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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY.DOCKET NO./TITLE	REQUEST ID
14/238,643	02/12/2014	David Ofer	TIA-10102/57	179925

Acknowledgement of Change to Small Entity Status

The entity status change request below filed through Private PAIR on 12/08/2022 has been accepted.

CERTIFICATIONS:

Change of Entity Status:

× 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.

This portion must be completed by the signatory or signatories making the entity status change in accordance with 37 CFR 1.4(d)(4).

Signature:	/Weston Gould/
Name:	Weston Gould
Registration Number:	59142



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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY.DOCKET NO./TITLE	REQUEST ID
14/238,643	02/12/2014	David Ofer	TIA-10102/57	179927

Acknowledgement of Loss of Entitlement to Entity Status Discount

The entity status change request below filed through Private PAIR on 12/08/2022 has been accepted.

CERTIFICATIONS:

Change of Entity Status:

✕ Applicant changing to regular undiscounted fee status.

NOTE: Checking this box will be taken to be notification of loss of entitlement to small or micro entity status, as applicable.

This portion must be completed by the signatory or signatories making the entity status change in accordance with 37 CFR 1.4(d)(4).

Signature:	/Weston Gould/
Name:	Weston Gould
Registration Number:	59142



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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY.DOCKET NO./TITLE	REQUEST ID
14/238,643	02/12/2014	David Ofer	TIA-10102/57	87402

Acknowledgement of Loss of Entitlement to Entity Status Discount

The entity status change request below filed through Private PAIR on 05/08/2019 has been accepted.

CERTIFICATIONS:

Change of Entity Status:

✕ Applicant changing to regular undiscounted fee status.

NOTE: Checking this box will be taken to be notification of loss of entitlement to small or micro entity status, as applicable.

This portion must be completed by the signatory or signatories making the entity status change in accordance with 37 CFR 1.4(d)(4).

Signature:	/Weston R. Gould/
Name:	Weston R. Gould
Registration Number:	59142



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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/238,643	12/08/2015	9209455	TIA-10102/57	1064

25006 7590 11/18/2015
DINSMORE & SHOHL LLP
PO BOX 7021
TROY, MI 48007-7021

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 117 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 Data Management (ODM) at (571)-272-4200.

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

David Ofer, Needham, MA;
Adrian W. Pullen, Boston, MA;
Suresh Sriamulu, Arlington, MA;

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.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: **Mail** Mail Stop ISSUE FEE
Commissioner for 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, 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)

DINSMORE & SHOHL LLP
2701 Troy Center Drive, Suite 330
Post Office Box 7021
Troy, Michigan 48007-7021

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 facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

Ann Andrusiak (Depositor's name)
Ann Andrusiak (Signature)
November 3, 2015 (Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/238,643	02/12/2014	David Ofer	TIA-10102/57	1064

TITLE OF INVENTION: POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	\$480.00			\$480.00	11/13/2015
EXAMINER	ART UNIT	CLASS-SUBCLASS				
P. F. Godenschwager	1767	252-182.100				

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).	2. For printing on the patent front page, list	
☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.	(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,	1 Dinsmore & Shohl LLP
☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. Use of a Customer Number is required.	(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.	2 Weston R. Gould, Ph.D.
		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

(B) RESIDENCE: (CITY and STATE OR COUNTRY)

TIAX LLC

Lexington, Massachusetts

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
☐ Publication Fee (No small entity discount permitted)
☐ Advance Order - # of Copies

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

- ☐ A check is enclosed.
☒ Payment by credit card. Form PTO-2038 is attached.
☐ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment, to Deposit Account Number 04-1133 (enclose an extra copy of this form).

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 /Weston R. Gould, Ph. D./

Date November 3, 2015

Typed or printed name Weston R. Gould, Ph. D.

Registration No. 59,142

Electronic Patent Application Fee Transmittal

Application Number:	14238643			
Filing Date:	12-Feb-2014			
Title of Invention:	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME			
First Named Inventor/Applicant Name:	David Ofer			
Filer:	Weston Gould/Ann Andrusiak			
Attorney Docket Number:	TIA-10102/57			
Filed as Small Entity				
Filing Fees for U.S. National Stage under 35 USC 371				
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	2501	1	480	480

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Extension-of-Time:				
Miscellaneous:				
Total in USD (\$)				480

Electronic Acknowledgement Receipt

EFS ID:	23968565
Application Number:	14238643
International Application Number:	
Confirmation Number:	1064
Title of Invention:	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME
First Named Inventor/Applicant Name:	David Ofer
Customer Number:	25006
Filer:	Weston Gould/Ann Andrusiak
Filer Authorized By:	Weston Gould
Attorney Docket Number:	TIA-10102/57
Receipt Date:	03-NOV-2015
Filing Date:	12-FEB-2014
Time Stamp:	10:30:40
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	\$480
RAM confirmation Number	9125
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)	doc00386620151103102816.pdf	128965 fec7b9a170bcc4eb44a860401f4c04c213063ba	no	1
Warnings:					
The page size in the PDF is too large. The pages should be 8.5 x 11 or A4. If this PDF is submitted, the pages will be resized upon entry into the Image File Wrapper and may affect subsequent processing					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30772 cd715038d226abc583c2e0f735072d99625f6e2	no	2
Warnings:					
Information:					
Total Files Size (in bytes):			159737		
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. <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.					



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www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

25006 7590 08/13/2015
GIFFORD, KRASS, SPRINKLE, ANDERSON & CITKOWSKI, P.C.
PO BOX 7021
TROY, MI 48007-7021

EXAMINER

GODENSCHWAGER, PETER F

ART UNIT

PAPER NUMBER

1767

DATE MAILED: 08/13/2015

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
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14/238,643

02/12/2014

David Ofer

TIA-10102/57

1064

TITLE OF INVENTION: POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
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nonprovisional

SMALL

\$480

\$0

\$0

\$480

11/13/2015

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 and an extra copy of the form should be submitted. 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: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: **Mail** **Mail Stop ISSUE FEE**
Commissioner for 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, 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)

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.

25006 7590 08/13/2015
GIFFORD, KRASS, SPRINKLE, ANDERSON & CITKOWSKI, P.C.
PO BOX 7021
TROY, MI 48007-7021

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 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	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/238,643	02/12/2014	David Ofer	TIA-10102/57	1064

TITLE OF INVENTION: POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	\$480	\$0	\$0	\$480	11/13/2015

EXAMINER	ART UNIT	CLASS-SUBCLASS
GODENSCHWAGER, PETER F	1767	252-182100

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; 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, 1 _____
- (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. 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

(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. The following fee(s) are submitted:

- ☐ Issue Fee
- ☐ Publication Fee (No small entity discount permitted)
- ☐ Advance Order - # of Copies _____

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

- ☐ A check is enclosed.
- ☐ Payment by credit card. Form PTO-2038 is attached.
- ☐ The director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

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. _____



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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Alexandria, Virginia 22313-1450
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/238,643	02/12/2014	David Ofer	TIA-10102/57	1064
25006 7590 08/13/2015 GIFFORD, KRASS, SPRINKLE, ANDERSON & CITKOWSKI, P.C PO BOX 7021 TROY, MI 48007-7021				
EXAMINER GODENSCHWAGER, PETER F				
ART UNIT		PAPER NUMBER		
1767				
DATE MAILED: 08/13/2015				

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.

