VertScan2.0（株式会社菱化 System 制造）测定表面形状，从而算出了表面粗糙度。测定区域设为 250 μm×188 μm 的范围，测定条件设为物镜 = 50 倍、镜筒 = 0.5×Body、连续变焦镜头 = NoRelay、滤波器 = 530white、测定模式 = Wave、视野尺寸 = 640×480。使用算术平均表面粗糙度 (Sa) 作为表面粗糙度。

[0179] （拉伸强度的测定）

[0180] 沿样品制备时的 MD 方向（流动方向）采取尺寸 15×150mm 的试验片，使用万能拉伸试验机，将夹盘间距离设为 100mm，以每分钟约 200mm 的速度拉伸试验片，测定其拉伸强度。单位用 N/15mm 表示。

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[0181] 〔制造例 1〕

[0182] 向聚酰胺酰亚胺类树脂溶液（东洋纺织社制造的商品名“VYLOMAX（バイロマックス）HR11NN”：固体成分浓度 15 重量%、溶剂 NMP、溶液粘度 20dPa·s/25℃）100 重量份中加入聚乙烯基吡咯烷酮（分子量 5.5 万）35 重量份作为水溶性聚合物制成制膜用的原液。在玻璃板上放置帝人杜邦社制的 PET 膜（厚度 100μm：商品名“HS74AS”）作为基体材料并使易粘接面向上，使用膜涂布机将保持在 25℃的原液流延在该 PET 膜上。流延时以膜涂布机与 PET 膜之间的间隙为 51μm 而进行。流延后，迅速地在湿度约 100%、温度 50℃的容器中保持 4 分钟。其后，浸渍于水中并使其凝固、清洗时，多孔膜自然地从 PET 膜上剥离。

[0183] 通过在室温下进行自然干燥而得到多孔膜。多孔膜的厚度为约 23μm。用电子显微镜观察该多孔膜，结果，存在于多孔膜的表面的孔的平均孔径为约 0.5μm，多孔膜内部为大致均质且在整体上存在平均孔径为约 0.5μm 的具有连通性的微孔。另外，多孔膜内部的孔隙率为 70%。测定多孔膜的透气度，结果为平均 4 秒（3 次的测定值 4 秒、4 秒、4 秒）。图 1 示出了制造例 1 中得到的多孔膜表面的电子显微镜照片（SEM 照片）。

[0184] 〔制造例 2〕

[0185] 向聚醚酰亚胺类树脂溶液（日本 GE Plastic 制造、商品名“ULTEM（ウルテム）1000P”：固体成分浓度 18 重量%、溶剂 NMP）100 重量份中加入聚乙烯基吡咯烷酮（分子量 5.5 万）30 重量份作为水溶性聚合物制成制膜用的原液。

[0186] 在玻璃板上放置作为基体材料的帝人杜邦社制的 PET 膜（厚度 100μm：商品名“HS74AS”）并使易粘接面向上，使用膜涂布机将保持在 25℃的原液流延在该 PET 膜上。流延时以膜涂布机与 PET 膜的间隙为 51μm 而进行。流延后，迅速地在湿度约 100%、温度 50℃的容器中保持 4 分钟。其后，浸渍水中并使其凝固、清洗时，多孔膜自然地从 PET 膜上剥离。通过在室温下进行自然干燥而得到多孔膜。多孔膜的厚度为约 24μm。用电子显微镜观察该多孔膜，结果，存在于多孔膜的表面的孔的平均孔径为约 1μm，多孔膜内部为大致均质且在整体上存在平均孔径为约 1μm 的具有连通性的微孔。另外，多孔膜内部的孔隙率为 73%。测定多孔膜的透气度，结果为平均 4 秒（3 次的测定值 3 秒、4 秒、4 秒）。图 2 示出了制造例 2 中得到的多孔膜表面的电子显微镜照片（SEM 照片）。

[0187] 〔实施例 1〕

[0188] 将制造例 1 的聚酰胺酰亚胺类多孔膜叠合在日本 VILENE 制造聚烯烃无纺布（厚度约 250μm、单位面积重量约 80g/m^2、密度约 0.36g/cm^3、透气度 0.1 秒：商品名“FT-330N”）上，并将其夹入进行了对折的 PET 膜（东丽社制造、厚度 100μm：制品名“lumiler S10”）之间，置于桌子上。将松下电器产业社制造蒸汽熨斗（产品编号：NI-R70）的温度设定设为中（约 150℃），在达到设定温度的状态下，连同 PET 膜从聚酰胺酰亚胺类多孔膜的侧进行了加热。蒸汽熨斗的移动速度设为约 60cm/ 分钟。

[0189] 通过上述的方法，得到聚酰胺酰亚胺类多孔膜和聚烯烃无纺布一体化的叠层体。叠层体的总厚度为约 313μm。在聚酰胺酰亚胺类多孔膜的一侧，玻璃化转变温度为约 300℃，因此没有观察到变化。

[0190] 对得到的叠层体进行胶带剥离实验，结果，无纺布和多孔膜没有发生界面剥离。用电子显微镜观察该叠层体，结果，多孔膜的表面存在的孔的平均孔径为约 0.5μm。测定叠层体的透气度，结果为平均 4 秒（3 次的测定值 4 秒、5 秒、4 秒），与叠层前的聚酰胺酰亚胺类

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多孔膜的值相同。没有观察到制备的叠层体引起透气性变差，也几乎没有偏差。

[0191] 另外，就高温放置后的变化率而言，a、b 均为 1.0%，几乎没有观察到叠层体由于高温放置引起形状变化。确认本叠层体在高温下形状稳定性优异。

[0192] [实施例 2]

[0193] 将制造例 1 的聚酰胺酰亚胺类多孔膜叠合在日本 VILENE 制造聚烯烃无纺布（厚度约 250 μm、单位面积重量约 80g/m^2、密度约 0.36g/cm^3、透气度 0.1 秒；商品名“FT-330N”）上，并将其夹入进行了对折的 PI 膜（东丽杜邦社制造、厚度 25 μm；制品名“Kapton（カプトン）100H”）之间。将 IRIS OHYAMA 社制层叠机（产品编号：LFA341D）的温度设定刻度设为 13（约 150℃），在达到设定温度的状态下连同 PI 膜一起从两侧进行加热。层叠机的层叠速度为约 47cm/ 分钟。

[0194] 通过上述的方法，得到聚酰胺酰亚胺类多孔膜和聚烯烃无纺布一体化的叠层体。叠层体的总厚度为约 249 μm。由于由于从两侧进行加热，因此聚烯烃无纺布的面的表面热熔融了一些、平滑性增加。在聚酰胺酰亚胺类多孔膜的一侧，玻璃化转变温度为约 300℃，因此，没有观察到变化。

[0195] 对得到的叠层体进行胶带剥离实验，结果，无纺布和多孔膜没有发生界面剥离。用电子显微镜观察该叠层体，结果，多孔膜的表面存在的孔的平均孔径为约 0.5 μm。测定叠层体的透气度，结果为平均 5 秒（测定值 5 秒、5 秒、4 秒），与叠层前的聚酰胺酰亚胺类多孔膜的值几乎相同，也几乎没有偏差。没有观察到制备的叠层体引起透气性变差。

[0196] 另外，就高温放置后的变化率而言，a、b 分别为 1.4%、1.5%，几乎没有观察到叠层体由于高温放置而引起形状变化。确认本叠层体在高温下形状稳定性优异。

[0197] [实施例 3]

[0198] 在实施例 2 中，使用广濑制纸制造的一面为聚酯、一面为聚丙烯的两层无纺布（厚度约 105 μm、单位面积重量约 50g/m^2、密度约 0.43g/cm^3、透气度 0.1 秒；商品名“05EP-50”）作为无纺布，将聚酰胺酰亚胺类多孔膜叠合在两层无纺布的聚丙烯侧上，除此之外，与实施例 2 同样的操作，得到无纺布和多孔膜一体化的叠层体。叠层体的总厚度为约 135 μm。从两侧进行加热，但聚酯的熔点为约 260℃，因此，聚酯无纺布一面的表面没有观察到变化。在聚酰胺酰亚胺类多孔膜的一侧，玻璃化转变温度为约 300℃，因此没有观察到变化。

[0199] 对得到的叠层体进行胶带剥离实验，结果，无纺布和多孔膜没有发生界面剥离。用电子显微镜观察该叠层体，结果，多孔膜的表面存在的孔的平均孔径为约 0.5 μm。测定叠层体的透气度，结果为平均 4 秒（3 次的测定值 4 秒、4 秒、4 秒），与叠层前的聚酰胺酰亚胺类多孔膜的值相同，也没有偏差。没有观察到制备的叠层体引起透气性变差。

[0200] 另外，就高温放置后的变化率而言，a、b 分别为 0%、0.5%，几乎没有观察到叠层体由于高温放置而引起形状变化。确认本叠层体在高温下的形状稳定性优异。

[0201] [实施例 4]

[0202] 在实施例 2 中，使用广濑制纸制造的一面为聚酯、一面为聚丙烯的两层无纺布（厚度约 93 μm、单位面积重量约 50g/m^2、密度约 0.42g/cm^3、透气度 0.1 秒；商品名“15EP-50”）作为无纺布，将聚酰胺酰亚胺类多孔膜叠合在两层无纺布的聚丙烯侧上，除此之外，与实施例 2 同样地操作，得到无纺布和多孔膜一体化的叠层体。叠层体的总厚度为约 131 μm。从两侧进行加热，但聚酯的熔点为约 260℃，因此，在聚酯无纺布一面的表面没有观察到变化。

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在聚酰胺酰亚胺类多孔膜的一侧，玻璃化转变温度为约 300℃，因此，没有观察到变化。

[0203] 对得到的叠层体进行胶带剥离实验，结果，无纺布和多孔膜没有发生界面剥离。用电子显微镜观察该叠层体，结果，多孔膜的表面存在的孔的平均孔径为约 0.5μm。测定叠层体的透气度，结果为平均 4 秒（3 次的测定值 4 秒、4 秒、4 秒），与叠层前的聚酰胺酰亚胺类多孔膜的值相同，也没有偏差。没有观察到制备的叠层体引起透气性变差。

[0204] 另外，就高温放置后的变化率而言，a、b 分别为 0.4%、0.5%，几乎没有观察到叠层体由于高温放置而引起形状变化。确认本叠层体在高温下的形状稳定性优异。

[0205] ［实施例 5］

[0206] 在实施例 2 中，使用广濑制纸制造聚烯烃无纺布（厚度约 13μm、单位面积重量约 2.6g/m^2、密度约 0.20g/cm^3、透气度 0.1 秒；商品名“06HOP-2”）作为无纺布，除此之外，进行与实施例 2 同样的操作，得到聚酰胺酰亚胺类多孔膜和聚烯烃无纺布一体化的叠层体。叠层体的总厚度为约 38μm。由于从两侧进行加热，因此聚烯烃无纺布一面的表面热熔融了一些，平滑性增加。在聚酰胺酰亚胺类多孔膜的一侧，玻璃化转变温度为约 300℃，因此没有观察到变化。

[0207] 对得到的叠层体进行胶带剥离实验，结果，无纺布和多孔膜没有引起界面剥离。用电子显微镜观察该叠层体，结果，多孔膜的表面存在的孔的平均孔径为约 0.5μm。测定叠层体的透气度，结果为平均 5 秒（3 次的测定值 4 秒、4 秒、5 秒），与叠层前的聚酰胺酰亚胺类多孔膜的值几乎相同。没有观察到制备的叠层体引起透气性变差。

[0208] 另外，就高温放置后的变化率而言，a、b 分别为 1.6%、0.7%，叠层体由于高温放置而引起的形状变化只是产生卷曲。确认本叠层体在高温下的形状稳定性优异。

[0209] ［实施例 6］

[0210] 在实施例 2 中，使用广濑制纸制造聚烯烃无纺布（厚度约 13μm、单位面积重量约 2.6g/m^2、密度约 0.20g/cm^3、透气度 0.1 秒；商品名“06HOP-2”）作为无纺布，使用制造例 2 的聚醚酰亚胺类多孔膜，除此之外，进行与实施例 2 同样的操作，得到聚醚酰亚胺类多孔膜和聚烯烃无纺布一体化的叠层体。叠层体的总厚度为约 39μm。由于从两侧进行加热，因此聚烯烃无纺布一面的表面热熔融了一些，平滑性增加。在聚醚酰亚胺类多孔膜的一侧，玻璃化转变温度为约 217℃，因此没有观察到变化。

[0211] 对得到的叠层体进行胶带剥离实验，结果，无纺布和多孔膜没有发生界面剥离。用电子显微镜观察该叠层体，结果，多孔膜的表面存在的孔的平均孔径为约 1μm。测定叠层体的透气度，结果为平均 4 秒（3 次的测定值 5 秒、4 秒、3 秒），与叠层前的聚醚酰亚胺类多孔膜的值相同，也仅为稍有偏差。没有观察到制备的叠层体引起透气性变差。

[0212] 另外，就高温放置后的变化率而言，a、b 分别为 0.2%、0.6%，叠层体由于高温放置而引起的形状变化只是产生卷曲。确认本叠层体在高温下的形状稳定性优异。

[0213] ［比较例 1］

[0214] 向聚酰胺酰亚胺类树脂溶液（东洋纺织社制造的商品名“VYLOMAX（バイロマックス）HR11NN”：固体成分浓度 15 重量%、溶剂 NMP、溶液粘度 20dPa·s/25℃）100 重量份中加入聚乙烯基吡咯烷酮（分子量 5.5 万）40 重量份作为水溶性聚合物来作为制膜用的原液。在玻璃板上放置日本 VILENE 社制的 PET 无纺布（厚度 130μm、单位面积重量约 90g/m^2、密度约 0.69g/cm^3、透气度 0.1 秒；商品名“MF-90”），在该无纺布上使用膜涂布机对保持

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在25℃的原液进行流延。流延时以膜涂布机和无纺布的间隙为51μm而进行。流延后，迅速地在湿度约100%、温度50℃的容器中保持4分钟。其后，浸渍于水中并使其凝固、清洗，接着，不从无纺布上剥离，而从水中取出，载置于纸巾上，在室温下进行自然干燥，由此得到无纺布和多孔膜一体化的叠层体。叠层体的总厚度为约147μm。

[0215] 对得到的叠层体进行胶带剥离实验，结果，无纺布和多孔膜没发生界面剥离。用电子显微镜观察该叠层体，结果，多孔膜与无纺布密合，多孔膜的表面存在的孔的平均孔径为约0.2μm，多孔膜内部为大致均质且整体上存在平均孔径为约0.2μm的具有连通性的微孔。另外，多孔膜内部的孔隙率为70%。测定叠层体的透气度，结果为平均136秒(3次的测定值142秒、170秒、96秒)。得知：与实施例1～6的叠层体样品相比，透气性非常差，另外，偏差也非常大。

[0216] 表1示出了将实施例1～6、比较例1的叠层体的表面粗糙度Sa的值。确认到：通过本发明的热熔粘(热封)得到的叠层体表面具有非常小的表面粗糙度，但通过比较例的涂布得到的叠层体表面具有相对地非常大的表面粗糙度。另外确认到：本发明的叠层体的表面平滑，且透气性高，但比较例中叠层体的多孔膜深深地进入无纺布内，因此，阻碍透气性。

[0217] 表1

[0218]

样品 (多孔叠层体)	算术平均表面粗糙Sa [μm]	透气度 [秒]
实施例1	0.15	4
实施例2	0.24	5
实施例3	0.17	4
实施例4	0.12	4
实施例5	0.12	5
实施例6	0.11	4
比较例1	0.52	136

[0219] 将高温放置实验的结果归纳于表2。另外，为了比较，进行了作为市售的聚烯烃类隔板的Celgard社制造的隔板(厚度约25μm、产品型号2500)的高温放置实验，结果，在试验后，隔板特别地沿一边方向显著地发生收缩，进而产生卷曲。确认到：聚烯烃类隔板在高温下形状稳定性非常差。另一方面，确认到：就本发明的叠层体而言，高温下的形状稳定性。

[0220] 表2

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[0221]

样品	a的变化率 [%]	b的变化率 [%]
实施例1	1	1
实施例2	1.4	1.5
实施例3	0	0.5
实施例4	0.4	0.5
实施例5	1.6	0.7
实施例6	0.2	0.6
Celgard 产品型号2500	1.2	22.1

[0222] 表3示出了实施例1～6的叠层体和制造例1～2的多孔膜的拉伸强度的测定结果。与制造例1～2的多孔膜相比，实施例1～6的叠层体的拉伸强度增大，确认操作性得到了改善。

[0223] 表3

[0224]

样品	拉伸强度 [N/15mm]
实施例1	48.5
实施例2	49.2
实施例3	44.5
实施例4	46.7
实施例5	4.0
实施例6	5.2
制造例1 (多孔膜)	2.3
制造例2 (多孔膜)	3.8

[0225] 工业实用性

[0226] 本发明的多孔膜叠层体由于空孔特性或表面平滑性优异，具有耐热性和柔软性，而且操作性及成形加工性优异，因此，特别可用作在高温下使用的过滤器、分离膜、隔板、或作为它们的一部分。

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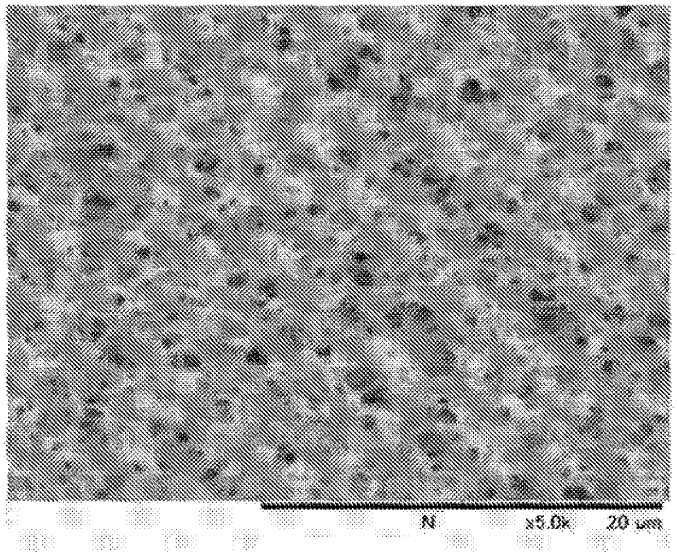


图 1

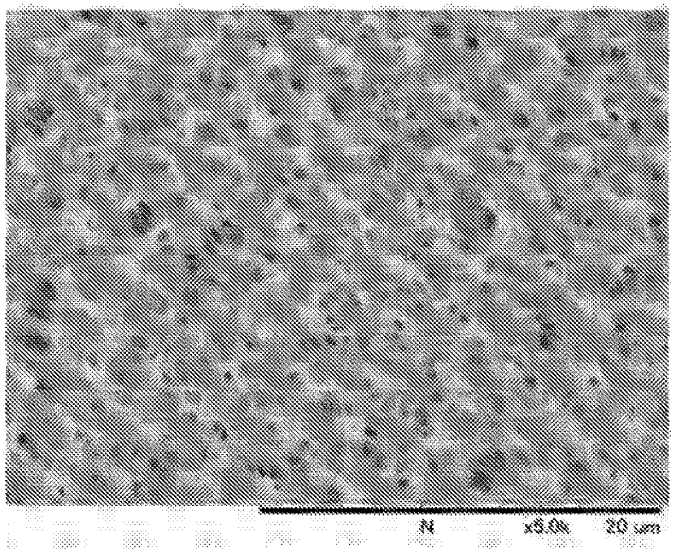


图 2

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Espacenet

CN205004376U Power battery's ceramic isolation membrane module for electric automobile

Applicants: SHENZHEN HONGTAI BATTERY TECH CO LTD

Inventors: ZHOU YONG,LYU JINGSHUANG,GAN FENGJIU

Classifications:
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Power battery's ceramic isolation membrane module for electric automobile

Abstract

The utility model provides a power battery's ceramic isolation membrane module for electric automobile, this power battery's ceramic isolation membrane module for electric automobile includes: PP membrane layer, the symmetry sets up two inorganic ceramic layers of PP membrane layer both sides, the symmetry sets up the tie coat in two inorganic ceramic layer outsides. The beneficial effects of the utility model are that: the stability of the heat of diaphragm is improved, mechanical properties is used for putting forward unfamiliar high temperature resistance, security, cycle life, low self discharge nature.