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 12 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. 14/238,643	Applicant(s) OFER ET AL.	
	Examiner PETER F. GODENSCHWAGER	Art Unit 1767	AIA (First Inventor to File) Status No

-- 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 the claim amendments filed October 13, 2014.
☐ 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 1-13 and 15. 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. _____.
 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) | 5. ☐ Examiner's Amendment/Comment |
| 2. ☒ Information Disclosure Statements (PTO/SB/08),
Paper No./Mail Date <u>2/12/2014</u> | 6. ☒ Examiner's Statement of Reasons for Allowance |
| 3. ☐ Examiner's Comment Regarding Requirement for Deposit
of Biological Material | 7. ☐ Other _____. |
| 4. ☐ Interview Summary (PTO-413),
Paper No./Mail Date _____. | |

/PETER F GODENSCHWAGER/
Primary Examiner, Art Unit 1767

The present application is being examined under the pre-AIA first to invent provisions.

ALLOWANCE

Claims 1-13 and 15 are allowed.

The following is an examiner's statement of reasons for allowance: The closest prior art, Shizuka et al. (US Pub. No. 2009/0104530), teaches a powder (particles) comprising a first composition having a lithium transition metal oxide including nickel that is layered and has an α -NaFeO₂ type structure (abstract, [0356]-[0361]). However, Shizuka et al. does not teach the particles wherein the grain boundary between crystallites comprises a second composition having a concentration of cobalt greater than the first composition. A search of the prior art did not reveal any teaching or suggestion to modify the particles of Shizuka et al. such that the grain boundary between crystallites comprises a second composition having a concentration of cobalt greater than the first composition.

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."

Correspondence

Any inquiry concerning this communication or earlier communications from the examiner should be directed to PETER F. GODENSCHWAGER whose telephone number is (571)270-3302. The examiner can normally be reached on Monday-Friday 7:30-4:00 EST.

Art Unit: 1767

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Mark Eashoo can be reached on (571) 272-1197. 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.

/PETER F GODENSCHWAGER/
Primary Examiner, Art Unit 1767
August 6, 2015

Search Notes 	Application/Control No. 14238643	Applicant(s)/Patent Under Reexamination OFER ET AL.
	Examiner PETER F GODENSCHWAGER	Art Unit 1767

CPC- SEARCHED		
Symbol	Date	Examiner
H01M 4/364, 3/366, 4/525	8/5/2015	PFG

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
inventor name search (eDAN)	8/5/2015	PFG
EAST search (see attached)	8/6/2015	PFG

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
H01M	4/364, 3/366, 4/525	8/6/2015	PFG

	/P.F.G./ Primary Examiner.Art Unit 1767
--	--

Issue Classification 	Application/Control No. 14238643	Applicant(s)/Patent Under Reexamination OFER ET AL.	
	Examiner PETER F GODENSCHWAGER	Art Unit 1767	

CPC						
Symbol					Type	Version
H01M		4	/	364	F	2013-01-01
C01G		51	/	42	I	2013-01-01
C01G		51	/	50	I	2013-01-01
C01G		53	/	42	I	2013-01-01
H01M		4	/	505	A	2013-01-01
H01M		4	/	525	I	2013-01-01
H01M		10	/	0525	I	2013-01-01
C01P		2002	/	54	A	2013-01-01
C01P		2002	/	85	A	2013-01-01
C01P		2004	/	03	A	2013-01-01
C01P		2004	/	04	A	2013-01-01
Y02E		60	/	122	A	2013-01-01
C01D		15	/	02	I	2013-01-01
H01M		2004	/	021	A	2013-01-01
			/			

CPC Combination Sets				
Symbol	Type	Set	Ranking	Version

NONE		Total Claims Allowed:	
		14	
(Assistant Examiner)	(Date)	O.G. Print Claim(s)	O.G. Print Figure
/PETER F GODENSCHWAGER/ Primary Examiner.Art Unit 1767	08/06/2015	1	1
(Primary Examiner)	(Date)		

Issue Classification 	Application/Control No. 14238643	Applicant(s)/Patent Under Reexamination OFER ET AL.
	Examiner PETER F GODENSCHWAGER	Art Unit 1767

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47															
Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	-	17												
2	2	-	18												
3	3	-	19												
4	4	-	20												
5	5														
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10	10														
11	11														
12	12														
13	13														
-	14														
14	15														
-	16														

NONE (Assistant Examiner) _____ (Date) _____		Total Claims Allowed: 14	
/PETER F GODENSCHWAGER/ Primary Examiner.Art Unit 1767 (Primary Examiner) _____ (Date) _____		O.G. Print Claim(s) 1	O.G. Print Figure 1



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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 P.O. Box 1450
 Alexandria, Virginia 22313-1450
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BIB DATA SHEET

CONFIRMATION NO. 1064

SERIAL NUMBER 14/238,643	FILING or 371(c) DATE 02/12/2014 RULE	CLASS 252	GROUP ART UNIT 1767	ATTORNEY DOCKET NO. TIA-10102/57	
APPLICANTS INVENTORS David Ofer, Needham, MA; Adrian W. Pullen, Boston, MA; /PFG/ Suresh Sriamulu, Arlington, MA; ** CONTINUING DATA ***** This application is a 371 of PCT/US2012/048602 07/27/2012 /PFG/ which claims benefit of 61/575,115 08/16/2011 ** FOREIGN APPLICATIONS ***** /PFG/ ** IF REQUIRED, FOREIGN FILING LICENSE GRANTED *** SMALL ENTITY ** 03/29/2014					
Foreign Priority claimed ☐ Yes ☒ No 35 USC 119(a-d) conditions met ☐ Yes ☒ No Verified and /PETER GODENSCHWAGER/ Acknowledged Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY MA	SHEETS DRAWINGS 9	TOTAL CLAIMS 19	INDEPENDENT CLAIMS 3
ADDRESS GIFFORD, KRASS, SPRINKLE, ANDERSON & CITKOWSKI, P.C PO BOX 7021 TROY, MI 48007-7021 UNITED STATES					
TITLE POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME					
FILING FEE RECEIVED 740	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		

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	("20140197357").PN.	US-PGPUB	OR	OFF	2015/08/05 12:02
S2	2	("20050181280" "20090104530").PN.	US-PGPUB; USPAT	ADJ	ON	2015/08/05 12:14
S3	19823	H01M4/525.CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 12:33
S4	628	"NaFeO.sub.2"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 12:35
S5	439	"alpha-NaFeO.sub.2"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 12:36
S6	282	(S4 OR S5) AND S3	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 12:37
S7	61	(S4 OR S5) AND S3 AND grain boundary	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 12:37
S8	7918	H01M4/364.CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 13:18
S9	12410	H01M4/366.CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 13:18
S10	19	(S4 OR S5) AND (S8 OR S9) AND grain boundary	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 13:22
S11	35	(S4 OR S5) AND (grain boundary) AND (cathode WITH active material)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT	ADJ	ON	2015/08/05 14:13

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	3077	H01M4/525.CPC.	US-PGPUB; UPAD	ADJ	ON	2015/08/06 08:00
L2	1242	H01M4/364.CPC.	US-PGPUB; UPAD	ADJ	ON	2015/08/06 08:00
L3	2258	H01M4/366.CPC.	US-PGPUB; UPAD	ADJ	ON	2015/08/06 08:01
L5	1	(crystallite AND particle AND (lithium OR Li) AND (nickel OR Ni) AND grain boundary AND	US-PGPUB;	ADJ	ON	2015/08/06 08:18

		("alpha-NaFeO.sub.2" OR "NaFeO.sub.2")).clm.	UPAD			
L6	1	(crystallite AND particle AND grain boundary AND ("alpha-NaFeO.sub.2" OR "NaFeO.sub.2")).clm.	US-PGPUB; UPAD	ADJ	ON	2015/08/06 08:18

8/ 6/ 2015 11:17:59 AM
C:\ Users\ pgodenschwager\ Documents\ EAST\ Workspaces\ 14_238643.wsp

PTO/SB/08a (07-09)

Approved for use through 07/31/2012. OMB 0651-0031

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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Substitute for form 1449/PTO INFORMATION DISCLOSURE STATEMENT BY APPLICANT <i>(Use as many sheets as necess ary)</i>				Complete if Known	
				Application Number	Not Yet Assigned
				Filing Date	Concurrently Herewith
				First Named Inventor	David Ofer
				Art Unit	N/A
				Examiner Name	Not Yet Assigned
Sheet	1	of	2	Attorney Docket Number	TIA-10102/57

U.S. PATENT DOCUMENTS					
Examiner Initials*	Cite No. ¹	Document Number	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		Number-Kind Code ² (if known)			
	AA*	US-2005/0181280	08-18-2005	Ceder et al.	
	AB*	US-2009/0104530	04-23-2009	Shizuka et al.	

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear	T ⁶
		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)				
	BA	JP-2008234872-A	10-02-2008	Sony Corp		√
	BB	KR-1020100099668	09-13-2010	Sony Corp.		√

Examiner Signature	/ PETER GODENSCHWAGER/	Date Considered	08/06/2015
-----------------------	------------------------	--------------------	------------

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. * CITE NO.: Those application(s) which are marked with an single asterisk (*) next to the Cite No. are not supplied (under 37 CFR 1.98(a)(2)(iii)) because that application was filed after June 30, 2003 or is available in the IFW. ¹ Applicant's unique citation designation number (optional). ² See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. ³ Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). ⁴ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁵ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁶ Applicant is to place a check mark here if English language Translation is attached.

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.

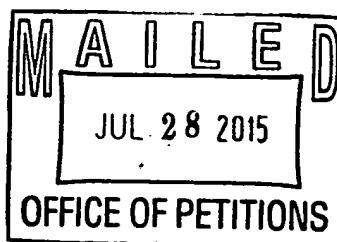
¹Applicant's unique citation designation number (optional). ²Applicant is to place a check mark here if English language Translation is attached.



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GIFFORD, KRASS, SPRINKLE,
ANDERSON & CITKOWSKI, P.C.
PO BOX 7021
TROY MI 48007-7021



In re Application of
OFER, et al
Application No.: 14/238,643
Filed: February 12, 2014
Attorney Docket No.: TIA-10102/57
For: POLYCRYSTALLINE METAL
OXIDE, METHODS OF MANUFACTURE
THEREOF, AND ARTICLES...

: DECISION ON REQUEST TO
: PARTICIPATE IN THE PATENT
: PROSECUTION HIGHWAY
: PROGRAM AND PETITION
: TO MAKE SPECIAL UNDER
: 37 CFR 1.102(a)

This is a decision on the request to participate in the Patent Prosecution Highway (PPH) program and the petition under 37 CFR 1.102(a), filed October 13, 2014, renewed June 10, 2015 and June 29, 2015, to make the above-identified application special.

The request and petition are **GRANTED**.

DISCUSSION

A grantable request to participate in the PPH pilot program and petition to make special require:

1. The U.S. application for which participation in the Global/IP5 PPH pilot program is requested: must have the same earliest date, whether this is the priority date or filing date, as that of a corresponding national or regional application filed with another Global/IP5 PPH participating office or a corresponding PCT international application for which one of the Global/IP5 PPH participating offices was the International Searching Authority (ISA) or the International Preliminary Examining Authority (IPEA).
2. Applicant must:
 - a. Ensure all the claims in the U.S. application must sufficiently correspond or be amended to sufficiently correspond to the allowable/patentable claim(s) in the corresponding Office of Earlier Examination (OEE) application and
 - b. Submit a claims correspondence table in English;
3. Examination of the U.S. application has not begun;
4. Applicant must submit:
 - a. Documentation of prior office action:
 - i. a copy of the office action(s) just prior to the "Decision to Grant a Patent" from each of the Global/IP5 PPH participating office application(s) containing the allowable/patentable claim(s) or
 - ii. if the allowable/patentable claims(s) are from a "Notification of Reasons for Refusal" then the Notification of Reasons for Refusal or

- iii. if the Global/IP5 PPH participating office application is a first action allowance then no office action from the Global/IP5 PPH participating office is necessary should be indicated on the request/petition form or
 - iv. the latest work product in the international phase of the OEE PCT application;
 - b. An English language translation of the Global/IP5 PPH participating office action or work product from (4)(a)(i)-(ii) or (iv) above;
5. Applicant must submit:
- a. An IDS listing the documents cited by the Global/IP5 PPH participating office examiner in the Global/IP5 PPH participating office action or work product (unless already submitted in this application)
 - b. Copies of the documents except U.S. patents or U.S. patent application publications (unless already submitted in this application);

The request to participate in the PPH pilot program and petition comply with the above requirements. Accordingly, the above-identified application has been accorded "special" status.

Telephone inquiries concerning this decision should be directed to the undersigned at (571) 272-6735.

All other inquiries concerning the examination or status of the application is accessible in the PAIR system at <http://www.uspto.gov/ebc/index.html>.

This application is being referred to the examiner for action on the merits commensurate with this decision.

/Diane Goodwyn/
Diane Goodwyn
Paralegal Specialist
Office of Petitions

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Utility Application of:
David Ofer et al.

Application No.: 14/238,643

Confirmation No.: 1064

Filed: February 12, 2014

Art Unit: 1761

For: POLYCRYSTALLINE METAL OXIDE,
METHODS OF MANUFACTURE THEREOF,
AND ARTICLES COMPRISING THE SAME

Examiner: Not Yet Assigned

**APPLICANT'S SUPPLEMENTAL RESPONSE TO DECISION ON APPLICANT'S
REQUEST TO PARTICIPATE IN THE PATENT PROSECUTION HIGHWAY
PROGRAM AND PETITION TO MAKE SPECIAL UNDER 37 CFR 1.102(a)**

MS Office of Petitions
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Madam:

In response to the Decision mailed May 19, 2015, Applicant respectfully submits the following:

The Written Opinion for PCT/US2012/048602 stated that claims 4-12 and 14 do not comply with PCT Rule 6.4(a) because multiple dependent claims should not serve as a basis for any other multiple dependent claims. The multiple dependent claims were later amended in the First Preliminary Amendment made of record February 14, 2014 to remove all instances of multiple dependencies. On October 13, 2014, Applicant filed a Second Preliminary Amendment

wherein the claims were amended to sufficiently correspond. As such, it is submitted that all claims are in patentable form and allowable at least as dependent from an allowable base claim.

In addition, only claims 1-13 and 15 were included in Applicant's Claims Correspondence Table submitted as part of Applicant's Request for Participation in the PPH Pilot Program. Claim 14 was inadvertently excluded. Attached is an updated Claims Correspondence Table including all claims, 1-15.

Applicant respectfully requests that the decision to dismiss Applicant's petition be reconsidered and overturned. If a telephone conference would aid in clarifying Applicant's position, their undersigned representative may be reached at the telephone and/or facsimile numbers provided below.