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Technical field

The utility model relates to the technical field of electric vehicles, in particular to a ceramic isolation membrane module for a power battery for an electric vehicle.

Background technique

With the development of the electric vehicle industry, the power battery has gradually become the core of electric vehicle components. The power battery has become the focus of new energy development because of its high working voltage, high energy density, good safety, no memory effect and no pollution. The field has broad application prospects in electric vehicles, wind power storage, solar power storage, mobile base stations, space technology, and defense industry.

At present, electric vehicles put forward extremely high requirements for the safety of power batteries. Currently, the diaphragms used in power batteries for electric vehicles are three-layer pp/pe/pp composite microporous membranes, or single-layer PP, PE single-layer micropores. Film, and coating film, due to the thin diaphragm thickness, generally 16-40μm before, in terms of thermal stability, the diaphragm is easy to shrink after high temperature to cause short circuit of the battery, mechanical properties are not strong, easy to ignite after acupuncture It brings certain safety hazards to the subsequent time of the battery.

Utility model content

The purpose of the utility model is to overcome the deficiencies of the prior art and to provide a ceramic separator module for a power battery for an electric vehicle.

The utility model is realized by the above technical solutions:

The utility model provides a ceramic isolation membrane module for a power battery for an electric vehicle, wherein the ceramic isolation membrane module of the power battery for an electric vehicle comprises: a PP diaphragm layer, two inorganic ceramics symmetrically disposed on two sides of the PP diaphragm layer The layer is symmetrically disposed on the outer side of the two inorganic ceramic layers.

Preferably, the PP separator layer has a thickness of 16-40 microns.

Preferably, the inorganic ceramic layer has a thickness of 2-3 microns.

Preferably, the bonding layer has a thickness of 2-3 microns.

The utility model has the beneficial effects of improving the thermal stability and mechanical properties of the diaphragm, and is used for improving the high temperature resistance, safety, cycle life and low self-discharge of the diaphragm.

DRAWINGS

BRIEF DESCRIPTION OF THE DRAWINGS Fig. 1 is a schematic view showing the structure of a ceramic separator assembly for a power battery for an electric vehicle according to an embodiment of the present invention.

Detailed ways

In order to make the objects, technical solutions and advantages of the present invention more comprehensible, the present invention will be further described in detail below with reference to the accompanying drawings and embodiments. It is understood that the specific embodiments described herein are merely illustrative of the invention and are not intended to limit the invention.

Please refer to FIG. 1. FIG. 1 is a schematic structural view of a ceramic isolation membrane module of a power battery for an electric vehicle according to the present invention.

The embodiment of the present invention provides a ceramic isolation membrane module for a power battery for an electric vehicle, and the ceramic insulation membrane assembly of the power battery for the electric vehicle includes: a PP membrane layer 1 symmetrically disposed on both sides of the PP membrane layer 1 Two inorganic ceramic layers 2 are symmetrically disposed on the outer side of the two inorganic ceramic layers 2.

Specifically, the PP separator layer 1 has a thickness of 16-40 microns. The inorganic ceramic layer 2 has a thickness of 2-3 μm. The bonding layer 3 has a thickness of 2-3 microns.

In order to facilitate a clear understanding of the diaphragm assembly provided by the embodiments of the present invention, the structure thereof will be described in detail below.

The ceramic separator for a power battery for an electric vehicle according to the present embodiment includes a PP separator having a thickness of 16 to 40 μm; the upper and lower layers of the separator are treated with the inorganic ceramic layer 2, and the inorganic ceramic layer 2 having a coating thickness of 2-3 μm.

The separator is unrolled through the stirred separator inorganic ceramic alumina mixed slurry, and after coating, it is baked at 70-90 degrees in an oven, and then a layer of 2-3 μm is applied to the treated separator. The baked diaphragm is then fabricated into a battery. The inorganic ceramic layer 2 can improve the thermal stability and mechanical properties of the separator, and is used for improving the high temperature resistance, safety, cycle life and low self-discharge of the separator. The bonding layer 3 can better bond the positive electrode tab, the negative electrode tab and the separator together, and enhance the electrochemical performance of the power battery, especially for reducing the internal resistance, improving the formation of the battery, improving the high temperature resistance and safety. Sex, cycle life, low self-discharge, the greater effect is to avoid the safety hazards caused by short circuits caused by the use of electric vehicles.

The above are only the preferred embodiments of the present invention, and are not intended to limit the present invention. Any modifications, equivalent substitutions and improvements made within the spirit and principles of the present invention are included in the present invention. Within the scope of protection.

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1.A ceramic separator module for a power battery for an electric vehicle, comprising: a PP separator layer, two inorganic ceramic layers symmetrically disposed on two sides of the PP separator layer, symmetrically disposed on the two inorganic ceramic layers The outer bonding layer.

2.A ceramic separator module for a power battery for an electric vehicle according to claim 1, wherein said PP separator layer has a thickness of 16 to 40 μm.

3.A ceramic separator module for a power battery for an electric vehicle according to claim 2, wherein said inorganic ceramic layer has a thickness of 2-3 μm.

4.A ceramic separator module for a power battery for an electric vehicle according to claim 2, wherein said bonding layer has a thickness of 2-3 μm.

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(12)实用新型专利

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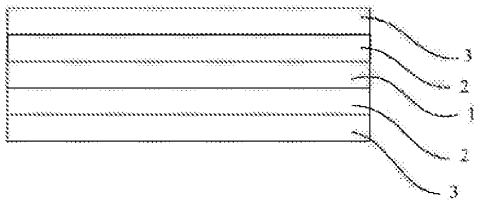
权利要求书1页 说明书2页 附图1页

(54)实用新型名称

一种电动汽车用动力电池的陶瓷隔离膜组件

(57)摘要

本实用新型提供了一种电动汽车用动力电池的陶瓷隔离膜组件，该电动汽车用动力电池的陶瓷隔离膜组件包括：PP隔膜层，对称设置在所述PP隔膜层两侧的两个无机陶瓷层，对称设置在所述两个无机陶瓷层外侧的粘结层。本实用新型的有益效果是：提高隔膜的热稳定性、机械性能，用来提隔膜的耐高温性、安全性、循环寿命、低自放电性。



CN 205004376 U

1. 一种电动汽车用动力电池的陶瓷隔离膜组件，其特征在于，包括：PP 隔膜层，对称设置在所述 PP 隔膜层两侧的两个无机陶瓷层，对称设置在所述两个无机陶瓷层外侧的粘结层。

2. 根据权利要求 1 所述的电动汽车用动力电池的陶瓷隔离膜组件，其特征在于，所述 PP 隔膜层的厚度为 16-40 微米。

3. 根据权利要求 2 所述的电动汽车用动力电池的陶瓷隔离膜组件，其特征在于，所述无机陶瓷层的厚度为 2-3 微米。

4. 根据权利要求 2 所述的电动汽车用动力电池的陶瓷隔离膜组件，其特征在于，所述粘结层的厚度为 2-3 微米。

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一种电动汽车用动力电池的陶瓷隔离膜组件

技术领域

[0001] 本实用新型涉及到电动车的技术领域，尤其涉及到一种电动汽车用动力电池的陶瓷隔离膜组件。

背景技术

[0002] 随着电动汽车行业的发展，动力电池逐渐成为电动汽车部件的核心，动力电池因其具有工作电压高、能量密度大、安全性好、无记忆效应、无污染等优点成为新能源开发的重点研究领域，在电动汽车、风光发电储能、太阳能发电储能、移动基站、空间技术、国防工业等诸多方面具有广阔的应用前景。

[0003] 目前，电动汽车对动力电池的安全性提出极高的要求，现在电动汽车用的动力电池基本使用的隔膜为三层 pp/pe/pp 复合微孔膜，或者单层 PP、PE 单层微孔膜、和涂布膜三种，由于隔膜厚度薄，一般为 16-40 μm 之前，在热稳定性方面差，高温后隔膜容易收缩给造成电池短路，机械性能不强，针刺后容易起火不齐，给电池的后续时候带来一定的安全隐患。

实用新型内容

[0004] 本实用新型的目的是为了克服现有技术的不足，提供了一种电动汽车用动力电池的陶瓷隔离膜组件。

[0005] 本实用新型是通过以上技术方案实现：

[0006] 本实用新型提供了一种电动汽车用动力电池的陶瓷隔离膜组件，该电动汽车用动力电池的陶瓷隔离膜组件包括：PP 隔膜层，对称设置在所述 PP 隔膜层两侧的两个无机陶瓷层，对称设置在所述两个无机陶瓷层外侧的粘结层。

[0007] 优选的，所述 PP 隔膜层的厚度为 16-40 微米。

[0008] 优选的，所述无机陶瓷层的厚度为 2-3 微米。

[0009] 优选的，所述粘结层的厚度为 2-3 微米。

[0010] 本实用新型的有益效果是：提高隔膜的热稳定性、机械性能，用来提隔膜的耐高温性、安全性、循环寿命、低自放电性。

附图说明

[0011] 图 1 是本实用新型实施例提供的电动汽车用动力电池的陶瓷隔离膜组件的结构示意图。

具体实施方式

[0012] 为了使本实用新型的目的、技术方案及优点更加清楚明白，以下结合附图及实施例，对本实用新型进行进一步详细说明。应当理解，此处所描述的具体实施例仅仅用以解释本实用新型，并不用于限定本实用新型。

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[0013] 请参阅图 1，图 1 是本实用新型提供的电动汽车用动力电池的陶瓷隔离膜组件的结构示意图。

[0014] 本实用新型实施例提供了一种电动汽车用动力电池的陶瓷隔离膜组件，该电动汽车用动力电池的陶瓷隔离膜组件包括：PP 隔膜层 1，对称设置在所述 PP 隔膜层 1 两侧的两个无机陶瓷层 2，对称设置在所述两个无机陶瓷层 2 外侧的粘结层 3。

[0015] 具体的，所述 PP 隔膜层 1 的厚度为 16-40 微米。所述无机陶瓷层 2 的厚度为 2-3 微米。所述粘结层 3 的厚度为 2-3 微米。

[0016] 为了方便对本实用新型实施例提供的隔膜组件有清晰的了解，下面对其结构进行详细的说明。

[0017] 本实施例提供的电动汽车用动力电池陶瓷隔膜包括 PP 隔膜，厚度为 16-40 微米厚；上下两层隔膜处理无机陶瓷层 2，涂层厚度 2-3 微米的无机陶瓷层 2。

[0018] 将隔膜展开通过搅拌好的隔膜无机陶瓷氧化铝混合浆料，涂布完后并使用烘箱 70-90 度温度烘烤干，后在处理好的隔膜上涂一层 2-3μm 的粘结层 3，烘烤干的隔膜再进行电池制作，无机陶瓷层 2 可提高隔膜的热稳定性、机械性能，用来提隔膜的耐高温性、安全性、循环寿命、低自放电性。粘结层 3 可将正极极片、负极极片和隔膜更好的粘合一起，增强动力电池的电化学性能，尤其是对减低内阻，提高电池化成的形成膜，提高耐高温性、安全性、循环寿命、低自放电性，更大的效果在于避免电动汽车使用过程中造成的短路等安全隐患。

[0019] 以上仅为本实用新型的较佳实施例而已，并不用以限制本实用新型，凡在本实用新型的精神和原则之内所作的任何修改、等同替换和改进等，均应包含在本实用新型的保护范围之内。

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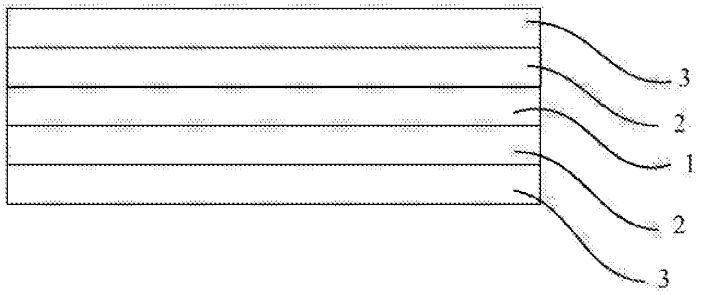


图 1

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Electronic Acknowledgement Receipt	
EFS ID:	44387671
Application Number:	17061427
International Application Number:	
Confirmation Number:	1915
Title of Invention:	POROUS FILM AND LITHIUM-ION BATTERY
First Named Inventor/Applicant Name:	Jianjian YI
Customer Number:	24341
Filer:	Yalei Sun/Edith Fuentes
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Application Type:	Utility under 35 USC 111(a)

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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		024607-02-5054US_IDS.pdf	165691 2ff097f1745d4ccb6c2f01cd62acf3a0ec260af9	yes	5

	Multipart Description/PDF files in .zip description				
	Document Description		Start	End	
	Transmittal Letter		1	4	
	Information Disclosure Statement (IDS) Form (SB08)		5	5	
Warnings:					
Information:					
2	Foreign Reference	CN102939675A.pdf	3770704 0c94cd908839708a7425e4ccc1e6f579cf0afc9a	no	30
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Information:					
3	Foreign Reference	CN103474602A.pdf	4705224 fa4bf08c8e969236205ff6e711bfe5b7b927ad57	no	19
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4	Foreign Reference	CN104871341A.pdf	5328488 cbed6da529fae3f337122b0420a817022991c58e	no	45
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Information:					
7	Non Patent Literature	Office-Action_CN201810322931-1_19AUG2021.pdf	431306 62a125e26ffdcc1322b35c343e602011c1c6887f	no	9
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8	Non Patent Literature	Yi_Office-Action-US16000764_22APR2020.pdf	317996 c4afad0126292828020fedabbdd0fef711c08a99	no	10
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Warnings:					
Information:					
		Total Files Size (in bytes):	23174393		

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<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Electronically filed November 29, 2021

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:	YI et al.	Confirmation No.:	1915
Serial No.:	17/061,427	Art Unit:	OPAP
Filed:	October 1, 2020	Examiner:	Central Docket
For:	Porous Film And Lithium-Ion Battery	Attorney Docket No.:	024607-02-5054-US

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In accordance with the duty of disclosure provisions of 37 C.F.R. §1.56, there is hereby provided certain information which the Examiner may consider material to the examination of the subject U.S. patent application. It is requested that the Examiner make this information of record if it is deemed material to the examination of the application.

1. Enclosures accompanying this Information Disclosure Statement are:

1a. ☒ A list of all patents, publications, applications, or other information submitted for consideration by the office.

1b. A legible copy of:

☒ Each foreign patent;

☐ Each publication or that portion which caused it to be listed on the PTO-1449;

☐ For each cited pending U.S. application, the application specification including the claims, and any drawing of the application, or portion of the application which caused it to be listed on the PTO-1449 including any claims directed to that portion;

☒ all other information or portion which caused it to be listed on the PTO-1449.

1c. ☐ An English language copy of search report(s) from a counterpart foreign application or PCT International Search Report.

1d. ☐ Explanations of relevancy (ATTACHMENT 1(d), hereto) or English language abstracts of the non-English language publications.

2. ☒ This Information Disclosure Statement is filed under 37 C.F.R. §1.97(b):

☐ Within three months of the filing date of a national application other than a continued prosecution application under §1.53(d);

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☐ Within three months of the date of entry of the national stage as set forth in §1.491 in an international application;

☒ Before the mailing of the first Office action on the merits;

☐ Before the mailing of a first Office action after the filing of a request for continued examination under §1.114.

3. ☐ This Information Disclosure Statement is filed under 37 C.F.R. §1.97(c) after the period specified in 37 C.F.R. §1.97(b), but before the mailing date of any of a final action under 37 C.F.R. §1.113, a notice of allowance under 37 C.F.R. §1.311 or an action that otherwise closes prosecution in the application.

(Check either Item 3a, 3b, 3c or 3d)

3a. ☐ The Certification Statement in Item 5 below is applicable. Accordingly, no fee is required.