Dated: June 29, 2015

Respectfully submitted,

Electronic signature: /Weston R. Gould, Ph. D./
Weston R. Gould, Ph. D.

Registration No.: 59,142
GIFFORD, KRASS, SPRINKLE, ANDERSON
& CITKOWSKI, P.C.
2701 Troy Center Drive, Suite 330
Post Office Box 7021
Troy, Michigan 48007-7021
(248) 647-6000
(248) 647-5210 (Fax)
Attorney for Applicant

REQUEST FOR PARTICIPATION IN THE GLOBAL/IP5 PATENT PROSECUTION HIGHWAY (PPH) PILOT PROGRAM IN THE USPTO

Application No.:	14/238,643-Conf. #1064	First Named Inventor:	David Ofer
Filing Date:	February 12, 2014	Attorney Docket No.:	TIA-10102/57

Title of the Invention: POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

THIS REQUEST FOR PARTICIPATION IN THE PPH PILOT PROGRAM ALONG WITH THE REQUIRED DOCUMENTS MUST BE SUBMITTED VIA EFS-WEB. INFORMATION REGARDING EFS-WEB IS AVAILABLE AT [HTTP://WWW.USPTO.GOV/PATENTS/PROCESS/FILE/EFS/](http://www.uspto.gov/patents/process/file/efs/).

APPLICANT HEREBY REQUESTS PARTICIPATION IN THE PATENT PROSECUTION HIGHWAY (PPH) PILOT PROGRAM AND PETITIONS TO MAKE THE ABOVE-IDENTIFIED APPLICATION SPECIAL UNDER THE PPH PILOT PROGRAM.

Office of earlier examination (OEE): PCT

OEE application number: PCT/US2012/048602

Both the OEE application and the above-identified U.S. application have the following earliest date (filing or priority date): July 27, 2012

Type of OEE work product relied upon: International Search Report and Written Opinion

Mailing date of OEE work product: February 26, 2013

I. Required Documents:

- a. A copy of the most recent office action prior to the decision to grant a patent or the most recent PCT work product (along with an English translation, if not in the English language):

☒ is attached.

☐ is already present in the U.S. application.

☐ is not attached because it is available to the USPTO via the Dossier Access System or WIPO's PATENTSCOPE system.

☐ is not attached because the decision to grant a patent was the first office action.

- b. (1) An information disclosure statement listing the documents cited in the OEE work product:

☐ is attached.

☒ has already been filed in the U.S. application.

☐ is not attached because no references were cited in the document in section a. above.

- (2) Copies of all cited documents (except for U.S. patents or U.S. patent application publications)

☐ are attached.

☒ have already been filed in the U.S. application.

☐ are not attached because no references were cited in the document in section a. above.

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 PARTICIPATION IN THE GLOBAL/IP5 PPH PILOT PROGRAM IN THE USPTO

(continued)

Application No.:	14/238,643-Conf. #1064	First Named Inventor:	David Ofer
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II. Claims Correspondence Table:

Claims in US Application	Patentable Claims in OEE Application	Explanation regarding the correspondence
1	1	Sufficiently correspond
2	2	Sufficiently correspond
3	3	Sufficiently correspond
4	4	See attached
5	5	See attached
6	6	See attached
7	7	See attached
8	8	See attached
9	9	See attached
10	10	See attached
11	11	See attached
12	12	See attached
13	13	Sufficiently correspond
14	14	See attached
15	15	Sufficiently correspond

III. All the claims in the US application sufficiently correspond to the patentable/allowable claims in the OEE application.

Signature	/Weston R. Gould, Ph. D./	Date	June 29, 2015
Name (Print/Typed)	Weston R. Gould, Ph. D.	Registration Number	59,142

**ADDENDUM TO
II. CLAIMS CORRESPONDENCE TABLE:**

<u>Claims in US Application</u>	<u>Patentable Claims in OEE Application</u>	<u>Explanation regarding the correspondence</u>
4	4	Claim 4 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency was corrected in the first preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 4 now properly depends from an allowable base claim – claim 1.
5	5	Claim 5 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 5 now properly depends from an allowable base claim – claim 1.
6	6	Claim 6 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 6 now properly depends from an allowable base claim – claim 1.
7	7	Claim 7 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple

dependent claim. The multiple dependency was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 7 now properly depends from an allowable base claim – claim 1.

8

8

Claim 8 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 8 now properly depends from an allowable base claim – claim 1.

9

9

Claim 9 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 9 now properly depends from an allowable base claim – claim 1.

10

10

Claim 10 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 10 now properly depends from an allowable base claim – claim 1.

11

11

Claim 11 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency

was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 11 now properly depends from an allowable base claim – claim 1.

12

12

Claim 12 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 12 now properly depends from an allowable base claim – claim 1.

14

14

Claim 14 was not reviewed at the international stage due to not being drafted in accordance with the second and third sentences of Rule 6.4(a) due to being a multiple dependent claim being dependent from a prior multiple dependent claim. The multiple dependency was corrected in the preliminary amendment filed 02/14/2014. A second preliminary amendment filed 10/13/2014 wherein the claims were amended to sufficiently correspond. As such, claim 14 now properly depends from an allowable base claim – claim 1.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference TIA0012PCT	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/US2012/048602	International filing date (<i>day/month/year</i>) 27 JULY 2012 (27.07.2012)	(Earliest) Priority Date (<i>day/month/year</i>) 16 AUGUST 2011 (16.08.2011)
Applicant TIAX LLC et al		

This International search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed

☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6bis(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☒ **Certain claims were found unsearchable** (See Box No. II)

3. ☐ **Unity of invention is lacking** (See Box No. III)

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. 1

☒ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figure is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2012/048602

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-12, 14
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees

POSCO Future M EX1005

POSCO Future M EX1005

Page 36

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/048602**A. CLASSIFICATION OF SUBJECT MATTER***C01G 49/00(2006.01)i, C01G 51/00(2006.01)i, C01D 1/00(2006.01)i, H01M 10/05(2010.01)i*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01G 49/00; H01M 4/48; H01M 10/0525; H01M 4/36; H01M 4/52; H01M 4/485

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: polycrystalline metal oxide, LiNiCoO, concentration of cobalt

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2008-234872 A (SONY CORP.) 02 October 2008 See abstract; paragraph [0014-0068]; claims 1-4	1-3, 13, 15
A	US 2005-0181280 A1 (GERBRAND CEDER et al.) 18 August 2005 See abstract; paragraph [0031-0045]; claims 1, 4	1-3, 13, 15
A	US 2009-0104530 A1 (SHIZUKA KENJI et al.) 23 April 2009 See abstract; paragraph [0481-0486]	1-3, 13, 15
A	KR 10-2010-0099668 A (LG CHEM. LTD.) 13 September 2010 See abstract; paragraph [0011-0026]	1-3, 13, 15

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

25 FEBRUARY 2013 (25.02.2013)

Date of mailing of the international search report

26 FEBRUARY 2013 (26.02.2013)

Name and mailing address of the ISA/KR



Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan
Civ. 302-701, Republic of Korea