3b. ☐ The $260 (large entity) fee set forth in 37 C.F.R. §1.17(p) in accordance with 37 C.F.R. §1.97(c) is to be charged to Morgan, Lewis & Bockius LLP Deposit Account No. 50-0310 (order no.).

3c. ☐ The $130 (small entity) fee set forth in 37 C.F.R. §1.17(p) in accordance with 37 C.F.R. §1.97(c) is to be charged to Morgan, Lewis & Bockius LLP Deposit Account No. 50-0310 (order no.).

3d. ☐ The $65 (micro entity) fee set forth in 37 C.F.R. §1.17(p) in accordance with 37 C.F.R. §1.97(c) is to be charged to Morgan, Lewis & Bockius LLP Deposit Account No. 50-0310 (order no.).

(Items 3b or 3c to be checked if any reference known for more than 3 months)

4. ☐ This Information Disclosure Statement is filed under 37 C.F.R. §1.97(d) after the period specified in 37 C.F.R. §1.97(c), but on or before the date of payment of the issue fee.

(Check Item 4a, and 4b, 4c or 4d)

4a. ☐ The Certification Statement in Item 5 below is applicable.

4b. ☐ The $260 (large entity) fee set forth in 37 C.F.R. §1.17(p) in accordance with 37 C.F.R. §1.97(c) is to be charged to Morgan, Lewis & Bockius LLP Deposit Account No. 50-0310 (order no.).

4c. ☐ The $130 (small entity) fee set forth in 37 C.F.R. §1.17(p) in accordance with 37 C.F.R. §1.97(c) is to be charged to Morgan, Lewis & Bockius LLP Deposit Account No. 50-0310 (order no.).

4d. ☐ The $65 (micro entity) fee set forth in 37 C.F.R. §1.17(p) in accordance with 37 C.F.R. §1.97(c) is to be charged to Morgan, Lewis & Bockius LLP Deposit Account No. 50-0310 (order no.).

5. ☐ Certification Statement (applicable if Item 3a or Item 4a is checked)

(Check either Item 5a, 5b, 5c or 5d)

5a. ☐ In accordance with 37 C.F.R. §1.97(e)(1), it is certified that each item of information contained in this information disclosure statement was first cited in a communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of this Information Disclosure Statement.

5b. ☐ In accordance with 37 C.F.R. §1.97(e)(2), it is certified that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 C.F.R. §1.56(c) more than three months prior to the filing of this information disclosure statement.

5c. ☐ Each item of information contained in this information disclosure statement was cited in a communication from a foreign patent office in a counterpart application, and the communication was not **received** by any individual designated in 37 C.F.R. §1.56(c) more than thirty days prior to the filing of this information disclosure statement.

5d. ☐ Pursuant to 37 C.F.R. §1.704(d), each item of information contained in this information disclosure statement was cited in a communication from a foreign patent office in a counterpart application, and the communication was not **received** by any individual designated in 37 C.F.R. §1.56(c) more than thirty days prior to the filing of this information disclosure statement.

6. ☒ Copies of each cited U.S. patent and each U.S. patent application publication are not enclosed pursuant to the USPTO OG Notice dated 05 August 2003 waiving the requirement under 37 C.F.R. 1.98(a)(2)(i) for U.S. patent applications filed after June 30, 2003.

7. ☐ This application is a continuation application under 37 C.F.R. §1.53(b) or (d).

(Check appropriate Items 7a, 7b and/or 7c)

7a. ☐ A Petition to Withdraw from issue under 37 C.F.R. §1.313(b)(5) is concurrently filed herewith.

7b. ☐ Copies of publications listed on Form PTO-1449 from prior application Serial No. , filed on , of which this application claims priority under 35 U.S.C. §120, are not being submitted pursuant to 37 C.F.R. §1.98(d).

7c. ☐ Copies of the publications listed on the attached Form PTO-1449 that were not previously cited in prior application Serial No. , filed on , are provided herewith.

8. ☐ This is a Supplemental Information Disclosure Statement. (Check Item 8a)

8a. ☐ This Supplemental Information Disclosure Statement under 37 C.F.R. §1.97(f) supplements the Information Disclosure Statement filed on . A bona fide attempt was made to comply with 37 C.F.R. §1.98, but inadvertent omissions were made. These omissions have been corrected herein. Accordingly, additional time is requested so that this Supplemental Information Disclosure Statement can be considered as if properly filed on .

Zhuhai CosMX Battery Co. - EX1002
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
Page 198 of 297

9. ☐ In accordance with 37 C.F.R. §1.98, a concise explanation of what is presently understood to be the relevance of each non-English language publication is:

(Check Item 9a, 9b, or 9c)

9a. ☐ satisfied because all non-English language publications were cited on the enclosed English language copy of the PCT International Search Report or the search report from a counterpart foreign application indicating the degree of relevance found by the foreign office.

9b. ☐ set forth in the application.

9c. ☐ enclosed as an attachment hereto.

10. ☒ The Commissioner is authorized to charge any additional fee required or credit any overpayment for this Information Disclosure Statement and/or Petition to Morgan, Lewis & Bockius LLP Deposit Account No. 50-0310 (order no. 024607-02-5054-US).

11. ☒ No admission is made that the information cited in this Statement is, or is considered to be, material to patentability nor a representation that a search has been made (other than a search report of a foreign counterpart application or PCT International Search Report if submitted herewith). 37 C.F.R. §§1.97(g) and (h).

Respectfully submitted,

Date: November 29, 2021

/Yalei Sun/ 57,765

Yalei Sun (Reg. No.)

MORGAN, LEWIS & BOCKIUS LLP
1400 Page Mill Road
Palo Alto, CA 94304
(650) 843-4000

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US

CONFIRMATION NO. 1915

PUBLICATION NOTICE

24341
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

OC000000122789392

Title:POROUS FILM AND LITHIUM-ION BATTERY

Publication No.US-2021-0020981-A1
Publication Date:01/21/2021

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently https://portal.uspto.gov/pair/PublicPair. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
17/061,427	10/01/2020	1727	1880	024607-02-5054-US	19	2

CONFIRMATION NO. 1915

UPDATED FILING RECEIPT

24341
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

OC000000121238989

Date Mailed: 11/10/2020

Receipt is acknowledged of this non-provisional utility patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF FIRST INVENTOR, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection.

Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a corrected Filing Receipt, including a properly marked-up ADS showing the changes with strike-through for deletions and underlining for additions. If you received a "Notice to File Missing Parts" or other Notice requiring a response for this application, please submit any request for correction to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections provided that the request is grantable.

Inventor(s)

Jianjian YI, Ningde City, CHINA;
Xinzhi ZHANG, Ningde City, CHINA;
Zengbin WEI, Ningde City, CHINA;
Xinghua TAO, Ningde City, CHINA;

Applicant(s)

NINGDE AMPEREX TECHNOLOGY LIMITED, Ningde City, CHINA;

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CON of 16/000,764 06/05/2018 PAT 10833355

Foreign Applications (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)
CHINA 201810322931.1 04/11/2018 No Access Code Provided

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

Projected Publication Date: 01/21/2021

Non-Publication Request: No

Early Publication Request: No

Title

POROUS FILM AND LITHIUM-ION BATTERY

Preliminary Class

429

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

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The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US

CONFIRMATION NO. 1915

24341
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

37 CFR 1.48(f)
ACKNOWLEDGEMENT LETTER

OC000000121238971

Date Mailed: 11/10/2020

NOTICE OF ACCEPTANCE OF REQUEST UNDER 37 CFR 1.48(f)

This is in response to the applicant's request under 37 CFR 1.48(f) submitted on 11/06/2020.

The request under 37 CFR 1.48(f) to correct the inventorship, to correct or update the name of an inventor, or to correct the order of names of joint inventors is accepted.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/hsarwari/

Doc Code: R48.REQ
Document Description: Request under Rule 48 correcting inventorship

PTO/AIA/40 (04-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR CORRECTION IN A PATENT APPLICATION RELATING TO INVENTORSHIP OR AN INVENTOR NAME, OR ORDER OF NAMES, OTHER THAN IN A REISSUE APPLICATION (37 CFR 1.48)

Application Number	17/061,427
Filing Date	October 1, 2020
First Named Inventor	Jianjian YI et al
Art Unit	1727
Examiner Name	To be assigned
Practitioner Docket Number	024607-02-5054-US

To: Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Applicant hereby **requests that the inventorship be corrected or changed, or that the name of the inventor or a joint inventor, or the order of the names of joint inventors, be changed,** in the above-identified application. **Note**: 37 CFR 1.48 applies to any request to correct inventorship filed on or after September 16, 2012, regardless of the application filing date. **Do not submit this form after payment of the issue fee or if the application has been patented.** See 37 CFR 1.324 for correction of inventorship in a patent.

Please check the applicable box(es) below.

For a nonprovisional application:

☐ 1. This request is to correct or change the inventorship in a **nonprovisional** application (**under 37 CFR 1.48(a)**) and includes:

☐ An application data sheet (ADS) in accordance with 37 CFR 1.76(c) with the corrected or updated information shown with markings (*e.g.*, underlining for insertions, strikethrough for deletions). See the Manual of Patent Examining Procedure (MPEP) section 601.05(a) for information about filing an ADS in an application filed on/after September 16, 2012. For information about filing a Supplemental ADS in an application filed before September 16, 2012, see MPEP 601.05(b).

☐ The processing fee set forth in 37 CFR 1.17(i). $ _____

☐ An inventor is being added. An inventor's oath or declaration by any actual inventor who has not yet executed an oath or declaration is required (see 37 CFR 1.48(b)). See MPEP 602.01(a) for information about an inventor's oath or declaration for an application filed on/after September 16, 2012 (*e.g.*, form **PTO/AIA/01**). For information about an inventor's oath or declaration for an application filed before September 16, 2012 (*e.g.*, form **PTO/SB/01**), see MPEP 602.01(b).

☐ This request is being filed after the first Office action on the merits has been given or mailed (see 37 CFR 1.48(c) and 1.17(d)). Check one of the following:

☐ This request to correct or change the inventorship is due solely to the cancellation of claims in the application.

OR

☐ The fee set forth in 37 CFR 1.17(d) is due (in addition to the fee set forth in 37 CFR 1.17(i)). $ _____

This collection of information is required by 37 CFR 1.48. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/40 (04-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR CORRECTION IN A PATENT APPLICATION RELATING TO INVENTORSHIP OR AN INVENTOR NAME, OR ORDER OF NAMES, OTHER THAN IN A REISSUE APPLICATION (37 CFR 1.48)

☒ 2. This request is to correct or update the name of the inventor or a joint inventor, or the order of names of joint inventors, in a **nonprovisional** application (**under 37 CFR 1.48(f)**) and includes:

☒ An application data sheet in accordance with 37 CFR 1.76(c) identifying the complete inventive entity, including the corrected or updated name of the inventor, or the new order of names shown with markings (*e.g.*, underlining for insertions, strikethrough for deletions). See the MPEP 601.05(a) for information about filing an ADS in an application filed on/after September 16, 2012. For information about filing a Supplemental ADS in an application filed before September 16, 2012, see MPEP 601.05(b).

☒ The processing fee set forth in 37 CFR 1.17(i). $ 140

For a provisional application:

☐ This request is to change or correct the inventorship, or correct or update the name of the inventor or a joint inventor, in a **provisional** application (**under 37 CFR 1.48(d)**) and includes:

☐ **Attached hereto** is a document that is signed by a party set forth in 37 CFR 1.33(b) and identifies each inventor by his or her legal name, in the preferred order. Note: the document may be an application data sheet in accordance with 37 CFR 1.76(c) that identifies the changes with markings (underlining for insertions, strikethrough for deletions).

☐ The processing fee set forth in 37 CFR 1.17(q). $ _____

Fee Payment Information:

☐ Applicant asserts small entity status. See 37 CFR 1.27.

☐ Applicant certifies micro entity status. See 37 CFR 1.29.
Form PTO/SB/15A or B or equivalent must either be enclosed or have been submitted previously

☐ A check in the amount of the fee is enclosed.

☐ Payment by credit card. Form PTO-2038 is attached.

☒ The Director is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 50-0310 (order no. 024607-02-5054-US).

☒ Payment made via EFS-Web.

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

I am the

☐ Applicant* ☐ attorney or agent of record Registration number _____ ☒ attorney or agent acting under 37 CFR 1.34 Registration number 57,765

Signature /Yalei Sun/

Typed or printed name Yalei Sun

Date November 6, 2020

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. *Juristic entities must be represented by a patent practitioner (See 37 CFR 1.31, applicable to any paper filed on or after September 16, 2012 that is presented on behalf of a juristic entity, regardless of application filing date). Submit multiple forms if more than one signature is required, see below**.

☒ ** Total of 1 forms are submitted.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PTO/AIA/01 (06-12)
Approved for use through 01/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number 16/000764 filed on June 5, 2018.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Xinghua Tao Date (Optional): JULY 24 2018

Signature: Tao Xinghua

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Electronic Patent Application Fee Transmittal

Application Number:	17061427
Filing Date:	01-Oct-2020
Title of Invention:	POROUS FILE AMD LITHIUM-ION BATTERY
First Named Inventor/Applicant Name:	Jianjian YI
Filer:	Yalei Sun/Jacqueline Yu
Attorney Docket Number:	024607-02-5054-US

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
PROCESSING FEE, EXCEPT PROV. APPLS.	1830	1	140	140
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**140**

Electronic Acknowledgement Receipt	
EFS ID:	41062483
Application Number:	17061427
International Application Number:	
Confirmation Number:	1915
Title of Invention:	POROUS FILE AMD LITHIUM-ION BATTERY
First Named Inventor/Applicant Name:	Jianjian YI
Customer Number:	24341
Filer:	Yalei Sun
Filer Authorized By:	
Attorney Docket Number:	024607-02-5054-US
Receipt Date:	06-NOV-2020
Filing Date:	01-OCT-2020
Time Stamp:	18:33:21
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$140
RAM confirmation Number	E2020A6I34381343
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		024607-02-5054-US_Request_for_Corrected_Filing_Receipt.pdf	3762693 68404463566485 6d1e1cb32ed333e9df1d93be11	yes	18

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Application Data Sheet	11	18
	Miscellaneous Incoming Letter	8	10
	Request under Rule 48 correcting inventorship	5	7
	Oath or Declaration filed	4	4
	Miscellaneous Incoming Letter	3	3
	Request for Corrected Filing Receipt	1	2

Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30504 efb5cdba47b3018358ee7a522f68a6559873a9a3	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	3793197		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/AIA/14 (11-15)
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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

SUPPLEMENTAL ADS

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	**17/061,427**
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Jianjian		YI	

Residence Information (Select One) ○ US Residency ◉ Non US Residency ○ Active US Military Service

City	Ningde City	Country of Residence [i]	CN

Mailing Address of Inventor:

Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	**State/Province**	FJ
Postal Code	352100	**Country** [i]	CN

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Xinzhi		ZHANG	

Residence Information (Select One) ○ US Residency ◉ Non US Residency ○ Active US Military Service

City	Ningde City	Country of Residence [i]	CN

Mailing Address of Inventor:

Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	**State/Province**	FJ
Postal Code	352100	**Country** [i]	CN

Inventor 3 Remove

Legal Name

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

SUPPLEMENTAL ADS

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	**17/061,427**
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Prefix	Given Name	Middle Name	Family Name	Suffix
	Zengbin		WEI	

Residence Information (Select One) ○ US Residency ◉ Non US Residency ○ Active US Military Service

City	Ningde City	Country of Residence [i]	CN

Mailing Address of Inventor:

Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	**State/Province**	FJ
Postal Code	352100	**Country** [i]	CN

Inventor 4 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Xinghua		TAO	

Residence Information (Select One) ○ US Residency ◉ Non US Residency ○ Active US Military Service

City	Ningde City	Country of Residence [i]	CN

Mailing Address of Inventor:

Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	**State/Province**	FJ
Postal Code	352100	**Country** [i]	CN

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	24341		
Email Address		Add Email	Remove Email

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

SUPPLEMENTAL ADS

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	**17/061,427**
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Application Information:

Title of the Invention	POROUS FILM AND LITHIUM-ION BATTERY		
Attorney Docket Number	024607-02-5054-US	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	3	**Suggested Figure for Publication (if any)**	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	◉ Customer Number	○ US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	24341		

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

SUPPLEMENTAL ADS

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	**17/061,427**
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status	Pending	Remove	
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	Continuation of	16000764	2018-06-05

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button.

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
201810322931.1	CN	2018-04-11	

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

SUPPLEMENTAL ADS

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	**17/061,427**
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

SUPPLEMENTAL ADS

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	**17/061,427**
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

◯ Assignee	◯ Legal Representative under 35 U.S.C. 117	◯ Joint Inventor
◯ Person to whom the inventor is obligated to assign.	◯ Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	NINGDE AMPEREX TECHNOLOGY LIMITED		
Mailing Address Information For Applicant:			
Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	**State/Province**	FJ
Country	CN	Postal Code	352100
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button.

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

SUPPLEMENTAL ADS

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	**17/061,427**
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button.

Signature:

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Yalei Sun/			Date (YYYY-MM-DD)	2020-11-06
First Name	Yalei	Last Name	Sun	Registration Number	57765

Additional Signature may be generated within this form by selecting the Add button.

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

SUPPLEMENTAL ADS

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	**17/061,427**
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Electronically filed November 6, 2020

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:	Jianjian YI et al.	Confirmation No.:	1915
Serial No.:	17/061,427	Art Unit:	1727
Filed:	October 1, 2020	Examiner:	To be Assigned
For:	*POROUS FILM AMD LITHIUM-ION BATTERY*	Attorney Docket No:	024607-02-5054-US

RESPONSE TO THE INFORMATIONAL NOTICE TO APPLICANT AND REQUEST FOR CORRECTED FILING RECEIPT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In response to the Informational Notice of Applicant mailed October 14, 2020, enclosed is a copy of the Informational Notice to Applicant and a copy of the executed Declaration from Inventor Xinghua TAO previously filed with the application on October 1, 2020.

The Applicant respectfully requests that a Corrected Filing Receipt be issued reflecting the following corrections to be made to the application to update Inventor's name, Zinghua TAO, to **Xinghua TAO**.

<Markup>

Jianjian YI, Ningde City, CHINA;
Xinzhi ZHANG, Ningde City, CHINA;
Zengbin WEI, Ningde City, CHINA;
~~**Zinghua**~~ **Xinghua TAO, Ningde City, CHINA**

<Clean>

Jianjian YI, Ningde City, CHINA;
Xinzhi ZHANG, Ningde City, CHINA;
Zengbin WEI, Ningde City, CHINA;
Xinghua TAO, Ningde City, CHINA

Attached is the Request to Correct Inventor Name under Rule 48, a marked-up copy of the Filing Receipt mailed October 14, 2020, and a Supplemental Application Data Sheet reflecting the desired change.

The Applicant also respectfully requests that the typographical errors in the Title of the Filing Receipt be corrected to show as **"POROUS FILM AND LITHIUM-ION BATTERY."** The Title is

correctly spelled as shown in the application documents filed on October 1, 2020 and in the attached Supplemental Application Data Sheet.

The Commissioner is hereby authorized to charge any required fees or credit any overpayments to Morgan, Lewis & Bockius LLP Deposit Account No. 50-0310 (order no. 024607-02-5054-US).

Respectfully submitted,

Date: November 6, 2020

/Yalei Sun/ 57,765

Yalei Sun (Reg. No.)
MORGAN, LEWIS & BOCKIUS LLP
1400 Page Mill Road
Palo Alto, CA 94304
Phone: (650) 843-4000

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US

CONFIRMATION NO. 1915

24341
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

INFORMAL NOTICE

OC000000120594043

Date Mailed: 10/14/2020

INFORMATIONAL NOTICE TO APPLICANT

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.53(f).

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

- A properly executed inventor's oath or declaration has not been received for the following inventor(s) *as named on the application data sheet:*
  Zinghua TAO
  An inventor's oath or declaration in compliance with 37 CFR 1.63 or 1.64 executed by or with respect to each inventor must be submitted no later than the date on which the issue fee is paid in response to a notice requiring such fee. See 37 CFR 1.53(f).
  If the name of the inventor provided on the ADS is not correct, applicant must submit a request to correct the inventor name according to 37 CFR 1.48(f), accompanied by the appropriate fee under 37 CFR 1.17(i) and a corrected ADS in compliance with 37 CFR 1.76(c), i.e., identifying the information that is being changed with underlining for insertions, and strike-through or brackets for text removed.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/fhadera/

Marked Up Filing Receipt

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
17/061,427	10/01/2020	1778	1880	024607-02-5054-US	19	2

CONFIRMATION NO. 1915

FILING RECEIPT

24341
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

OC000000120594042

Date Mailed: 10/14/2020

Receipt is acknowledged of this non-provisional utility patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF FIRST INVENTOR, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection.

Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a corrected Filing Receipt, including a properly marked-up ADS showing the changes with strike-through for deletions and underlining for additions. If you received a "Notice to File Missing Parts" or other Notice requiring a response for this application, please submit any request for correction to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections provided that the request is grantable.

Inventor(s)

Jianjian YI, Ningde City, CHINA;
Xinzhi ZHANG, Ningde City, CHINA;
Zengbin WEI, Ningde City, CHINA;
~~Zinghua TAO~~, Ningde City, CHINA; **Xinghua TAO**

Applicant(s)

NINGDE AMPEREX TECHNOLOGY LIMITED, Ningde City, CHINA;

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CON of 16/000,764 06/05/2018

Foreign Applications (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)
CHINA 201810322931.1 04/11/2018 No Access Code Provided

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

Marked Up Filing Receipt

If Required, Foreign Filing License Granted: 10/13/2020

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 17/061,427**

Projected Publication Date: 01/21/2021

Non-Publication Request: No

Early Publication Request: No

Title

~~POROUS FILE AMD LITHIUM-ION BATTERY~~ POROUS FILM AND LITHIUM-ION BATTERY

Preliminary Class

210

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

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LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 17/061,427

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	320
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	700
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	800
TOTAL CLAIMS (37 CFR 1.16(i))	19 minus 20 =	*			OR	x 100 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	2 minus 3 =	*				x 480 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1820

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
17/061,427	10/01/2020	1778	1880	024607-02-5054-US	19	2

CONFIRMATION NO. 1915

24341
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

FILING RECEIPT

OC000000120594042

Date Mailed: 10/14/2020

Receipt is acknowledged of this non-provisional utility patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF FIRST INVENTOR, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection.

Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a corrected Filing Receipt, including a properly marked-up ADS showing the changes with strike-through for deletions and underlining for additions. If you received a "Notice to File Missing Parts" or other Notice requiring a response for this application, please submit any request for correction to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections provided that the request is grantable.

Inventor(s)

Jianjian YI, Ningde City, CHINA;
Xinzhi ZHANG, Ningde City, CHINA;
Zengbin WEI, Ningde City, CHINA;
Zinghua TAO, Ningde City, CHINA;

Applicant(s)

NINGDE AMPEREX TECHNOLOGY LIMITED, Ningde City, CHINA;

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CON of 16/000,764 06/05/2018

Foreign Applications (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)
CHINA 201810322931.1 04/11/2018 No Access Code Provided

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

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The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 17/061,427**

Projected Publication Date: 01/21/2021

Non-Publication Request: No

Early Publication Request: No

Title

POROUS FILE AMD LITHIUM-ION BATTERY

Preliminary Class

210

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

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Title 37, Code of Federal Regulations, 5.11 & 5.15

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NOT GRANTED

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UNITED STATES PATENT AND TRADEMARK OFFICE

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United States Patent and Trademark Office
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
17/061,427	10/01/2020	Jianjian YI	024607-02-5054-US

CONFIRMATION NO. 1915

24341
Morgan, Lewis & Bockius LLP (PA)
1400 Page Mill Road
Palo Alto, CA 94304-1124

INFORMAL NOTICE

OC000000120594043

Date Mailed: 10/14/2020

INFORMATIONAL NOTICE TO APPLICANT

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.53(f).

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

- A properly executed inventor's oath or declaration has not been received for the following inventor(s) *as named on the application data sheet:*
  Zinghua TAO
  An inventor's oath or declaration in compliance with 37 CFR 1.63 or 1.64 executed by or with respect to each inventor must be submitted no later than the date on which the issue fee is paid in response to a notice requiring such fee. See 37 CFR 1.53(f).
  If the name of the inventor provided on the ADS is not correct, applicant must submit a request to correct the inventor name according to 37 CFR 1.48(f), accompanied by the appropriate fee under 37 CFR 1.17(i) and a corrected ADS in compliance with 37 CFR 1.76(c), i.e., identifying the information that is being changed with underlining for insertions, and strike-through or brackets for text removed.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/fhadera/

United States Patent and Trademark Office

Office of the Chief Financial Officer

Document Code:WFEE

User :C46910

Sale Accounting Date:10/13/2020

Sale Item Reference Number	Effective Date
17061427	10/01/2020

Document Number	Fee Code	Fee Code Description	Amount Paid	Payment Method
I20200C034183537	1051	LATE FILING FEE FOR OATH OR DECLARATION	$160.00	Deposit Account

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Jianjian		YI	

Residence Information (Select One) ○ US Residency ◉ Non US Residency ○ Active US Military Service

City	Ningde City	Country of Residence [i]	CN

Mailing Address of Inventor:

Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	**State/Province**	FJ
Postal Code	352100	**Country** [i]	CN

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Xinzhi		ZHANG	

Residence Information (Select One) ○ US Residency ◉ Non US Residency ○ Active US Military Service

City	Ningde City	Country of Residence [i]	CN

Mailing Address of Inventor:

Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	**State/Province**	FJ
Postal Code	352100	**Country** [i]	CN

Inventor 3 Remove

Legal Name

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Prefix	Given Name	Middle Name	Family Name	Suffix
	Zengbin		WEI	

Residence Information (Select One) ◯ US Residency ◉ Non US Residency ◯ Active US Military Service

City	Ningde City	Country of Residence [i]	CN

Mailing Address of Inventor:

Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	State/Province	FJ
Postal Code	352100	Country [i]	CN

Inventor 4 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Zinghua		TAO	

Residence Information (Select One) ◯ US Residency ◉ Non US Residency ◯ Active US Military Service

City	Ningde City	Country of Residence [i]	CN

Mailing Address of Inventor:

Address 1	No. 1, Xingang Road		
Address 2	Zhangwan Town, Jiaocheng Zone		
City	Ningde City	State/Province	FJ
Postal Code	352100	Country [i]	CN

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ An Address is being provided for the correspondence Information of this application.

Customer Number	24341		
Email Address		Add Email	Remove Email

PTO/AIA/14 (11-15)
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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Application Information:

Title of the Invention	POROUS FILM AND LITHIUM-ION BATTERY		
Attorney Docket Number	024607-02-5054-US	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	3	**Suggested Figure for Publication (if any)**	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	◉ Customer Number	○ US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	24341		

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status	Pending	Remove	
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	Continuation of	16000764	2018-06-05

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button.

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
201810322931.1	CN	2018-04-11	

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

PTO/AIA/14 (11-15)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	024607-02-5054-US
	Application Number	
Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

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B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

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Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

◯ Assignee	◯ Legal Representative under 35 U.S.C. 117	◯ Joint Inventor
◯ Person to whom the inventor is obligated to assign.	◯ Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:	

If the Applicant is an Organization check here. ☒

Organization Name	NINGDE AMPEREX TECHNOLOGY LIMITED

Mailing Address Information For Applicant:

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City	Ningde City	**State/Province**	FJ
Country	CN	Postal Code	352100
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button.

Assignee Information including Non-Applicant Assignee Information:

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Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
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Signature:

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Yalei Sun/			Date (YYYY-MM-DD)	2020-10-01
First Name	Yalei	Last Name	Sun	Registration Number	57765

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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	POROUS FILM AND LITHIUM-ION BATTERY

As the below named inventor, I hereby declare that:

This declaration is directed to:

- ☐ The attached application, or
- ☒ United States application or PCT international application number 16/000764 filed on June 5, 2018.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

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LEGAL NAME OF INVENTOR

Inventor: Xinghua Tao Date (Optional): JULY 24 2018

Signature: Tao Xinghua

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

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LEGAL NAME OF INVENTOR

Inventor: Zengbin Wei Date (Optional): July 24 2018

Signature: Wei Zengbin

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LEGAL NAME OF INVENTOR

Inventor: Jianjian Yi Date (Optional): July 24 2018

Signature: Yi JianJian

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The above-identified application was made or authorized to be made by me.

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LEGAL NAME OF INVENTOR

Inventor: Xinzhi Zhang Date (Optional): July 20 2018.

Signature: Zhang XinZhi

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

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POROUS FILM AND LITHIUM-ION BATTERY

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation application of U.S. Patent Application No. 16/000,764, filed on June 5, 2018, which claims priority to Chinese Patent Application No. 201810322931.1 filed on April 11, 2018, the contents of which are incorporated by reference herein.

TECHNICAL FIELD

[0002] The present application relates to the field of energy storage devices, and in particular, to a porous film and a lithium-ion battery.

BACKGROUND

[0003] Non-aqueous secondary batteries, particularly lithium-ion batteries, are widely used in portable electronic devices such as notebook computers, digital cameras, camcorders, and cellphones due to their high energy density and good rate performance. In recent years, the application of lithium-ion batteries as the power supply for new energy vehicles is also promoting the development of lithium-ion battery technology. In the cycle process of the lithium-ion battery, with the progress of charging and discharging, a gap will be created between the electrode and the separator, resulting in a reduction of the cycle capacity of the lithium-ion battery and thereby having an influence on its service life. Therefore, there is an urgent need for a technical solution to solve the problem of the gap issue between the separator and the electrode so as to improve the service life of the lithium-ion battery.

SUMMARY OF THE APPLICATION

[0004] In order to solve the problem in the prior art, a porous film and a lithium-ion battery are provided according to the present application.

[0005] According to a first aspect of the application, a porous film is provided, including: a binder; and inorganic particles, wherein the porous film contains pores formed by the

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binder, the pores at least includes a part of the inorganic particles, and the average wall thickness between the pores is in a range of 20 nm to 500 nm.

[0006] In the porous film described above, the porous film has an average pore size of 0.3 μm to 20 μm.

[0007] In the porous film described above, the inorganic particles have particle sizes such that particle size having a volume accumulation of 10% (Dv10) is in a range of 0.015 μm to 3 μm, particle size having a volume accumulation of 50% (Dv50) is in a range of 0.2 μm to 5 μm, and particle size having a volume accumulation of 90% (Dv90) is in a range of 1 μm to 10 μm. Particle size having a volume accumulation of 10% (Dv10) refers to particle sizes which reach 10% of the cumulative volume from the side of small particle size in the granularity distribution on a volume basis. Particle size having a volume accumulation of 50% (Dv50) refers to particle sizes which reach 50% of the cumulative volume from the side of small particle size in the granularity distribution on a volume basis. Particle size having a volume accumulation of 90% (Dv90) refers to particle sizes which reach 90% of the cumulative volume from the side of small particle size in the granularity distribution on a volume basis.

[0008] In the porous film described above, particle size having a volume accumulation of 10% (Dv10) is less than particle size having a volume accumulation of 50% (Dv50), and particle size having a volume accumulation of 50% (Dv50) is less than particle size having a volume accumulation of 90% (Dv90).

[0009] In the porous film described above, the particle sizes of the inorganic particles satisfy that: the ratio of particle size having a volume accumulation of 90% (Dv90) to particle size having a volume accumulation of 10% (Dv10) is in a range of 2 to 100.

[0010] In the porous film described above, a pore size distribution coefficient (D) of the pores in the porous film is in a range of 1 to 5.

[0011] In the porous film described above, the inorganic particles are at least one of alumina, silica, magnesia, titanium oxide, hafnium dioxide, tin oxide, cerium dioxide, nickel oxide, zirconia, zinc oxide, calcium oxide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate.

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[0012] In the porous film described above, the binder is at least one of polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylic acid salt, sodium carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene.

[0013] In the porous film described above, the porous film has a porosity of 20% to 90%, and the porous film has a thickness of 0.2 to 10 μm.

[0014] In the porous film described above, a volume ratio of the inorganic particles to the binder is in a range of 0.2 to 3.0.

[0015] According to a second aspect of the application, a lithium-ion battery is provided, including: a positive electrode; a negative electrode; a separator arranged between the positive electrode and the negative electrode; and non-aqueous electrolyte; and a porous film, wherein the porous film is the porous film according to the first aspect of the application.

[0016] In the lithium-ion battery described above, the porous film is arranged on a surface of at least one of the positive electrode, the negative electrode and the separator.

[0017] The porous film provided by the application has excellent adhesion, and meanwhile the pore structure of the porous film can still be well maintained after being immersed in the electrolyte, thereby reducing the probability of pore blockage of the porous film and enabling the porous film to have high ionic conductivity. Therefore, the rate performance of the lithium-ion battery is greatly improved, and the provided lithium-ion battery has excellent rate performance and cycle performance.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

[0018] Fig 1 is an electronic microscope image (1000 times magnification) of the pore structure of the lower surface (namely, the surface of the porous film away from the porous substrate) of the porous film according to example 3.

[0019] Fig 2 is an electronic microscope image (5000 times magnification) of the pore structure of the lower surface of the porous film according to example 3.

[0020] Fig 3 is an electronic microscope image (1000 times magnification) of the pore

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structure of the lower surface of the porous film according to comparative example 3.

DETAILED DESCRIPTION OF THE PREFERRED EXAMPLES

[0021] Exemplary examples will be described in details below. While these exemplary examples may be implemented in various forms, the application should not be construed as limited to the examples of the application set forth herein. Rather, these examples are provided with the purpose of making the disclosure of the application thorough and complete and fully conveying the scope of the application to those skilled in the art.

[0022] According to a first aspect of the present application, a porous film is provided, including a binder and inorganic particles of different particle sizes, and the inorganic particles are fixed by the binder. Since the porous film includes the binder, the porous film has good adhesion, which can prevent the porous film from detaching during the use of the lithium-ion battery, and enables the lithium-ion battery to have a high safety performance. Moreover, the average pore size of the porous film is larger and the pore sizes are distributed uniformly, so that the porous film has good electrolyte diffusion and absorption capability and high ionic conductivity, the polarization reaction inside the lithium-ion battery can be reduced, thereby improving the rate performance of the lithium-ion battery. In addition, since the average wall thickness between the adjacent pores in the porous film is low, the binder (usually a polymer, for example, polyvinylidene fluoride) can be prevented from swelling in the electrolyte and blocking the pores of the porous film after the porous film is subjected to the soaking process in the electrolyte during the preparation of the lithium-ion battery. Therefore, the pore structure in the porous film can be more retained, smoothness of the lithium ion transport channel is ensured, and the polarization reaction inside the lithium-ion battery is reduced, thereby the rate performance of the lithium-ion battery can be further improved. In addition, due to the presence of inorganic particles in the porous film, the stability of the pore structure is enhanced. Therefore, the pore structure is not softened and closed after the soaking process in the electrolyte and the high-temperature and high-pressure process in the forming stage, the possibility of the pore structure being compressed and

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damaged is reduced, smoothness of the lithium ion transport channel is ensured, and the polarization reaction inside the lithium-ion battery is reduced, ensuring that the lithium-ion battery has a high rate performance.

[0023] In the porous film, inorganic particles are at least one of alumina, silica, magnesia, titanium oxide, hafnium dioxide, tin oxide, cerium dioxide, zirconia, nickel oxide, zinc oxide, calcium oxide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate. The inorganic particles may contain polar functional groups selected from a hydroxyl group. The surface of the inorganic particles containing polar functional groups is more easily combined with the non-solvent (third solvent) in the coagulating solution described below in the preparation process, which is advantageous for the diffusion of the third solvent into the porous film along the surface of the inorganic particles. Thus, large pore structures are formed in the vicinity of the inorganic particles, and the pore structures with large average pore sizes and small average wall thickness between the adjacent pores are easily obtained.