Authorized officer

LEE, Jin Hong



POSCO Future Materials
POSCO Future Materials

Page 3/7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/048602

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2008-234872 A	02.10.2008	None	
US 2005-0181280 A1	18.08.2005	US 2002-0048706 A1 US 2005-0175529 A1 US 2008-0099734 A1 US 7026071 B2	25.04.2002 11.08.2005 01.05.2008 11.04.2006
US 2009-0104530 A1	23.04.2009	CN 101379637 A CN 102044672 A CN 102044673 A EP 2006937 A2 EP 2006937 A9 JP 04-591716 B2 JP 04-591717 B2 JP 04-613943 B2 JP 2008-103308 A JP 2008-108692 A JP 2008-305777 A JP 2010-278015 A JP 2011-003551 A JP 4591716 B2 JP 4591717 B2 JP 4613943 B2 KR 10-2008-0108222 A WO 2007-116971 A1	04.03.2009 04.05.2011 04.05.2011 24.12.2008 08.07.2009 24.09.2010 24.09.2010 29.10.2010 01.05.2008 08.05.2008 18.12.2008 09.12.2010 06.01.2011 01.12.2010 01.12.2010 19.01.2011 12.12.2008 18.10.2007
KR 10-2010-0099668 A	13.09.2010	EP 2405511 A2 US 2012-0225343 A1 WO 2010-101396 A2 WO 2010-101396 A3	11.01.2012 06.09.2012 10.09.2010 10.09.2010

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:
EHRlich GRANT M.

CANTOR COLBURN LLP 20 CHURCH STREET 22ND
FLOOR HARTFORD CT 06103 USA

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

Date of mailing
(day/month/year) 26 FEBRUARY 2013 (26.02.2013)

Applicant's or agent's file reference

TIA0012PCT

FOR FURTHER ACTION

See paragraph 2 below

International application No.

PCT/US2012/048602

International filing date (day/month/year)

27 JULY 2012 (27.07.2012)

Priority date(day/month/year)

16 AUGUST 2011 (16.08.2011)

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

C01G 49/00(2006.01)i, C01G 51/00(2006.01)i, C01D 1/00(2006.01)i, H01M 10/05(2010.01)i

Applicant

TIAX LLC et al

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon
Metropolitan City, 302-701,
Republic of Korea
Facsimile No. 82-42-472-7140

Date of completion of this opinion

25 FEBRUARY 2013 (25.02.2013)

Authorized officer

LEE, Jin Hong

Telephone No.82-42-481-8649



**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US2012/048602

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of :

- ☒ the international application in the language in which it was filed
- ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of:

a. a sequence listing filed or furnished

- ☐ on paper
- ☐ in electronic form

b. time of filing or furnishing

- ☐ contained in the international application as filed.
- ☐ filed together with the international application in electronic form.
- ☐ furnished subsequently to this Authority for the purposes of search.

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US2012/048602

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application

☒ claims Nos. 4-12, 14

because:

☐ the said international application, or the said claims Nos. _____
relate to the following subject matter which does not require an international search (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. _____
are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. _____ are so inadequately supported
by the description that no meaningful opinion could be formed (*specify*):

☒ no international search report has been established for said claims Nos. 4-12, 14

☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.

☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.

☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rule 13ter.1(a) or (b).

☐ See Supplemental Box for further details.

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US2012/048602

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-3,13,15	YES
	Claims	NONE	NO
Inventive step (IS)	Claims	1-3,13,15	YES
	Claims	NONE	NO
Industrial applicability (IA)	Claims	1-3,13,15	YES
	Claims	NONE	NO

2. Citations and explanations :

Reference is made to the following documents:

D1: JP 2008-234872 A (SONY CORP.) 02 October 2008
D2: US 2005-0181280 A1 (GERBRAND CEDER et al.) 18 August 2005
D3: US 2009-0104530 A1 (SHIZUKA KENJI et al.) 23 April 2009
D4: KR 10-2010-0099668 A (LG CHEM. LTD.) 13 September 2010

1. Novelty and Inventive step

1.1. Independent Claims 1, 13 and 15

The subject matters of claims 1, 13 and 15 differ from those of the prior art documents in that a concentration of cobalt in the grain boundary is greater than that in the crystallites. And they are not obvious to a person skilled in the art by the documents, taken alone or in combination. Therefore, claims 1, 13 and 15 meet the requirements of PCT Article 33(2) and (3) with respect to novelty and inventive step.

1.2. Dependent Claims 2-3

Claims 2-3 are dependent on claim 1, and therefore meet the requirements of PCT Article 33(2) and (3).

2. Industrial Applicability

Claims 1-3, 13 and 15 are industrially applicable under PCT Article 33(4).

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/US2012/048602

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

Claims 4-12 and 14 do not comply with PCT Rule 6.4(a) because multiple dependent claims should not serve as a basis for any other multiple dependent claim.

Electronic Acknowledgement Receipt

EFS ID:	22777229
Application Number:	14238643
International Application Number:	
Confirmation Number:	1064
Title of Invention:	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME
First Named Inventor/Applicant Name:	David Ofer
Customer Number:	25006
Filer:	Weston Gould/Ann Andrusiak
Filer Authorized By:	Weston Gould
Attorney Docket Number:	TIA-10102/57
Receipt Date:	29-JUN-2015
Filing Date:	12-FEB-2014
Time Stamp:	18:22:24
Application Type:	U.S. National Stage under 35 USC 371

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	Petition to make Special under PCT- Patent Pros Hwy	SCAN_A2_043890.pdf	906350 1ead1a49429c4b97f2589310723c8265268007cb	no	16

Warnings:

Information:

Total Files Size (in bytes):

906350

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.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Utility Application of:
David Ofer et al.

Application No.: 14/238,643

Confirmation No.: 1064

Filed: February 12, 2014

Art Unit: 1761

For: POLYCRYSTALLINE METAL OXIDE,
METHODS OF MANUFACTURE THEREOF,
AND ARTICLES COMPRISING THE SAME

Examiner: Not Yet Assigned

**APPLICANT'S RESPONSE TO DECISION ON APPLICANT'S REQUEST TO
PARTICIPATE IN THE PATENT PROSECUTION HIGHWAY PROGRAM
AND PETITION TO MAKE SPECIAL UNDER 37 CFR 1.102(a)**

MS Office of Petitions
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Madam:

In response to the Decision mailed May 19, 2015, Applicant respectfully submits the following:

The Written Opinion for PCT/US2012/048602 stated that claims 4-12 and 14 do not comply with PCT Rule 6.4(a) because multiple dependent claims should not serve as a basis for any other multiple dependent claims. The multiple dependent claims were incorrectly submitted and were later amended to remove all instances of multiple dependencies.

In addition, only claims 1-13 and 15 were included in Applicant's Claims Correspondence Table submitted as part of Applicant's Request for Participation in the PPH Pilot Program. Claim 14 was inadvertently excluded. Attached is an updated Claims Correspondence Table including all claims, 1-15.

Applicant respectfully requests that the decision to dismiss Applicant's petition be reconsidered and overturned. If a telephone conference would aid in clarifying Applicant's position, their undersigned representative may be reached at the telephone and/or facsimile numbers provided below.

Dated: June 10, 2015

Respectfully submitted,

Electronic signature: /Weston R. Gould, Ph. D./
Weston R. Gould, Ph. D.

Registration No.: 59,142

GIFFORD, KRASS, SPRINKLE, ANDERSON
& CITKOWSKI, P.C.

2701 Troy Center Drive, Suite 330

Post Office Box 7021

Troy, Michigan 48007-7021

(248) 647-6000

(248) 647-5210 (Fax)

Attorney for Applicant

Electronic Acknowledgement Receipt

EFS ID:	22586598
Application Number:	14238643
International Application Number:	
Confirmation Number:	1064
Title of Invention:	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME
First Named Inventor/Applicant Name:	David Ofer
Customer Number:	25006
Filer:	Weston Gould/Ann Andrusiak
Filer Authorized By:	Weston Gould
Attorney Docket Number:	TIA-10102/57
Receipt Date:	10-JUN-2015
Filing Date:	12-FEB-2014
Time Stamp:	12:08:54
Application Type:	U.S. National Stage under 35 USC 371

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	Petition to make Special under PCT- Patent Pros Hwy	SCAN_A2_043093.pdf	83324 386fa0a904ba3c31c74943f91e1d6d32558c ae2d	no	2

Warnings:

Information:

Total Files Size (in bytes):

83324

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

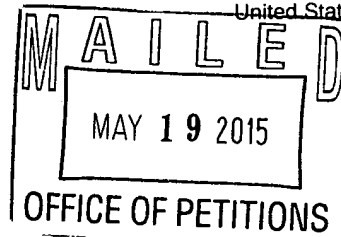
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will 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.



UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450
www.uspto.gov

**GIFFORD, KRASS, SPRINKLE,
ANDERSON & CITKOWSKI, P.C.
PO BOX 7021
TROY MI 48007-7021**



**In re Application of
OFER, et al**

Application No.: 14/238,643

Filed: February 12, 2014

Attorney Docket No.: TIA-10102/57

For: POLYCRYSTALLINE METAL

**OXIDE, METHODS OF MANUFACTURE
THEREOF, AND ARTICLES...**

**: DECISION ON REQUEST TO
: PARTICIPATE IN THE PATENT
: PROSECUTION HIGHWAY
: PROGRAM AND PETITION
: TO MAKE SPECIAL UNDER
: 37 CFR 1.102(a)**

This is a decision on the request to participate in the Patent Prosecution Highway (PPH) program and the petition under 37 CFR 1.102(a), filed October 13, 2014, to make the above-identified application special.

The request and petition are **DISMISSED**.

DISCUSSION

A grantable request to participate in the PPH pilot program and petition to make special require:

1. The U.S. application for which participation in the Global/IP5 PPH pilot program is requested must have the same earliest date, whether this is the priority date or filing date, as that of a corresponding national or regional application filed with another Global/IP5 PPH participating office or a corresponding PCT international application for which one of the Global/IP5 PPH participating offices was the International Searching Authority (ISA) or the International Preliminary Examining Authority (IPEA).
2. Applicant must:
 - a. Ensure all the claims in the U.S. application must sufficiently correspond or be amended to sufficiently correspond to the allowable/patentable claim(s) in the corresponding Office of Earlier Examination (OEE) application and
 - b. Submit a claims correspondence table in English;
3. Examination of the U.S. application has not begun;
4. Applicant must submit:
 - a. Documentation of prior office action:
 - i. a copy of the office action(s) just prior to the "Decision to Grant a Patent" from each of the Global/IP5 PPH participating office application(s) containing the allowable/patentable claim(s) or
 - ii. if the allowable/patentable claims(s) are from a "Notification of Reasons for Refusal" then the Notification of Reasons for Refusal or
 - iii. if the Global/IP5 PPH participating office application is a first action allowance then no office action from the Global/IP5 PPH participating office is necessary should be indicated on the request/petition form or
 - iv. the latest work product in the international phase of the OEE PCT application;
 - b. An English language translation of the Global/IP5 PPH participating office action or work product from (4)(a)(i)-(ii) or (iv) above;

5. Applicant must submit:

- a. An IDS listing the documents cited by the Global/IP5 PPH participating office examiner in the Global/IP5 PPH participating office action or work product (unless already submitted in this application)
- b. Copies of the documents except U.S. patents or U.S. patent application publications (unless already submitted in this application);

Conditions (1) and (3-5) above are considered to have been met. However, the request to participate in the PPH pilot program and petition fails to comply with the conditions, (2).

Regarding the requirement of condition (2), applicant has not ensured that all claims in the U.S. application for which participation in the PPH program is requested sufficiently correspond to the patentable/allowable claims in the OEE application. In this regard, the Claims Correspondence Table filed October 13, 2014, indicates the claims in the US application sufficiently correspond to claims, which were consider to not contain an opinion in the OEE application as it relates to novelty, inventive step and industrial applicability. Please see the Written Opinion (ISA/237). Clarification is needed.

Applicant is given **ONE** opportunity within a time period of **ONE MONTH or THIRTY DAYS**, whichever is longer, from the mailing date of this decision to correct the deficiencies. **NO EXTENSION OF TIME UNDER 37 CFR 1.136 IS PERMITTED.** If the deficiencies are not corrected with the time period given, the application will await action in its regular turn.

Response must be filed via the Electronic Filing System (EFS) using the document description: Petition to make special under Patent Pros Hwy. Any preliminary amendments and IDS submitted with the PPH documents must be separately indexed as a preliminary amendment and IDS, respectively.

Telephone inquiries concerning this decision should be directed to the undersigned at (571) 272-6735.

All other inquiries concerning the examination or status of the application is accessible in the PAIR system at <http://www.uspto.gov/ebc.index.html>.

/Diane Goodwyn/
Diane Goodwyn
Paralegal Specialist
Office of Petitions

REQUEST FOR PARTICIPATION IN THE GLOBAL/IP5 PATENT PROSECUTION HIGHWAY (PPH) PILOT PROGRAM IN THE USPTO

Application No.:	14/238,643-Conf. #1064	First Named Inventor:	David Ofer
Filing Date:	February 12, 2014	Attorney Docket No.:	TIA-10102/57

Title of the Invention: POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

THIS REQUEST FOR PARTICIPATION IN THE PPH PILOT PROGRAM ALONG WITH THE REQUIRED DOCUMENTS MUST BE SUBMITTED VIA EFS-WEB. INFORMATION REGARDING EFS-WEB IS AVAILABLE AT [HTTP://WWW.USPTO.GOV/PATENTS/PROCESS/FILE/DFS/](http://www.uspto.gov/patents/process/file/efs/).

APPLICANT HEREBY REQUESTS PARTICIPATION IN THE PATENT PROSECUTION HIGHWAY (PPH) PILOT PROGRAM AND PETITIONS TO MAKE THE ABOVE-IDENTIFIED APPLICATION SPECIAL UNDER THE PPH PILOT PROGRAM.

Office of earlier examination (OEE): PCT

OEE application number: PCT/US2012/048602

Both the OEE application and the above-identified U.S. application have the following earliest date (filing or priority date): July 27, 2012

Type of OEE work product relied upon: International Search Report and Written Opinion

Mailing date of OEE work product: February 26, 2013

I. Required Documents:

- a. A copy of the most recent office action prior to the decision to grant a patent or the most recent PCT work product (along with an English translation, if not in the English language):

☒ is attached.

☐ is already present in the U.S. application.

☐ is not attached because it is available to the USPTO via the Dossier Access System or WIPO's PATENTSCOPE system.

☐ is not attached because the decision to grant a patent was the first office action.

- b. (1) An information disclosure statement listing the documents cited in the OEE work product:

☐ is attached.

☒ has already been filed in the U.S. application.

☐ is not attached because no references were cited in the document in section a. above.

- (2) Copies of all cited documents (except for U.S. patents or U.S. patent application publications)

☐ are attached.

☒ have already been filed in the U.S. application.

☐ are not attached because no references were cited in the document in section a. above.