[0024] The particle sizes of the inorganic particles satisfy that the particle size having a volume accumulation of 10% (Dv10) is in a range of 0.015 μm to 3 μm, the particle size having a volume accumulation of 50% (Dv50) is in a range of 0.2 μm to 5 μm, and the particle size having a volume accumulation of 90% (Dv90) is in a range of 1 μm to 10 μm. The particle size (Dv10) having a volume accumulation of 10% refers to particle sizes which reach 10% of the cumulative volume from the side of small particle size in the granularity distribution on a volume basis. The particle size (Dv50) having a volume accumulation of 50% refers to particle sizes which reach 50% of the cumulative volume from the side of small particle size in the granularity distribution on a volume basis. The particle size (Dv90) having a volume accumulation of 90% refers to particle sizes which reach 90% of the cumulative volume from the side of small particle size in the granularity distribution on a volume basis. For example, the inorganic particles having large particle sizes and a narrow peak distribution are used, therefore the exchange speed between the non-solvent (third solvent) in the coagulation solution and the organic solvent (first solvent) in the coating solution can be increased during the formation of the porous film, and a porous film structure with a larger

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average pore size and smaller average wall thickness between the adjacent pores is formed. Within this range, if the particle sizes of the inorganic particles become smaller, the exchange speed between the non-solvent (third solvent) in the coagulation solution and the organic solvent (first solvent) in the coating solution is decreased during the formation of the porous film, the development of the pore structure is slower, the average pore size of the formed pore is decreased, and the average wall thickness between adjacent pores is increased. Conversely, if the particle sizes of the inorganic particles become larger, the exchange speed between the non-solvent (third solvent) in the coagulation solution and the organic solvent (first solvent) in the coating solution is increased, the development of the pore structure is faster, the average pore size of the formed pore is increased, and the average wall thickness between adjacent pores is decreased. However, if the particle sizes of the inorganic particles are too small and are beyond this range, the exchange between the non-solvent (third solvent) in the coagulation solution and the organic solvent (first solvent) in the coating solution will be adversely affected, and it is difficult to form a pore with a large average pore size. If the particle sizes of the inorganic particles are too large and are beyond this range, the surface of the formed porous film is not uniform, the strength of the porous film is decreased, and the adhesion force of the porous film is decreased.

[0025] In some examples, the inorganic particles have particle sizes such that Dv10 is in a range of 1.0 μm to 1.6 μm, Dv50 is in a range of 2.0 μm to 2.6 μm, and Dv90 is in a range of 3.0 μm to 4.0 μm.

[0026] In the above-described porous film, the particle size distribution of the inorganic particles satisfies Dv90/Dv10= 2~100. If Dv90/Dv10 is greater than 100, which will lead to the particle size distribution of the inorganic particles being too wide, the uniformity of the formed pores is poor, and polarization reactions will easily occur in the lithium-ion battery.

[0027] In the above-described porous film, the average wall thickness between adjacent pores is in a range of 20 nm to 500 nm, and the average pore size of the porous film is in a range of 0.3 μm to 20 μm. The average pore size of the porous film according to the present application is larger, so that the porous film has good electrolyte diffusion and absorption capability and high ionic conductivity, and the polarization reaction inside the lithium-ion

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battery can be reduced, thereby improving the rate performance of the lithium-ion battery. In addition, since the average wall thickness between adjacent pores in the porous film is low, the binder (typically a polymer, for example, polyvinylidene fluoride) can be prevented from swelling in the electrolyte and blocking the pores of the porous film after the porous film is subject to a soaking process in the electrolyte during the preparation of the lithium-ion battery. Therefore, the pore structure in the porous film can be maintained, smoothness of the lithium ion transport channel is ensured and the polarization reaction inside the lithium-ion battery is reduced, the rate performance of the lithium-ion battery can be further improved.

[0028] In the above-described porous film, the pore size distribution coefficient D of the pores in the porous film is in a range of 1 to 5. R10 represents pore sizes which reach 10% of the cumulative pore sizes from the side of small pore size in the pore size distribution curve (the pore sizes of 10% of the pores are less than R10). R90 represents pore sizes which reach 90% of the cumulative pore sizes from the side of small pore size in the pore size distribution curve (the pore sizes of 90% of the pores are less than R90). The pore size distribution coefficient D is equal to R90/R10. The closer to 1 the pore size distribution coefficient D is, the more uniform the pore sizes in the porous film will be, and thus the porous film will have better rate performance and cycle performance.

[0029] In the above-mentioned porous film, the porous film has a thickness of 0.2 μm to 10 μm. If the thickness of the porous film is larger, the gas permeability of the porous film becomes deteriorated, and the rate performance of the lithium-ion battery is decreased. If the thickness of the porous film is smaller, the adhesive force of the porous film is reduced, and the porous film tends to fall off due to a poor adhesive force when applied in a lithium-ion battery, resulting in deteriorated safety performance of the lithium-ion battery. In some examples, the porous film has a thickness of 1 μm to 3 μm.

[0030] In the above-described porous film, the porous film has a porosity of 20% to 90%. In some examples, the porous film has a porosity of 40% to 60%.

[0031] In the above-described porous film, the binder is at least one of polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylic acid salt, sodium carboxymethylcellulose,

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polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene.

[0032] In the above-described porous film, the volume ratio of the inorganic particles to the binder in the porous film is in a range of 0.2 to 3.0. If the volume ratio of them is lower than 0.2, the average pore size of the porous film is reduced, the porosity is decreased, and the rate performance of the lithium-ion battery is deteriorated drastically. If the volume ratio of them is greater than 3.0, the adhesive force of the porous film is reduced. When the porous film is applied to a lithium-ion battery, the porous film tends to fall off due to poor adhesion, resulting in deteriorated safety performance of the lithium-ion battery.

[0033] According to a second aspect of the present application, a method for preparing a porous film is provided, which is used for preparing the porous film according to the first aspect of the present application, including steps of: (1) mixing inorganic particles with a binder, and then adding a first solvent and uniformly stirring the mixture to obtain a coating solution, wherein the binder is dissolved in the first solvent; (2) uniformly coating the coating solution on at least one surface of a substrate to form a wet film; (3) immersing the substrate with the wet film into a coagulation solution for phase transformation, wherein the coagulation solution includes a second solvent and a third solvent, and the second solvent and the third solvent are miscible with each other; (4) performing a drying process after the phase transformation is completed, to obtain the substrate whose surface is provided with a porous film, wherein the average wall thickness between adjacent pores in the porous film is in a range of 20 nm to 500 nm, and the average pore size of the porous film is not less than 0.3 μm.

[0034] The above-mentioned substrate may be one of a separator, a positive electrode, and a negative electrode.

[0035] In the above-described method for preparing the porous film, the porous film is prepared using the principle of phase transformation (i.e., non-solvent induced phase separation, NIPS). In the coating solution obtained in the step (1), the first solvent is oily, and the binder (for example, polyvinylidene fluoride) may be dissolved in the first solvent. The third solvent contained in the coagulation solution in step (3) is one or more selected from

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deionized water, ethanol, propanol, acetone, dimethyl carbonate and diethyl carbonate, and the binder is insoluble in the third solvent (for example, deionized water). Therefore, after the coating solution is coated on the substrate and then immersed in the coagulation solution, since the first solvent in the coating solution is extracted into the third solvent (for example, deionized water) in the coagulation solution, the binder in the coating solution is coagulated and separated out, thus forming a porous film.

[0036] In the above-described preparation method for the porous film, in step (1), the first solvent is at least one of N-methylpyrrolidone (NMP), dimethylacetamide (DMAC), dimethylformamide (DMF), triethyl phosphate (TEP), and dimethyl sulfoxide (DMSO). The porous film formed using NMP has the largest average pore size and the highest porosity, the porous film formed using DMF has the smallest average pore size and the lowest porosity, and the porous film formed using DMAC has the average pore size and a porosity between that of the porous films formed using NMP and DMF respectively.

[0037] In the above-described method for preparing the porous film, the solid content of the coating solution in step (1) is in a range of 7% to 25%. Within this range, if the solid content of the coating solution is increased, the viscosity of the coating solution is increased, the exchange speed between the third solvent in the coagulation solution and the first solvent in the coating solution becomes lower, and both the average pore size and porosity of the formed porous film are decreased. Conversely, if the solid content of the coating solution is decreased, both the average pore size and porosity of the porous film are increased. However, if the solid content of the coating solution is too high and is beyond this range, the porous film cannot meet the requirement of gas permeability, and the porous film cannot be used in the lithium-ion battery; if the solid content of the coating solution is too low and is below this range, the strength of the porous film is decreased, and it is difficult to form a film on the surface of the substrate. In some examples, the coating solution has a solid content of 10% to 20%.

[0038] In the above-described method for preparing the porous film, the temperature of the coating solution in step (1) is in a range of 15 degrees Celsius to 30 degrees Celsius. In some examples, the temperature of the coating solution is in a range of 20 degrees Celsius to

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25 degrees Celsius.

[0039] In the above-described method for preparing the porous film, the coating of the coating solution in step (2) may be performed using a common coating method, such as roll coating, a gas knife coating, rod coating, scraper coating, gravure coating, screen coating, die coating, micro gravure coating, dip coating or the like. In some examples, the dip coating method is selected as the coating method of the coating solution.

[0040] In the above-described preparation method, the second solvent in step (3) is one or more selected from N-methylpyrrolidone (NMP), dimethylacetamide (DMAC), dimethylformamide (DMF), triethyl phosphate (TEP), and dimethyl sulfoxide (DMSO). The second solvent in step (3) may be the same as the first solvent added in step (1).

[0041] In the above-described preparation method, in step (3), the mass percentage of the second solvent in the coagulation solution is in a range of 20% to 60%. If the content of the second solvent in the coagulation solution is decreased, it is advantageous for the increase of the average pore size and porosity of the porous film. However, if the content of the second solvent is too low, a dense skin may be formed on the surface of the porous film which is away from the substrate, resulting in deteriorated gas permeability of the porous film. If the content of the second solvent is too high, a complete porous structure cannot be formed or the formed porous film has a very low average pore size and a high wall thickness. In some examples, the mass percentage of the second solvent in the coagulation solution is in a range of 30% to 40%.

[0042] In the above-described method for preparing the porous film, the temperature of the coagulation solution in step (3) is in a range of 15 degrees Celsius to 30 degrees Celsius. In some examples, the temperature of the coagulation solution is in a range of 20 degrees Celsius to 25 degrees Celsius.

[0043] In the above-described method for preparing the porous film, in step (3), the period for phase transformation is in a range of 10 s to 90 s. In some examples, the period for phase transformation is in a range of 20 s to 60 s.

[0044] In the above-described method for preparing the porous film, in step (4), the drying temperature is in a range of 60 degrees Celsius to 70 degrees Celsius, and the drying

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period is less than 1 min.

[0045] According to a third aspect of the present application, a separator including the porous film according to the first aspect of the present application is provided.

[0046] The separator includes a porous substrate and a porous film. The porous film is arranged on the surface of the porous substrate. In the above-described separator, there is no particular limitation on the type of the porous substrate, and it may be selected as actually required. Specifically, the porous substrate is at least one of polyethylene film (PE), polypropylene film (PP), polyethylene/polypropylene dual-layer film (PE/PP), polypropylene/polyethylene/polypropylene three-layer film (PP/PE/PP), non-woven fabric, polyimide, polyacrylonitrile porous film (PAN), and glass fiber film.

[0047] A method for preparing the above-described separator is further provided according to the present application, which is used for preparing the separator according to the third aspect of the present application, and which includes steps of: (1) mixing inorganic particles with a binder, and then adding a first solvent and uniformly stirring the mixture to obtain a coating solution, wherein the binder is dissolved in the first solvent; (2) uniformly coating the coating solution on a surface of the porous substrate (for example, polyethylene) to form a wet film; (3) immersing the porous substrate (for example, polyethylene) with the wet film into a coagulation solution for phase transformation, wherein the coagulation solution includes a second solvent and a third solvent, and the second solvent and the third solvent are miscible with each other; (4) performing a drying process after the phase transformation is completed to obtain a separator in which a porous film is arranged on the surface of the porous substrate (for example, polyethylene), wherein the average wall thickness between adjacent pores in the porous film is in a range of 20 nm to 500 nm, and the average pore size of the porous film is not less than 0.3 μm.

[0048] In the above-described method for preparing the separator, the parameter setting of the preparation process is consistent with that of the preparation process of the porous film according to the second aspect of the present application, and only the substrate is changed to porous substrate.

[0049] According to a fourth aspect of the present application, an electrode including the

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porous film according to the first aspect of the present application is provided. The electrode includes a current collector and an active material layer. The active material layer is arranged on the surface of the current collector, and the porous film is arranged on the surface of the active material layer which is away from the current collector.

[0050] In the above-described electrode, the electrode may be either a positive electrode or a negative electrode, depending on the current collector and the active material used. There is no particular limitation on the type of the current collector, and it can be selected as actually required. Specifically, the current collector is at least one of aluminum foil, copper foil, nickel foil, titanium foil, silver foil, nickel-copper alloy foil, aluminum-zirconium alloy foil , stainless steel foil and graphene film.

[0051] A method for preparing an electrode is further provided according to the application, which is used for preparing the electrode according to the fourth aspect of the present application, including steps of: (1) mixing inorganic particles with a binder, and then adding a first solvent and uniformly stirring the mixture to obtain a coating solution, wherein the binder is dissolved in the first solvent; (2) mixing an active material, a conductive agent and a binder, adding an organic solvent (such as N-methylpyrrolidone) into the mixture, uniformly stirring the mixture under the action of a vacuum stirrer to obtain an electrode slurry, and uniformly coating the electrode slurry on the current collector and then drying to form an active material layer (electrode) on the current collector; (3) uniformly coating the coating solution on the surface of the electrode to form a wet film; (4) immersing the electrode with the wet film into a coagulation solution for phase transformation, wherein the coagulation solution includes a second solvent and a third solvent, and the second solvent and the third solvent are miscible with each other; (5) performing a drying process after the phase transformation to obtain an electrode whose surface is provided with a porous film, wherein the average wall thickness between adjacent pores in the porous film is in a range of 20 nm to 500 nm, and the average pore size of the porous film is not less than 0.3 μm. The electrode may be either a positive electrode or a negative electrode.

[0052] In the method for preparing the electrode described above, the parameter setting of the preparation process is consistent with that of the preparation process of the porous film

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according to the second aspect of the present application.

[0053] According to a fifth aspect of the present application, a lithium-ion battery is provided. The lithium-ion battery includes the separator according to the third aspect of the present application, or includes the electrode according to the fourth aspect of the present application, or includes both the separator according to the third aspect of the present application and the electrode according to the fourth aspect of the present application. The electrode may be either a positive electrode or a negative electrode.

[0054] In the above-described lithium-ion battery, the positive electrode includes a positive electrode material capable of intercalation and deintercalation of lithium (Li) (hereinafter sometimes referred to as "positive electrode material capable of intercalation / deintercalation of lithium (Li)"). Examples of the positive electrode material capable of intercalation / deintercalation of lithium (Li) may include one or more of lithium cobaltate, nickel cobalt lithium manganate, nickel cobalt lithium aluminate, lithium manganate, iron manganese lithium phosphate, lithium vanadium phosphate, lithium oxide vanadium phosphate, lithium iron phosphate, lithium titanate, and lithium-rich manganese-based materials.

[0055] In the above-mentioned positive electrode material, the chemical formula of lithium cobaltate may be expressed as $Li_xCo_aM1_bO_{2-c}$, wherein M1 represents at least one selected from the group consisting of nickel (Ni), manganese (Mn), magnesium (Mg), aluminum (Al), boron (B), titanium (Ti), vanadium (V), chromium (Cr), ferrum (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), strontium (Sr), tungsten (W), yttrium (Y), lanthanum (La), zirconium (Zr), and silicon (Si), and the values of x, a, b, and c are respectively within the following ranges: $0.8\leq x\leq 1.2$, $0.8\leq a\leq 1$, $0\leq b\leq 0.2$, $-0.1\leq c\leq 0.2$.

[0056] In the above-mentioned positive electrode material, the chemical formula of nickel cobalt lithium manganate or nickel cobalt lithium aluminate may be expressed as $Li_yNi_dM2_eO_{2-f}$, wherein M2 represents at least one selected from the group consisting of cobalt (Co), manganese (Mn), magnesium (Mg), aluminum (Al) , boron (B), titanium (Ti), vanadium (V), chromium (Cr), ferrum (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), yttrium (Sr), tungsten (W), zirconium (Zr), and silicon (Si), and the

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values of y, d, e, and f are respectively within the following ranges: $0.8 \leq y \leq 1.2$, $0.3 \leq d \leq 0.98$, $0.02 \leq e \leq 0.7$, $-0.1 \leq f \leq 0.2$.

[0057] In the above-mentioned positive electrode material, the chemical formula of lithium manganate is expressed as $Li_zMn_{2-g}M3_gO_{4-h}$, wherein M3 represents at least one selected from the group consisting of cobalt (Co), nickel (Ni), magnesium (Mg), aluminum (Al), boron (B), titanium (Ti), vanadium (V), chromium (Cr), ferrum (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), strontium (Sr), and tungsten (W), and the values of z, g and h are respectively within the following ranges: $0.8 \leq z \leq 1.2$, $0 \leq g < 1.0$, and $-0.2 \leq h \leq 0.2$.

[0058] The negative electrode includes a negative electrode material capable of intercalation and deintercalation of lithium (Li) (hereinafter, sometimes referred to as "negative electrode material capable of intercalation/ deintercalation of lithium (Li)"). Examples of the negative electrode material capable of intercalation/deintercalation of lithium (Li) may include a carbon material, a metal compound, an oxide, a sulfide, a nitride of lithium such as LiN_3, lithium metal, a metal which formed an alloy with lithium, and a polymer material. Examples of carbon materials may include low graphitized carbon, easily graphitized carbon, artificial graphite, natural graphite, mesocarbon microbeads, soft carbon, hard carbon, pyrolytic carbon, coke, glassy carbon, organic polymer compound sintered body, carbon fiber and active carbon. Wherein coke may include pitch coke, needle coke, and petroleum coke. The organic polymer compound sintered body refers to materials obtained by calcining a polymer material such as a phenol plastic or a furan resin at a suitable temperature and carbonizing them, and some of these materials are classified into low graphitized carbon or easily graphitized carbon. Examples of polymeric materials may include polyacetylene and polypyrrole.

[0059] Among these negative electrode materials capable of intercalation /deintercalation of lithium (Li), further, materials whose charge and discharge voltages are close to the charge and discharge voltages of lithium metal are selected. This is because that the lower the charge and discharge voltages of the negative electrode material are, the more easily the battery can have a higher energy density. The carbon material can be selected as the negative electrode

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material, since the crystal structure of the carbon material has only small changes during charging and discharging. Therefore, good cycle characteristics and high charge and discharge capacities can be obtained. In particular, graphite can be selected, since it can provide a high electrochemical equivalent and energy density.

[0060] In addition, the negative electrode material capable of intercalation /deintercalation of lithium (Li) may include elemental lithium metal, metal elements and semi-metal elements capable of forming an alloy together with lithium (Li), alloys and compounds including such elements, etc. In particular, they are used together with the carbon material, since good cycle characteristics and high energy density can be obtained in this case. In addition to alloys including two or more metal elements, alloys used herein further include alloys including one or more metal elements and one or more semi-metal elements. The alloys may be in the following forms of solid solutions, eutectic crystals (eutectic mixtures), intermetallic compounds, and mixtures thereof. Examples of metal elements and semi-metal elements may include tin (Sn), lead (Pb), aluminum (Al), indium (In), silicon (Si), zinc (Zn), antimony (Sb), bismuth (Bi), cadmium (Cd), magnesium (Mg), boron (B), gallium (Ga), germanium (Ge), arsenic (As), silver (Ag), zirconium (Zr), yttrium (Y), and hafnium (Hf). Examples of the above-described alloys and compounds may include a material expressed as a chemical formula: $Ma_sMb_tLi_u$ and a material expressed as a chemical formula: $Ma_pMc_qMd_r$. In these chemical formulas, Ma represents at least one of metal elements and semi-metal elements capable of forming alloys with lithium, Mb represents at least one of these metal elements and semi-metal elements other than lithium and Ma, Mc represents at least one of the non-metal elements, Md represents at least one of these metal elements and semi-metal elements other than Ma, and s, t, u, p, q, and r satisfy $s>0$, $t\geq 0$, $u\geq 0$, $p>0$, $q>0$, and $r\geq 0$, respectively. In addition, an inorganic compound that does not include lithium (Li) may be used in the negative electrode, such as MnO_2, V_2O_5, V_6O_{13}, NiS, and MoS.

[0061] The lithium-ion battery described above further includes an electrolyte, which may be one or more of a gel electrolyte, a solid electrolyte, and an liquid electrolyte. The liquid electrolyte includes a lithium salt and a non-aqueous solvent.

[0062] The lithium salt is at least one of $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiClO_4$, $LiB(C_6H_5)_4$,

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$LiCH_3SO_3$, $LiCF_3SO_3$, $LiN(SO_2CF_3)_2$, $LiC(SO_2CF_3)_3$, $LiSiF_6$, LiBOB, and lithium difluoborate. For example, $LiPF_6$ is used as a lithium salt, since it can provide high ionic conductivity and improve cycle performance.

[0063] The non-aqueous solvent may be a carbonate compound, a carboxylic acid ester compound, an ether compound, other organic solvents or combinations thereof.

[0064] The carbonate compound may be a chain carbonate compound, a cyclic carbonate compound, a fluorinated carbonate compound or combinations thereof.

[0065] Examples of chain carbonate compounds include diethyl carbonate (DEC), dimethyl carbonate (DMC), dipropyl carbonate (DPC), methylpropyl carbonate (MPC), ethyl propyl carbonate (EPC), methyl ethyl carbonate (MEC) and combinations thereof. Examples of the cyclic carbonate compounds include ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), vinyl ethylene carbonate (VEC), and combinations thereof. Examples of the fluorocarbonate compound include fluoroethylene carbonate (FEC), 1,2-difluoroethylene carbonate, 1,1-difluoroethylene carbonate, 1,1,2-trifluoroethylene carbonate, 1,1,2,2-tetrafluoroethylene carbonate, 1-fluoro-2-methylethyl carbonate, 1-fluoro-1-methyl-ethylene carbonate, 1,2-difluoro-1-methylethylene carbonate, 1,1,2-trifluoro-2-methylethyl carbonate, trifluoromethyl ethylene carbonate, and combinations thereof.

[0066] Examples of carboxylic acid ester compounds include methyl acetate, ethyl acetate, n-propyl acetate, tert-butyl acetate, methyl propionate, ethyl propionate, γ-butyrolactone, decanolactone, valerolactone, mevalonolactone, caprolactone, methyl formate, and combinations thereof.

[0067] Examples of ether compounds include dibutyl ether, tetraethylene glycol dimethyl ether, diethylene glycol dimethyl ether, 1,2-dimethoxyethane, 1,2-diethoxyethane, ethoxy methoxy ethane, 2-methyltetrahydrofuran, tetrahydrofuran, and combinations thereof.

[0068] Examples of other organic solvents include dimethyl sulfoxide, 1,2-dioxolane, sulfolane, methyl sulfolane, 1,3-dimethyl-2-imidazolidinone, N-methyl-2-pyrrolidone, formamide, dimethylformamide, acetonitrile, trimethyl phosphate, triethyl phosphate, trioctyl phosphate, phosphate esters, and combinations thereof.

[0069] The electrode assembly of the lithium-ion battery to which the porous film of the

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present application is applied includes not only a wound type electrode assembly, but also a laminated (stacked) type electrode assembly and a folded type electrode assembly.

[0070] The present application is further described in details with examples below. It should be understood that these examples are only for illustrating the application but are not intended to limit the scope of the application. In the examples, only the case where the electrode assembly of the lithium-ion battery is wound type is illustrated, but the application is not limited thereto.

[0071] In the following examples, reagents, materials, and instruments used are commercially available unless otherwise specified.

[0072] Example 1

[0073] (1) Preparation of negative electrode

[0074] The negative electrode active material (artificial graphite), the binder (styrene-butadiene rubber), and the conductive agent (conductive carbon black (Super P)) are mixed uniformly with deionized water at a mass ratio of 92:3:5 to prepare a negative electrode slurry, then the negative electrode slurry is coated uniformly on front and rear surfaces of the negative electrode current collector copper foil, then a negative electrode active material layer is formed by drying the coated negative electrode current collector copper foil at 85 degrees Celsius, followed by cold pressing, slitting and cutting processes and a negative electrode tab is welded so as to obtain a negative electrode.

[0075] (2) Preparation of positive electrode

[0076] The positive electrode active material (lithium cobaltate ($LiCoO_2$)), the binder (polyvinylidene fluoride (PVDF)) and the conductive agent (conductive carbon black (Super P)) are dissolved in the solvent (N-methylpyrrolidone (NMP)) at a mass ratio of 97:1.5:1.5. A positive electrode slurry is prepared by stirring uniformly the mixture, then the positive electrode slurry is coated uniformly on front and rear surfaces of the positive electrode current collector aluminum foil, then a positive electrode active material layer is formed by drying the coated positive electrode current collector aluminum foil at 85 degrees Celsius, followed by cold pressing, slitting and cutting processes and a positive electrode tab is welded so as to obtain a positive electrode.

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[0077] (3) Preparation of separator

[0078] Inorganic particles (boehmite) are mixed with the binder (polyvinylidene fluoride) at a volume ratio of 1.2, and then N-methylpyrrolidone (first solvent) is added and uniformly stirred to obtain a coating solution, wherein the coating solution has a solid content of 7%. The coating solution is coated onto a porous substrate (polyethylene) using the dip coating method to form a wet film. The porous substrate (polyethylene) with a wet film is immersed in a coagulation solution containing deionized water (third solvent) and N-methylpyrrolidone (NMP, second solvent) for phase transformation, wherein the mass percentage of N-methylpyrrolidone (second solvent) in the coagulation solution is 40%, and the coating solution and the coagulation solution are at the temperature of 25 degrees Celsius. After being immersed in the coagulation solution for 30 seconds, the porous substrate (polyethylene) with a wet film is dried in an oven at 60 degrees Celsius to obtain a separator with a porous film. The particle size distribution of inorganic particles (boehmite) is such that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0079] (4) Preparation of electrolyte

[0080] A solution prepared with lithium salt $LiPF_6$ and a non-aqueous organic solvent (ethylene carbonate (EC): diethyl carbonate (DEC): ethyl methyl carbonate (EMC): vinylene carbonate (VC) = 8:85:5:2, by mass ratio) at a mass ratio of 8:92 is used as the electrolyte.

[0081] (5) Preparation of lithium-ion battery

[0082] An electrode assembly is obtained by winding the positive electrode, the separator and the negative electrode, and followed by packaging, injection of the electrolyte, forming, and suction molding processes are performed to obtain the lithium-ion battery.

[0083] Example 2

[0084] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 10%.

[0085] Example 3

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[0086] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%.

[0087] Example 4

[0088] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 20%.

[0089] Example 5

[0090] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 25%.

[0091] Example 6

[0092] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and dimethylacetamide (DMAC) is selected as the second solvent.

[0093] Example 7

[0094] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and dimethylformamide (DMF) is selected as the second solvent.

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[0095] Example 8

[0096] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and the particle size distribution of inorganic particles (boehmite) is that Dv10 is 0.015 μm, Dv50 is 0.2 μm and Dv90 is 1.5 μm.

[0097] Example 9

[0098] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and the particle size distribution of inorganic particles (boehmite) is that Dv10 is 0.2 μm, Dv50 is 1.0 μm and Dv90 is 2.0 μm.

[0099] Example 10

[0100] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and the particle size distribution of inorganic particles (boehmite) is that Dv10 is 1.6 μm, Dv50 is 2.6 μm and Dv90 is 4.6 μm.

[0101] Example 11

[0102] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and the particle size distribution of inorganic particles (boehmite) is that Dv10 is 2.2 μm, Dv50 is 3.5 μm and Dv90 is 5.8 μm.

[0103] Example 12

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[0104] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and the particle size distribution of inorganic particles (boehmite) is that Dv10 is 3.0 μm, Dv50 is 5.0 μm and Dv90 is 10.0 μm.

[0105] Example 13

[0106] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and the mass percentage of N-methylpyrrolidone in the coagulation solution is 20%.

[0107] Example 14

[0108] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, and the mass percentage of N-methylpyrrolidone in the coagulation solution is 60%.

[0109] Example 15

[0110] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 15%, alumina is selected as inorganic particles, and the particle size distribution of alumina particles is that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0111] Example 16

[0112] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the

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same as that described in Example 1, except that the solid content of the coating solution is 15%, magnesium hydroxide is selected as inorganic particles, and the particle size distribution of magnesium hydroxide particles is that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0113] Example 17

[0114] (1) Preparation of negative electrode

[0115] The negative electrode active material (artificial graphite), the binder (styrene-butadiene rubber), and the conductive agent (conductive carbon black (Super P)) are mixed uniformly with deionized water at a mass ratio of 92:3:5 to prepare a negative slurry, then the negative slurry is coated uniformly on front and rear surfaces of the negative electrode current collector copper foil, then a negative electrode active material layer is formed by drying the coated negative electrode current collector copper foil at 85 degrees Celsius, followed by cold pressing, slitting and cutting processes and a negative electrode tab is welded to obtain a negative electrode.

[0116] (2) Preparation of positive electrode

[0117] The positive electrode active material (lithium cobaltate ($LiCoO_2$)), the binder (polyvinylidene fluoride (PVDF)), and the conductive agent (conductive carbon black (Super P)) are dissolved in the solvent (N-methylpyrrolidone (NMP)) at a mass ratio of 97:1.5:1.5. A positive slurry is prepared by stirring uniformly the mixture, then the positive slurry is coated uniformly on front and rear surfaces of the positive electrode current collector (aluminum foil), then a positive electrode active material layer is formed by drying the coated positive electrode current collector aluminum foil at 85 degrees Celsius. Inorganic particles (boehmite) are mixed with the binder PVDF at a volume ratio of 1.2, and then N-methylpyrrolidone (first solvent) is added and uniformly stirred to obtain a coating solution, wherein the coating solution has a solid content of 15 %. The coating solution is coated onto the positive electrode current collector on which a positive electrode active material layer is arranged by the dip coating method to form a wet film. The positive electrode current collector with a wet film is then immersed in a coagulation solution containing deionized water (third solvent) and N-methylpyrrolidone (second solvent) for phase transformation,

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wherein the mass percentage of N-methylpyrrolidone in the coagulation solution is 40%, and the coating solution and the coagulation solution are both at the temperature of 25 degrees Celsius. After being immersed in the coagulation solution for 30 seconds, the positive electrode current collector with a wet film is dried in an oven at 60 degrees Celsius, then cold pressing, slitting and cutting processes are performed and a positive electrode tab is welded to obtain a positive electrode with a porous film. The particle size distribution of inorganic particles (boehmite) is such that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0118] (3) Preparation of separator

[0119] A polyethylene porous substrate is used as a separator.

[0120] (4) Preparation of electrolyte

[0121] A solution prepared with lithium salt $LiPF_6$ and a non-aqueous organic solvent (ethylene carbonate (EC): diethyl carbonate (DEC): ethyl methyl carbonate (EMC): vinylene carbonate (VC) = 8:85:5:2, by a mass ratio) at a mass ratio of 8:92 is used as the electrolyte.

[0122] (5) Preparation of lithium-ion battery

[0123] An electrode assembly is obtained by winding the positive electrode, the separator and the negative electrode, and then packaging, injection of the electrolyte, forming, and suction molding processes are performed to obtain the lithium-ion battery.

[0124] Example 18

[0125] (1) Preparation of negative electrode

[0126] The negative electrode active material (artificial graphite), the binder (styrene-butadiene rubber), and the conductive agent (conductive carbon black (Super P)) are mixed uniformly with the solvent (N-methylpyrrolidone (NMP)) at a mass ratio of 92:3:5 to prepare a negative slurry, then the negative slurry is coated uniformly on front and rear surfaces of the negative electrode current collector (copper foil), then a negative electrode active material layer is formed by drying the coated negative electrode current collector copper foil at 85 degrees Celsius. Inorganic particles (boehmite) are mixed with the binder (PVDF) at a volume ratio of 1.2, and then N-methylpyrrolidone (first solvent) is added and uniformly stirred to obtain a coating solution, wherein the coating solution has a solid content of 15 %. The coating solution is coated onto the negative electrode current collector on which the

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negative electrode active material layer is provided by the dip coating method to form a wet film. The negative electrode current collector with a wet film is then immersed in a coagulation solution containing deionized water (third solvent) and N-methylpyrrolidone (second solvent) for phase transformation, wherein the mass percentage of N-methylpyrrolidone in the coagulation solution is 40%, and the coating solution and the coagulation solution are both at the temperature of 25 degrees Celsius. After being immersed in the coagulation solution for 30 seconds, the negative electrode current collector with a wet film is dried in an oven at 60 degrees Celsius, and then cold pressing, slitting and cutting processes are performed and a negative electrode tab is welded to obtain a negative electrode. The particle size distribution of inorganic particles (boehmite) is such that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0127] (2) Preparation of positive electrode

[0128] The positive electrode active material (lithium cobaltate ($LiCoO_2$)), the binder (polyvinylidene fluoride (PVDF)), and the conductive agent (conductive carbon black (Super P)) are dissolved in the solvent (N-methylpyrrolidone (NMP)) at a mass ratio of 97:1.5:1.5. A positive slurry is prepared by stirring uniformly the mixture, then the positive slurry is coated uniformly on front and rear surfaces of the positive electrode current collector aluminum foil, then a positive electrode active material layer is formed by drying the coated positive electrode current collector aluminum foil at 85 degrees Celsius, and then cold pressing, slitting and cutting processes are performed and a positive electrode tab is welded to obtain a positive electrode.

[0129] (3) Preparation of separator

[0130] A polyethylene porous substrate is used as a separator.

[0131] (4) Preparation of electrolyte

[0132] A solution prepared with lithium salt $LiPF_6$ and a non-aqueous organic solvent (ethylene carbonate (EC): diethyl carbonate (DEC): ethyl methyl carbonate (EMC): vinylene carbonate (VC) = 8:85:5:2, by a mass ratio) at a mass ratio of 8:92 is used as the electrolyte.

[0133] (5) Preparation of lithium-ion battery

[0134] An electrode assembly is obtained by winding the positive electrode, the separator

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and the negative electrode, and packaging, injection of the electrolyte, forming, and suction molding processes are performed to obtain the lithium-ion battery.

[0135] Example 19

[0136] (1) Preparation of negative electrode

[0137] The negative electrode active material (artificial graphite), the binder (styrene-butadiene rubber), and the conductive agent (conductive carbon black (Super P)) are mixed uniformly with the solvent (N-methylpyrrolidone (NMP)) at a mass ratio of 92:3:5 to prepare a negative slurry, then the negative slurry is coated uniformly on front and rear surfaces of the negative electrode current collector (copper foil), then a negative electrode active material layer is formed by drying the coated negative electrode current collector copper foil at 85 degrees Celsius, then cold pressing, slitting and cutting processes are performed and a negative electrode tab is welded to obtain a negative electrode.

[0138] (2) Preparation of positive electrode

[0139] The positive electrode active material (lithium cobaltate ($LiCoO_2$)), the binder (polyvinylidene fluoride (PVDF)) and the conductive agent (conductive carbon black (Super P)) are dissolved in the solvent (N-methylpyrrolidone (NMP)) at a mass ratio of 97:1.5:1.5. A positive slurry is prepared by stirring uniformly the mixture, then the positive slurry is coated uniformly on front and rear surfaces of the positive electrode current collector aluminum foil, then a positive electrode active material layer is formed by drying the coated positive electrode current collector aluminum foil at 85 degrees Celsius. Inorganic particles (boehmite) are mixed with the binder (PVDF) at a volume ratio of 1.2, and then N-methylpyrrolidone (first solvent) is added and uniformly stirred to obtain a coating solution, wherein the coating solution has solid content of 15%. The coating solution is coated onto the positive electrode current collector on which the positive electrode active material layer is provided by the dip coating method to form a wet film. The positive electrode current collector with a wet film is then immersed in a coagulation solution containing deionized water (third solvent) and N-methylpyrrolidone (second solvent) for phase transformation, wherein the mass percentage of N-methylpyrrolidone in the coagulation solution is 40%, and the coating solution and the coagulation solution are both at the temperature of 25 degrees

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Celsius. After being immersed in the coagulation solution for 30 seconds, the positive electrode current collector with a wet film is dried in an oven at 60 degrees Celsius, and then cold pressing, slitting and cutting processes are performed and a positive electrode tab is welded to obtain a positive electrode with a porous film. The particle size distribution of inorganic particles boehmite is such that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0140] (3) Preparation of separator

[0141] Inorganic particles (boehmite) are mixed with the binder (PVDF) at a volume ratio of 1.2, and then N-methylpyrrolidone (first solvent) is added and uniformly stirred to obtain a coating solution, wherein the coating solution has a solid content of 15 %. The coating solution is coated onto a porous substrate (polyethylene) by the dip coating method to form a wet film. The porous substrate (polyethylene) with a wet film is immersed in a coagulation solution containing deionized water (third solvent) and N-methylpyrrolidone (second solvent) for phase transformation, wherein the mass percentage of N-methylpyrrolidone in the coagulation solution is 40%, and the coating solution and the coagulation solution are both at the temperature of 25 degrees Celsius. After being immersed in the coagulation solution for 30 seconds, the porous substrate (polyethylene) with a wet film is dried in an oven at 60 degrees Celsius to obtain a separator with a porous film. The particle size distribution of inorganic particles (boehmite) is such that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0142] (4) Preparation of electrolyte

[0143] A solution prepared with lithium salt $LiPF_6$ and a non-aqueous organic solvent (ethylene carbonate (EC): diethyl carbonate (DEC): ethyl methyl carbonate (EMC): vinylene carbonate (VC) = 8:85:5:2, by a mass ratio) at a mass ratio of 8:92 is used as the electrolyte.

[0144] (5) Preparation of lithium-ion battery

[0145] An electrode assembly is obtained by winding the positive electrode, the separator and the negative electrode, and then packaging, injection of the electrolyte, forming, and suction molding processes are performed to obtain the lithium-ion battery.

[0146] Example 20

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[0147] (1) Preparation of negative electrode

[0148] The negative electrode active material (artificial graphite), the binder (styrene-butadiene rubber), and the conductive agent (conductive carbon black (Super P)) are mixed uniformly with the solvent (N-methylpyrrolidone (NMP)) at a mass ratio of 92:3:5 to prepare a negative slurry, then the negative slurry is coated uniformly on front and rear surfaces of the negative electrode current collector copper foil, and then a negative electrode active material layer is formed by drying the coated negative electrode current collector copper foil at 85 degrees Celsius. Inorganic particles (boehmite) are mixed with the binder (PVDF) at a volume ratio of 1.2, and then N-methylpyrrolidone (first solvent) is added and uniformly stirred to obtain a coating solution, wherein the coating solution has a solid content of 15 %. The coating solution is coated onto the negative electrode current collector on which the negative electrode active material layer is provided by the dip coating method to form a wet film. The negative electrode current collector with a wet film is immersed in a coagulation solution containing deionized water (third solvent) and N-methylpyrrolidone (second solvent) for phase transformation, wherein the mass percentage of N-methylpyrrolidone in the coagulation solution is 40%, and the coating solution and the coagulation solution are both at the temperature of 25 degrees Celsius. After being immersed in the coagulation solution for 30 seconds, the negative electrode current collector with a wet film is dried in an oven at 60 degrees Celsius, then cold pressing, slitting and cutting processes are performed and a negative electrode tab is welded to obtain a negative electrode with a porous film. The particle size distribution of inorganic particles (boehmite) is such that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0149] (2) Preparation of positive electrode

[0150] The positive electrode active material (lithium cobaltate ($LiCoO_2$)), the binder (polyvinylidene fluoride (PVDF)), and the conductive agent (conductive carbon black (Super P)) are dissolved in the solvent (N-methylpyrrolidone (NMP)) at a mass ratio of 97:1.5:1.5. A positive slurry is prepared by stirring uniformly the mixture, then the positive slurry is coated uniformly on front and rear surfaces of the positive electrode current collector aluminum foil, then a positive electrode active material layer is formed by drying the coated positive

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electrode current collector aluminum foil at 85 degrees Celsius, then cold pressing, slitting and cutting processes are performed and a positive electrode tab is welded to obtain a positive electrode.

[0151] (3) Preparation of separator

[0152] Inorganic particles (boehmite) are mixed with the binder (PVDF) at a volume ratio of 1.2, and then N-methylpyrrolidone (first solvent) is added and uniformly stirred to obtain a coating solution, wherein the coating solution has a solid content of 15%. The coating solution is coated onto a porous substrate (polyethylene) using the dip coating method to form a wet film. The porous substrate (polyethylene) with a wet film is immersed in a coagulation solution containing deionized water (third solvent) and N-methylpyrrolidone (second solvent) for phase transformation, wherein the mass percentage of N-methylpyrrolidone in the coagulation solution is 40%, and the coating solution and the coagulation solution are both at the temperature of 25 degrees Celsius. After being immersed in the coagulation solution for 30 seconds, the porous substrate (polyethylene) with a wet film is dried in an oven at 60 degrees Celsius to obtain a separator with a porous film. The particle size distribution of inorganic particles (boehmite) is such that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0153] (4) Preparation of electrolyte

[0154] A solution prepared with lithium salt $LiPF_6$ and a non-aqueous organic solvent (ethylene carbonate (EC): diethyl carbonate (DEC): ethyl methyl carbonate (EMC): vinylene carbonate (VC) = 8:85:5:2, by a mass ratio) at a mass ratio of 8:92 is used as the electrolyte.

[0155] (5) Preparation of lithium-ion battery

[0156] An electrode assembly is obtained by winding the positive electrode, the separator and the negative electrode, and then packaging, injection of the electrolyte, forming, and suction molding processes are performed to obtain the lithium-ion battery.

[0157] Comparative example 1

[0158] In this comparative example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1.

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[0159] The separator is prepared as follows.

[0160] The boehmite and polyvinylidene fluoride at a volume ratio of 1.2 are added into deionized water and uniformly mixed to prepare a slurry, and the solid content of the slurry is 45%. Then, the slurry is uniformly coated onto front and rear surfaces of the porous substrate (polyethylene) using the micro gravure coating method to form a wet film. After the wet film is dried in an oven, a separator is obtained. The particle size distribution of inorganic particles (boehmite) is that Dv10 is 0.9 μm, Dv50 is 1.8 μm and Dv90 is 3.0 μm.

[0161] Comparative example 2

[0162] In this comparative example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 4%.

[0163] Comparative example 3

[001] In this example, the preparation methods for the negative electrode, the positive electrode, the electrolyte, and the lithium-ion battery are the same as the corresponding preparation methods described in Example 1. The preparation method of the separator is the same as that described in Example 1, except that the solid content of the coating solution is 30%.

[0164] Parameters of Examples 1-20 and comparative examples 1-3 are shown in Table 1 below.

Table 1

	Position of porous film	Solid content of the coating solution	Inorganic particle/ μm				Second solvent	Content of second solvent in coagulation solution
			Type	Dv10	Dv50	Dv90		
Example 1	surfaces of separator	7%	boehmite	0.9	1.8	3.0	NMP	40%
Example 2	surfaces of separator	10%	boehmite	0.9	1.8	3.0	NMP	40%
Example 3	surfaces of separator	15%	boehmite	0.9	1.8	3.0	NMP	40%
Example 4	surfaces of separator	20%	boehmite	0.9	1.8	3.0	NMP	40%

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Example 5	surfaces of separator	25%	boehmite	0.9	1.8	3.0	NMP	40%
Example 3	surfaces of separator	15%	boehmite	0.9	1.8	3.0	NMP	40%
Example 6	surfaces of separator	15%	boehmite	0.9	1.8	3.0	DMAC	40%
Example 7	surfaces of separator	15%	boehmite	0.9	1.8	3.0	DMF	40%
Example 8	surfaces of separator	15%	boehmite	0.015	0.2	1.5	NMP	40%
Example 9	surfaces of separator	15%	boehmite	0.2	1.0	2.0	NMP	40%
Example 3	surfaces of separator	15%	boehmite	0.9	1.8	3.0	NMP	40%
Example 10	surfaces of separator	15%	boehmite	1.6	2.6	4.6	NMP	40%
Example 11	surfaces of separator	15%	boehmite	2.2	3.5	5.8	NMP	40%
Example 12	surfaces of separator	15%	boehmite	3.0	5.0	10.0	NMP	40%
Example 13	surfaces of separator	15%	boehmite	0.9	1.8	3.0	NMP	20%
Example 3	surfaces of separator	15%	boehmite	0.9	1.8	3.0	NMP	40%
Example 14	surfaces of separator	15%	boehmite	0.9	1.8	3.0	NMP	60%
Example 15	surfaces of separator	15%	alumina	0.9	1.8	3.0	NMP	40%
Example 16	surfaces of separator	15%	magnesium hydroxide	0.9	1.8	3.0	NMP	40%
Example 3	surfaces of separator	15%	boehmite	0.9	1.8	3.0	NMP	40%
Example 17	surfaces of positive electrode	15%	boehmite	0.9	1.8	3.0	NMP	40%

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Example 18	surfaces of negative electrode	15%	boehmite	0.9	1.8	3.0	NMP	40%
Example 19	surfaces of separator and positive electrode	15%	boehmite	0.9	1.8	3.0	NMP	40%
Example 20	surfaces of separator and negative electrode	15%	boehmite	0.9	1.8	3.0	NMP	40%
Comparative Example 1	surfaces of separator	/	boehmite	0.9	1.8	3.0	/	/
Comparative Example 2	surfaces of separator	4%	boehmite	0.9	1.8	3.0	NMP	40%
Comparative Example 3	surfaces of separator	30%	boehmite	0.9	1.8	3.0	NMP	40%

[0165] Performance test

[0166] The performances of the porous film and the lithium-ion battery including the porous film prepared in Examples 1-20 and comparative examples 1-3 are tested, and the test method is described as follows.

[0167] (1) Thickness test of porous film

[0168] A separator sample or an electrode sample provided with a porous film is placed on a thickness gauge (Model VL-50 LITEMATIC from Naitutoyo company) using a 5 mm flat bottom probe with a speed of 50 mm/min and a pressure of 0.01 N. Each separator sample or electrode sample provided with the porous film is measured for 60 thickness points, and the average thickness is taken as the measured value. The thickness of the porous film is equal to the thickness of the separator or the electrode coated with the porous film minus the thickness of the separator sample or the electrode sample without the porous film. In a case that there are two porous films, the thickness is divided by 2 to obtain the thickness of each porous layer.

[0169] (2) Gas permeability test of porous film

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[0170] A 100mm x 100mm separator sample provided with a porous film is cut and tested using a US Gurley 4110 N permeability tester with a test gas of 100 cc, and the period that the test gas passes completely through the separator provided with the porous film is recorded as a Gurley value. The Gurley value of the porous film is equal to the Gurley value of the separator provided with the porous film minus the Gurley value of the separator without the porous film (i.e., a pure porous substrate). In a case that the electrode includes a porous film, since the current collector itself is gas-tight, the gas permeability of the porous film cannot be evaluated according to such a method.

[0171] (3) Porosity test of porous film

[0172] The length, width, and thickness of a separator sample or an electrode sample provided with a porous film are measured, the thickness of the porous film is obtained using the above-described method, and the apparent volume V1 of the porous film is obtained through calculation. The true volume V20 of the separator sample or the electrode sample provided with the porous film is measured using a true density meter (AccuPyc II Model 1340 Gas Pycnometer, Micromeritics Company), and the true volume V0 of the separator sample or the electrode sample without the porous film having the same area is measured. The true volume V2 of the porous film is equal to V20-V0, and the porosity of the porous film is equal to 1-V2/V1.

[0173] (4) Average pore size test of porous film

[0174] The area of the porous film that needs to be measured is observed using the Model Sigma-02-33 Scanning Electron Microscope from Zeiss, and images are saved. The maximum diameter L1 in the transverse direction and the maximum diameter L2 in the longitudinal direction for each pore in the images are measured, and the pore size of the pore is equal to (L1+L2)/2. Pore sizes of 200 adjacent pores are measured and an average value thereof is taken as the average pore size of the porous film.

[0175] (5) Pore size distribution coefficient test of porous film

[0176] The area of the porous film that needs to be measured is observed using the Model Sigma-02-33 Scanning Electron Microscope from Zeiss, and images are saved. Pore sizes of 200 adjacent pores are measured to obtain a pore size distribution curve. R10 represents pore

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sizes which reach 10% of the cumulative pore sizes from the side of small pore size in the pore size distribution curve (the pore sizes of 10% of the pores are less than R10). R90 represents pore sizes which reach 90% of the cumulative pore sizes from the side of small pore size in the pore size distribution curve (the pore sizes of 90% of the pores are less than R90). The pore size distribution coefficient D is equal to R90/R10. The closer to 1 the pore size distribution coefficient D is, the more uniform the pore sizes will be. The higher the pore size distribution coefficient D is, the poorer the uniformity of the pore sizes will be.

[0177] (6) Average wall thickness test between adjacent pores in the porous film

[0178] The area of the porous film that needs to be measured is observed using the Model Sigma-02-33 Scanning Electron Microscope from Zeiss, and images are saved. The wall thicknesses between each two adjacent pores among 200 adjacent pores are measured and an average value thereof is taken as the average wall thickness between adjacent pores in the porous film.

[0179] (7) Rate performance test of lithium-ion battery

[0180] At 25 degrees Celsius, the lithium-ion battery is discharged to 3.0 V at a constant current of 0.2 C, rested for 10 minutes, then charged to 4.4 V at a constant current of 0.7 C, then charged to 0.02 C at a constant voltage of 4.4 V, and rested for 10 min, and is further discharged at a constant current of 0.2 C until the voltage is 3.0 V. The discharge capacity at this point is measured and recorded as Q1. Then, the lithium-ion battery is charged to 4.4 V at a constant current of 0.7C, is then charged to 0.02C at a constant voltage of 4.4 V, rested for 10 minutes, then discharged at a constant current of 2 C until the voltage is 3.0 V. The discharge capacity at this point is measured and recorded as Q2.

[0181] 2 C/0.2 C rate performance (%) of the lithium-ion battery is equal to Q2/Q1 x 100%.

[0182] (8) Cycle performance test of lithium-ion battery

[0183] At 25 degrees Celsius, the lithium-ion battery is charged to 4.4 V at a constant current of 0.7 C, is then charged to 0.02 C at a constant voltage of 4.4 V, rested for 10 minutes, is discharged to 3.0 V at a constant current of 1 C, and rested for 10 minutes. The discharge capacity at this point is measured and recorded as Q3. The above-described

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procedures are regarded as one cycle of charge and discharge; 200 cycles are performed, and the discharge capacity after the 200 cycles is recorded as Q4.

[0184] The capacity retention rate (%) of the lithium-ion battery after 200 cycles is equal to Q4/Q3 x 100%.

[0185] Test results

[0186] The measured results of Examples 1-20 and comparative examples 1-3 are shown in Table 2 below.

Table 2

	Porous film						Lithium-ion battery	
	Gurley value (s/100cc)	Thickness (μm)	Porosity	Average pore size(μm)	Pore size distribution coefficient D	Average wall thickness (nm)	Rate performance	Cycle performance
Example 1	24	2.4	58%	12	1.5	20	80.50%	86.70%
Example 2	28	2.4	55%	7.8	2.1	90	84.20%	91.10%
Example 3	32	2.4	53%	5	2.5	180	87.30%	95.30%
Example 4	41	2.4	49%	3.6	3.6	320	83.90%	90.70%
Example 5	55	2.4	46%	1.5	4.5	500	79.70%	85.30%
Example 3	32	2.4	53%	5	2.5	180	87.30%	95.30%
Example 6	35	2.4	52%	4.5	3	220	85.10%	92.30%
Example 7	39	2.4	50%	3.7	3.2	300	82.90%	90.00%
Example 8	45	2.4	48%	3.0	3.8	410	84.50%	91.50%
Example 9	40	2.4	50%	4.0	3.4	320	85.40%	92.10%
Example 3	32	2.4	53%	5	2.5	180	87.30%	95.30%
Example 10	30	3.0	54%	5.5	2.2	160	86.30%	92.40%
Example 11	28	4.0	55%	6.9	2.0	100	82.40%	89.80%
Example 12	26	8.0	57%	8.9	1.8	70	80.20%	86.50%
Example 13	39	2.4	51%	8.1	3.6	50	82.20%	89.30%
Example 3	32	2.4	53%	5	2.5	180	87.30%	95.30%

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Example 14	34	2.4	52%	3.5	2.3	300	84.10%	90.20%
Example 15	43	2.4	49%	2.5	3.0	240	80.20%	85.20%
Example 16	38	2.4	51%	3.1	2.9	230	85.20%	89.70%
Example 3	32	2.4	53%	5	2.5	180	87.30%	95.30%
Example 17	/	2.4	53%	4.9	2.6	180	86.90%	94.60%
Example 18	/	2.4	53%	5.1	2.6	180	87.20%	94.90%
Example 19	/	2.4	53%	4.9	2.7	180	85.50%	93.50%
	32	2.4	53%	5	2.5	180		
Example 20	/	2.4	53%	5.1	2.6	180	85.70%	92.90%
	32	2.4	53%	5	2.4	180		
Example 1	36	2.4	46%	/	/	/	68.80%	70.10%
Example 2	20	2.4	61%	18	1.3	12	73.70%	76.30%
Example 3	91	2.4	42%	0.5	5.3	600	72.70%	73.60%

[0187] As can be seen from the relevant data in Table 2 above, the porous film according to the Examples of the present application has a higher porosity, and the lithium-ion battery has better rate performance and cycle performance.

[0188] As can be seen from the analysis of the relevant data of Examples 1-5 and comparative examples 2-3, if the solid content of the coating solution is increased, the viscosity of the coating solution is increased, the exchange speed between the non-solvent (third solvent) in the coagulation solution and the organic solvent (first solvent) in the coating solution becomes lower, the average pore size of the formed porous film is decreased, the average wall thickness between the adjacent pores is increased, the porosity of the porous film is decreased, and the gas permeability of the porous film is deteriorated. However, if the solid content of the coating solution is too low (for example, comparative example 2), it is difficult to form a porous film, and the electrochemical performance of the lithium-ion battery is drastically degraded. The porous film in Example 3 has a larger average pore size, uniform pore size distribution, and a small average wall thickness between adjacent pores. If the solid content of the coating solution is too high (for example, comparative example 3), the porosity of the porous film is too low and the gas permeability of the porous film is very

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poor. Referring to Fig 3, it can be seen that a small pore size structure tends to be formed in the porous film, and the average wall thickness between the adjacent pores is large, which seriously affects the cycle performance and rate performance of the lithium-ion battery.

[0189] As can be seen from the analysis of the relevant data of Example 3 and Examples 15 and 16, the rate performance and cycle performance of the lithium-ion battery is more significantly improved with the inorganic particles containing polar functional groups. This is because the surface of the inorganic particles containing polar functional groups is more easily combined with the non-solvent (third solvent), i.e., deionized water in the coagulating solution, which is advantageous for the diffusion of the deionized water into the porous film along the surface of the inorganic particles, and thus large pore structures are formed in the vicinity of the inorganic particles, and the pore structures with large average pore sizes and a small average wall thickness between the adjacent pores are easily obtained.

[0190] As can be seen from the analysis of the relevant data of Example 3, Example 6 and Example 7, if different organic solvents (second solvent) are selected, the pore structures in the obtained porous films are also different. The porous film formed with NMP has the largest average pore size and the highest porosity, the porous film formed with DMF has the smallest average pore size and the lowest porosity, and the porous film formed with DMAC has the average pore size and a porosity between those of the porous films formed with NMP and DMF respectively.

[0191] As can be seen from the analysis of the relevant data of Example 3 and Examples 8-12, the particle size of the inorganic particles has an effect on the improvement of the rate performance and cycle performance of the lithium-ion battery. If the particle size of the inorganic particles is increased, the exchange speed between the non-solvent (third solvent) in the coagulation solution and the organic solvent (first solvent) in the coating solution is increased, the development of the pore structure is faster, the average pore size of the formed pore is increased, and the average wall thickness between adjacent pores is decreased.

[0192] As can be seen from the analysis of the relevant data of Example 3 and Examples 13-14, the content of the organic solvent (second solvent) in the coagulation solution has a great effect on the rate performance and cycle performance of the lithium-ion battery. If the

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content of the organic solvent (second solvent) in the coagulation solution is reduced, the average pore size of the pores in the porous film is increased. As can be seen from the analysis of the relevant data of Example 1 and Examples 17-20, the porous film of the application may be formed separately on the separator, the positive electrode, and the negative electrode, or may also be formed on both the separator and the positive electrode or formed on both the separator and the negative electrode. The lithium-ion battery has good rate performance and cycling performance in either case.

[0193] It should be understood by those skilled in the art that the above-described Examples are only illustrative examples. Various changes, substitutions, and alterations could be made to the application without departing from the spirit and scope of the application.

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CLAIMS

What is claimed is:

1. A porous film, comprising:

a binder; and

inorganic particles;

wherein the porous film comprises pores formed by the binder, the pores at least comprises a part of the inorganic particles, wherein the inorganic particles have particle sizes that Dv10 is in a range of 0.015 μm to 3 μm, Dv50 is in a range of 0.2 μm to 5 μm, and Dv90 is in a range of 1 μm to 10 μm; Dv10 of the inorganic particles is less than Dv50 of the inorganic particles, and Dv50 of the inorganic particles is less than Dv90 of the inorganic particles, and the inorganic particles have particle sizes that the ratio of Dv90 to Dv10 is in a range of 2 to 100.

2. The porous film according to claim 1, wherein the porous film has an average pore size of 0.3 μm to 20 μm.

3. The porous film according to claim 1, wherein the average wall thickness between the pores is in a range of 20 nm to 500 nm.

4. The porous film according to claim 1, wherein a pore size distribution coefficient of the pores in the porous film is in a range of 1 to 5.

5. The porous film according to claim 1, wherein the inorganic particles are at least one selected from the group consisting of alumina, silica, magnesia, titanium oxide, hafnium dioxide, tin oxide, cerium dioxide, nickel oxide, zirconia, zinc oxide, calcium oxide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate.

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6. The porous film according to claim 1, wherein the binder is at least one selected from the group consisting of polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylic acid salt, sodium carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene.

7. The porous film according to claim 1, wherein the porous film has a porosity of 20% to 90%.

8. The porous film according to claim 1, wherein the porous film has a thickness of 0.2 to 10 μm.

9. The porous film according to claim 1, wherein a volume ratio of the inorganic particles to the binder is in a range of 0.2 to 3.0.

10. A lithium-ion battery, comprising:

a positive electrode;

a negative electrode;

a separator, arranged between the positive electrode and the negative electrode; non-aqueous electrolyte; and

a porous film, comprising:

a binder; and

inorganic particles;

wherein the porous film comprises pores formed by the binder, the pores at least comprises a part of the inorganic particles, wherein the inorganic particles have particle sizes that Dv10 is in a range of 0.015 μm to 3 μm, Dv50 is in a range of 0.2 μm to 5 μm, Dv90 is in a range of 1 μm to 10 μm; Dv10 of the inorganic particles is less than Dv50 of the inorganic particles, and Dv50 of the inorganic particles is less than Dv90 of the inorganic particles; and the inorganic particles have particle sizes that the ratio of Dv90 to Dv10 is in a

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range of 2 to 100.

11. The lithium-ion battery according to claim 10, wherein the porous film has an average pore size of 0.3 μm to 20 μm.

12. The lithium-ion battery according to claim 10, wherein the average wall thickness between the pores is in a range of 20 nm to 500 nm.

13. The lithium-ion battery according to claim 10, wherein a pore size distribution coefficient of the pores in the porous film is in a range of 1 to 5.

14. The lithium-ion battery according to claim 10, wherein the inorganic particles are at least one selected from the group consisting of alumina, silica, magnesia, titanium oxide, hafnium dioxide, tin oxide, cerium dioxide, nickel oxide, zirconia, zinc oxide, calcium oxide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate.

15. The lithium-ion battery according to claim 10, wherein the binder is at least one selected from the group consisting of polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylic acid salt, sodium carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene.

16. The lithium-ion battery according to claim 10, wherein the porous film has a porosity of 20% to 90%.

17. The lithium-ion battery according to claim 10, wherein the porous film has a thickness of 0.2 to 10 μm.

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18. The lithium-ion battery according to claim 10, wherein a volume ratio of the inorganic particles to the binder is in a range of 0.2 to 3.0.

19. The lithium-ion battery according to claim 10, wherein the porous film is arranged on a surface of at least one selected from the group consisting of the positive electrode, the negative electrode and the separator.

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ABSTRACT

A porous film, including a binder and inorganic particles. The porous film includes pores formed by the binder. The pores at least include a part of the inorganic particles. The inorganic particles have particle sizes that Dv10 is in a range of 0.015 μm to 3 μm, Dv50 is in a range of 0.2 μm to 5 μm, and Dv90 is in a range of 1 μm to 10 μm. Dv10 of the inorganic particles is less than Dv50 of the inorganic particles, and Dv50 of the inorganic particles is less than Dv90 of the inorganic particles, and the inorganic particles have particle sizes that the ratio of Dv90 to Dv10 is in a range of 2 to 100.

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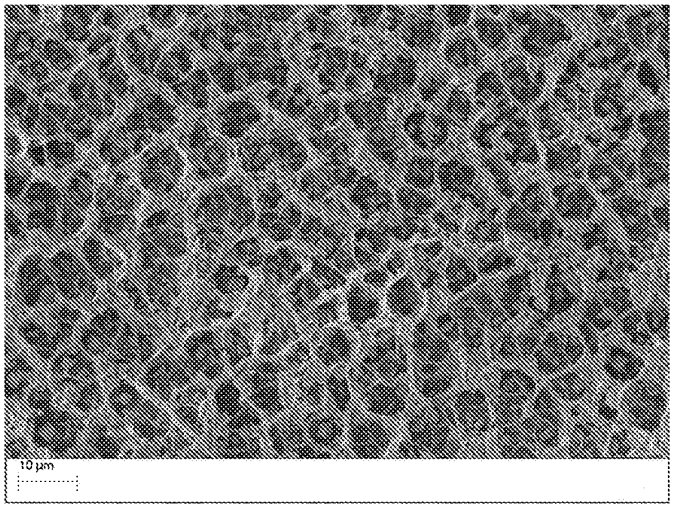


FIG. 1

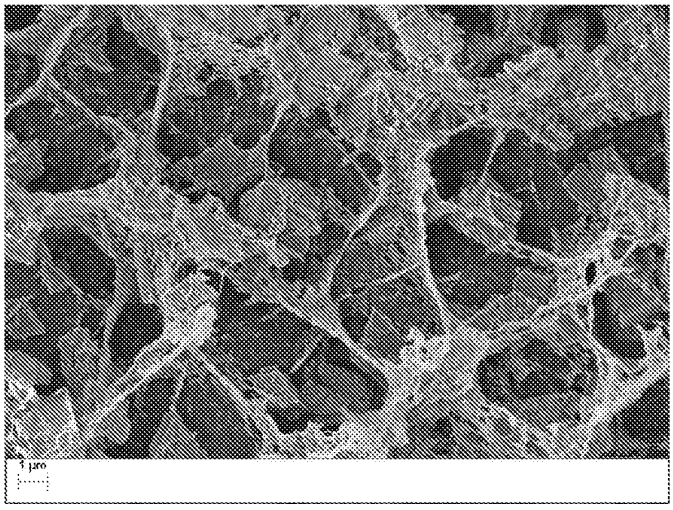


FIG. 2

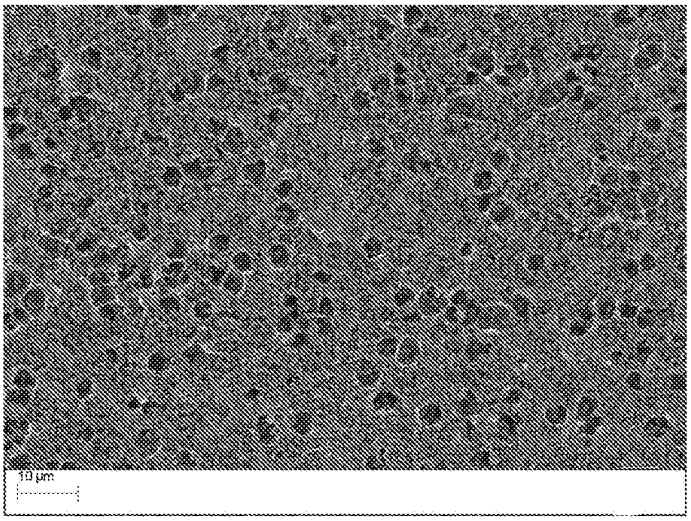


FIG. 3

Electronic Patent Application Fee Transmittal	
Application Number:	
Filing Date:	
Title of Invention:	POROUS FILE AMD LITHIUM-ION BATTERY
First Named Inventor/Applicant Name:	Jianjian YI
Filer:	Yalei Sun/Cheryl Rogers
Attorney Docket Number:	024607-02-5054-US
Filed as Large Entity	
Filing Fees for Utility under 35 USC 111(a)	

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPLICATION FILING	1011	1	300	300
UTILITY SEARCH FEE	1111	1	660	660
UTILITY EXAMINATION FEE	1311	1	760	760
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**1720**

Electronic Acknowledgement Receipt	
EFS ID:	40741211
Application Number:	17061427
International Application Number:	
Confirmation Number:	1915
Title of Invention:	POROUS FILE AMD LITHIUM-ION BATTERY
First Named Inventor/Applicant Name:	Jianjian YI
Customer Number:	24341
Filer:	Yalei Sun
Filer Authorized By:	
Attorney Docket Number:	024607-02-5054-US
Receipt Date:	01-OCT-2020
Filing Date:	
Time Stamp:	20:10:24
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1720
RAM confirmation Number	E202001K10507499
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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		024607-02-5054-US_Application.pdf	2454836 3262f1a150171a46c92872346e71489cd17f f842	yes	58

Multipart Description/PDF files in .zip description

Document Description	Start	End
Transmittal of New Application	1	1
Fee Worksheet (SB06)	2	2
Application Data Sheet	3	10
Oath or Declaration filed	11	14
Specification	15	51
Claims	52	55
Abstract	56	56
Drawings-only black and white line drawings	57	58

Warnings:

Information:

2	Fee Worksheet (SB06)	fee-info.pdf	34770 6ebd21d287aae486378bd459f10524d339 d0bb5e	no	2

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Information:

Total Files Size (in bytes):	2489606

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UTILITY PATENT APPLICATION TRANSMITTAL (Only for new nonprovisional applications under 37 CFR § 1.53(b))	Attorney Docket No.	024607-02-5054-US
	First Inventor	Jianjian YI, et al.
	Title	POROUS FILM AND LITHIUM-ION BATTERY
	Electronically filed	October 1, 2020

APPLICATION ELEMENTS
See MPEP Chapter 600 concerning utility patent application contents.

Address to: **Commissioner for Patents**
P.O. Box 1450
Alexandria, VA 22313-1450

1. ☐ Fee Transmittal Form *(with duplicate for fee processing)*
2. ☐ Applicant claims Small Entity status, see 37 C.F.R. § 1.27
3. ☒ Specification [Total Pages 42]
4. ☒ Drawing(s) *(35 USC § 113)* [Total Sheets 3]
5. ☒ Oath or Declaration [Total Pages 4]
   a. ☐ Newly executed *(original or copy)*
   b. ☒ Copy from a prior application *(37 CFR § 1.63(d))*
6. ☒ Application Data Sheet, see 37 C.F.R. § 1.76
7. ☐ CD-ROM or CD-R in duplicate, large table or Computer Program *(Appendix)*
   ☐ Landscape Table on CD
8. ☐ Nucleotide and/or Amino Acid Sequence Submission *(if applicable, all necessary)*
   a. ☐ Computer Readable Form (CRF)
   b. ☐ Specification Sequence Listing on
      i. ☐ CD-ROM or CD-R (2 copies); or
      ii. ☐ Paper
   c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

9. ☐ Assignment Papers *(cover sheet & document(s))*
   Name of Assignee:
10. ☐ 37 CFR § 3.73(c) Statement
    a. ☐ Power of Attorney
11. ☐ English Translation Document *(if applicable)*
12. ☐ Information Disclosure Statement and PTO-1449
    a. ☐ Copies of citations attached
13. ☐ Preliminary Amendment
14. ☐ Return Receipt Postcard *(MPEP 503)*
15. ☐ Certified Copy of Priority Document(s) *(if foreign priority is claimed)*
16. ☐ Non-Publication Request under 35 U.S.C. § 122 (b)(2)(B)(i)
17. ☐ Other:

Note: (1) Benefit claims under 37 CFR 1.78 and foreign priority claims under 1.55 **MUST** be included in an Application Data Sheet (ADS).
(2) For applications filed under 35 U.S.C. 111, the application must contain an ADS specifying the applicant if the applicant is an assignee, person to whom the inventor is under an obligation to assign, or person who otherwise shows sufficient proprietary interest in the matter. See 37 CFR 1.46(b).

19. CORRESPONDENCE ADDRESS: Customer Number 24341

Signature	/Yalei Sun/	Date	October 1, 2020
Name (Print/Type)	Yalei Sun	Registration No. (Attorney/Agent)	57,765

C:\Users\mp074366\Desktop\ATL Application\024607-02-5054-US\024607-02-5054-US Utility Patent

UTILITY PATENT APPLICATION FEE TRANSMITTAL *(Only for new nonprovisional applications under 37 CFR § 1.53(b))*	Attorney Docket No.	024607-02-5054-US
	First Inventor	Jianjian YI, et al.
	Title	POROUS FILM AND LITHIUM-ION BATTERY
	Electronically filed	October 1, 2020

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

BASIC FILING, SEARCH AND EXAMINATION FEES

Application Type	Filing Fees	Search Fees	Examination Fees	Fees Paid ($)
Utility	$ 300	$ 660	$ 760	$ 1720

EXCESS CLAIM FEES

Type	No. Filed	Less	Extra	Extra Rate ($)	Fee ($)
Total Claims	19	- 20	0	$ 100 each	0
Independent	2	- 3	0	$ 460 each	0
			Multiple Dependency Fee If Applicable ($820)		0

APPLICATION SIZE FEE (Specification and Drawings)

Total Sheets	Extra Sheets	No. of each add'l 50 or fraction thereof	Fee ($)
45 x .75- 100	/ 50	(round up to whole no.) x $400	0

Sub Total	1720
Applicant qualifies for the 50% Reduction for Independent Inventor, Nonprofit Organization or Small Business Concern plus electronic filing discount of $75	
TOTAL FILING FEE	**1720**

Please charge the total filing fee and any other additional fees to Morgan, Lewis & Bockius LLP Deposit Account 50-0310 (order no. 024607-02-5054-US).

Respectfully submitted,

Date: October 1, 2020

/Yalei Sun/ 57,765

Yalei Sun (Reg. No.)

MORGAN, LEWIS & BOCKIUS LLP
1400 Page Mill Road
Palo Alto, CA 94304
(650) 843-4000

DocCode – SCORE

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Application Number: 17061427 Document Date: 10/01/2020

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