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 PARTICIPATION IN THE GLOBAL/IP5 PPH PILOT PROGRAM IN THE USPTO (continued)

Application No.:	14/238,643-Conf. #1064	First Named Inventor:	David Ofer
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II. Claims Correspondence Table:

Claims in US Application	Patentable Claims in OEE Application	Explanation regarding the correspondence
1	1	Sufficiently correspond
2	2	Sufficiently correspond
3	3	Sufficiently correspond
4	4	Sufficiently correspond
5	5	Sufficiently correspond
6	6	Sufficiently correspond
7	7	Sufficiently correspond
8	8	Sufficiently correspond
9	9	Sufficiently correspond
10	10	Sufficiently correspond
11	11	Sufficiently correspond
12	12	Sufficiently correspond
13	13	Sufficiently correspond
15	15	Sufficiently correspond

III. All the claims in the US application sufficiently correspond to the patentable/allowable claims in the OEE application.

Signature	/Weston R. Gould, Ph. D./	Date	October 13, 2014
Name (Print/Typed)	Weston R. Gould, Ph. D.	Registration Number	59,142



(51) International Patent Classification:

C01G 49/00 (2006.01) C01D 1/00 (2006.01)

C01G 51/00 (2006.01) H01M 10/05 (2010.01)

(21) International Application Number:

PCT/US2012/048602

(22) International Filing Date:

27 July 2012 (27.07.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/575,115 16 August 2011 (16.08.2011) US

(71) Applicant (for all designated States except US): TIAX LLC [US/US]; 35 Hartwell Avenue, Lexington, Massachusetts 02421 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): OFER, David [US/US]; 37 Booth Street, Needham, Massachusetts 02494 (US). PULLEN, Adrian W. [US/US]; 65 Boylston St., #3, Boston, Massachusetts 02130 (US). SRIRAMULU, Suresh [US/US]; 23 Virginia Road, Arlington, Massachusetts 02476 (US).

(74) Agent: EHRLICH, Grant M.; Cantor Colburn LLP, 20 Church Street, 22nd Floor, Hartford, Connecticut 06103 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

[Continued on next page]

(54) Title: POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

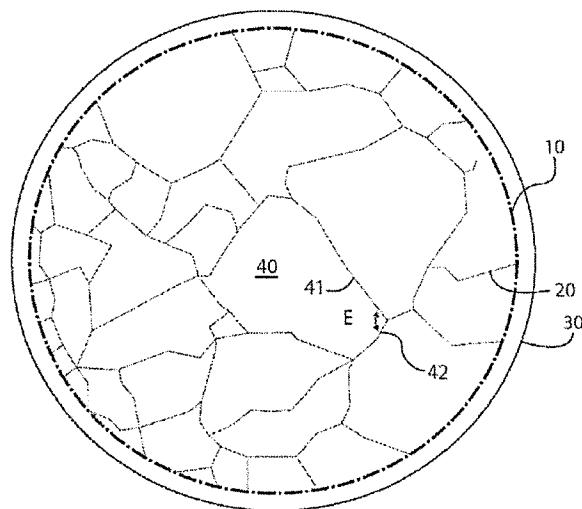


FIG. 1

(57) Abstract: A particle, including: a plurality of crystallites including a first composition having a layered α -NaFeO₂-type structure and including lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel in an amount of about 0.1 to about 0.79 mole, per mole of the first composition, cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and including a second composition having the layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.



Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

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

(88) Date of publication of the international search report:

4 July 2013

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2012/048602

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-12, 14
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/048602**A. CLASSIFICATION OF SUBJECT MATTER***C01G 49/00(2006.01)i, C01G 51/00(2006.01)i, C01D 1/00(2006.01)i, H01M 10/05(2010.01)i*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01G 49/00; H01M 4/48; H01M 10/0525; H01M 4/36; H01M 4/52; H01M 4/485

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: polycrystalline metal oxide, LiNiCoO, concentration of cobalt

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2008-234872 A (SONY CORP.) 02 October 2008 See abstract; paragraph [0014-0068]; claims 1-4	1-3, 13, 15
A	US 2005-0181280 A1 (GERBRAND CEDER et al.) 18 August 2005 See abstract; paragraph [0031-0045]; claims 1, 4	1-3, 13, 15
A	US 2009-0104530 A1 (SHIZUKA KENJI et al.) 23 April 2009 See abstract; paragraph [0481-0486]	1-3, 13, 15
A	KR 10-2010-0099668 A (LG CHEM. LTD.) 13 September 2010 See abstract; paragraph [0011-0026]	1-3, 13, 15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

25 FEBRUARY 2013 (25.02.2013)

Date of mailing of the international search report

26 FEBRUARY 2013 (26.02.2013)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan
City, 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

LEE, Jin Hong

Telephone No. 82-42-481-8649



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/048602

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2008-234872 A	02.10.2008	None	
US 2005-0181280 A1	18.08.2005	US 2002-0048706 A1 US 2005-0175529 A1 US 2008-0099734 A1 US 7026071 B2	25.04.2002 11.08.2005 01.05.2008 11.04.2006
US 2009-0104530 A1	23.04.2009	CN 101379637 A CN 102044672 A CN 102044673 A EP 2006937 A2 EP 2006937 A9 JP 04-591716 B2 JP 04-591717 B2 JP 04-613943 B2 JP 2008-103308 A JP 2008-108692 A JP 2008-305777 A JP 2010-278015 A JP 2011-003551 A JP 4591716 B2 JP 4591717 B2 JP 4613943 B2 KR 10-2008-0108222 A WO 2007-116971 A1	04.03.2009 04.05.2011 04.05.2011 24.12.2008 08.07.2009 24.09.2010 24.09.2010 29.10.2010 01.05.2008 08.05.2008 18.12.2008 09.12.2010 06.01.2011 01.12.2010 01.12.2010 19.01.2011 12.12.2008 18.10.2007
KR 10-2010-0099668 A	13.09.2010	EP 2405511 A2 US 2012-0225343 A1 WO 2010-101396 A2 WO 2010-101396 A3	11.01.2012 06.09.2012 10.09.2010 10.09.2010

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

EHRlich GRANT M.

CANTOR COLBURN LLP 20 CHURCH STREET 22ND
FLOOR HARTFORD CT 06103 USA

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

Date of mailing

(day/month/year)

26 FEBRUARY 2013 (26.02.2013)

Applicant's or agent's file reference

TIA0012PCT

FOR FURTHER ACTION

See paragraph 2 below

International application No.

PCT/US2012/048602

International filing date (day/month/year)

27 JULY 2012 (27.07.2012)

Priority date(day/month/year)

16 AUGUST 2011 (16.08.2011)

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

C01G 49/00(2006.01)i, C01G 51/00(2006.01)i, C01D 1/00(2006.01)i, H01M 10/05(2010.01)i

Applicant

TIAX LLC et al

1. This opinion contains indications relating to the following items:



Box No. I

Basis of the opinion



Box No. II

Priority



Box No. III

Non-establishment of opinion with regard to novelty, inventive step and industrial applicability



Box No. IV

Lack of unity of invention



Box No. V

Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement



Box No. VI

Certain documents cited



Box No. VII

Certain defects in the international application



Box No. VIII

Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon
Metropolitan City, 302-701,
Republic of Korea
Facsimile No. 82-42-472-7140



Date of completion of this opinion

25 FEBRUARY 2013 (25.02.2013)

Authorized officer

LEE, Jin Hong

Telephone No. 82-42-481-8649



**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US2012/048602

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of :
 - ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a))
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of:
 - a. a sequence listing filed or furnished
 - ☐ on paper
 - ☐ in electronic form
 - b. time of filing or furnishing
 - ☐ contained in the international application as filed.
 - ☐ filed together with the international application in electronic form.
 - ☐ furnished subsequently to this Authority for the purposes of search.
4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
5. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US2012/048602

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application

☒ claims Nos. 4-12, 14

because:

☐ the said international application, or the said claims Nos. _____
relate to the following subject matter which does not require an international search (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. _____
are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. _____ are so inadequately supported
by the description that no meaningful opinion could be formed (*specify*):

☒ no international search report has been established for said claims Nos. 4-12, 14

☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.

☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.

☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rule 13ter.1(a) or (b).

☐ See Supplemental Box for further details.

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US2012/048602

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-3,13,15	YES
	Claims	NONE	NO
Inventive step (IS)	Claims	1-3,13,15	YES
	Claims	NONE	NO
Industrial applicability (IA)	Claims	1-3,13,15	YES
	Claims	NONE	NO

2. Citations and explanations :

Reference is made to the following documents:

D1: JP 2008-234872 A (SONY CORP.) 02 October 2008
D2: US 2005-0181280 A1 (GERBRAND CEDER et al.) 18 August 2005
D3: US 2009-0104530 A1 (SHIZUKA KENJI et al.) 23 April 2009
D4: KR 10-2010-0099668 A (LG CHEM. LTD.) 13 September 2010

1. Novelty and Inventive step

1.1. Independent Claims 1, 13 and 15

The subject matters of claims 1, 13 and 15 differ from those of the prior art documents in that a concentration of cobalt in the grain boundary is greater than that in the crystallites. And they are not obvious to a person skilled in the art by the documents, taken alone or in combination. Therefore, claims 1, 13 and 15 meet the requirements of PCT Article 33(2) and (3) with respect to novelty and inventive step.

1.2. Dependent Claims 2-3

Claims 2-3 are dependent on claim 1, and therefore meet the requirements of PCT Article 33(2) and (3).

2. Industrial Applicability

Claims 1-3, 13 and 15 are industrially applicable under PCT Article 33(4).

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US2012/048602

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

Claims 4-12 and 14 do not comply with PCT Rule 6.4(a) because multiple dependent claims should not serve as a basis for any other multiple dependent claim.

Electronic Acknowledgement Receipt

EFS ID:	20399873
Application Number:	14238643
International Application Number:	
Confirmation Number:	1064
Title of Invention:	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME
First Named Inventor/Applicant Name:	David Ofer
Customer Number:	25006
Filer:	Weston Gould/Ann Andrusiak
Filer Authorized By:	Weston Gould
Attorney Docket Number:	TIA-10102/57
Receipt Date:	13-OCT-2014
Filing Date:	12-FEB-2014
Time Stamp:	16:40:04
Application Type:	U.S. National Stage under 35 USC 371

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		SCAN_A2_034285.pdf	1023119 ac6e2fd41905582eb29c7deadeb1fd830ed62dc	yes	19

Multipart Description/PDF files in .zip description			
Document Description	Start	End	
Preliminary Amendment	1	7	
Petition to make special under Patent Prosecution Hwy	8	9	
Miscellaneous Incoming Letter	10	19	

Warnings:

The page size in the PDF is too large. The pages should be 8.5 x 11 or A4. If this PDF is submitted, the pages will be resized upon entry into the Image File Wrapper and may affect subsequent processing

Information:

Total Files Size (in bytes):	1023119
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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.

Docket No.: TIA-10102/57
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Utility Application of:
David Ofer et al.

Application No.: 14/238,643

Confirmation No.: 1064

Filed: February 12, 2014

Art Unit: N/A

For: POLYCRYSTALLING METAL OXIDE,
METHODS OF MANUFACTURE THEREOF,
AND ARTICLES COMPRISING THE SAME

Examiner: Not Yet Assigned

SECOND PRELIMINARY AMENDMENT UNDER 37 C.F.R. 1.115

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

Dear Madam:

INTRODUCTORY COMMENTS

Prior to examination on the merits, please amend the above-identified U.S. patent application as follows:

AMENDMENTS TO THE CLAIMS

1. (Currently Amended) A particle, comprising:
a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising
lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,
nickel in an amount of about 0.1 to about 0.79 mole, per mole of the first composition,
cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and
oxygen; and
a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having the layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof,
wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.
2. (Original) The particle of claim 1, wherein the grain boundary is substantially rectilinear in cross-section.
3. (Previously Presented) The particle of claim 1, wherein a direction of a surface of the grain boundary is different than a direction of a tangent of a nearest outer surface of the particle.
4. (Previously Presented) The particle of claim 1, wherein the particle comprises a first grain boundary and a second grain boundary, wherein the first grain boundary and the second grain boundary are each directly on a same crystallite of the plurality of crystallites, and wherein the first grain boundary and second grain boundary intersect at an angle determined by a crystal structure of the first composition.

5. (Previously Presented) The particle of claim 1,
having an average grain boundary length of about 50 to about 1000 nanometers,
having an average grain boundary thickness of about 1 to about 200 nanometers,
wherein the grain boundary has a length of about 50 to about 1000 nanometers, wherein
the length is parallel to a surface of an adjacent crystallite, and
wherein the grain boundary has a thickness of about 1 to about 200 nanometers, wherein
the thickness is perpendicular to the crystallite surface.

6. (Previously Presented) The particle of claim 1, wherein
the second composition comprises
lithium in an amount of about 0.1 to about 1.3 moles, per mole of the second
composition,
nickel in an amount of about 0.1 to about 0.95 mole, per mole of the second composition,
cobalt in an amount of about 0.02 to about 0.99 mole, per mole of the second
composition, and
oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the second
composition.

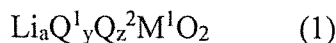
7. (Previously Presented) The particle of claim 1, wherein
the first composition may further comprise an additional metal, wherein the additional
metal of the first composition is present in an amount of about 0.01 to about 0.9 mole, per mole
of the first composition;
the second composition further comprises an additional metal, wherein the additional
metal of the second composition is present in an amount of about 0.01 to about 0.9 mole, per
mole of the second composition; and
the additional metal of the first and second compositions each independently comprise
Mg, Sr, Ca, Cu, Zn, Mn, Al, V, Ba, Zr, Ti, Cr, Fe, Mo, B, or a combination thereof.

8. (Previously Presented) The particle of claim 1, wherein

the first composition comprises Mn, and the Mn is present in the first composition in an amount of about 0.01 to about 0.6 mole, per mole of the first composition, and

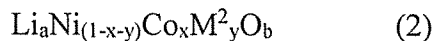
the second composition comprises Mn, and the Mn is present in the second composition in an amount of about 0.01 to about 0.6 mole, per mole of the second composition.

9. (Previously Presented) The particle of claim 1, wherein
the first and second compositions each independently comprise a composition of
Formula 1:



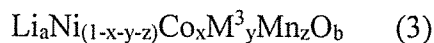
wherein Q^1 is Mg, Sr, Ca, Cu, Zn, or a combination thereof, Q^2 is Mn, Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga, or B, or a combination thereof, M^1 is Ni and Co, $0.1 \leq a \leq 1.2$, $0 < y \leq 0.2$, and $0 \leq z \leq 0.6$; or

the first and second compositions each independently comprise a composition of
Formula 2



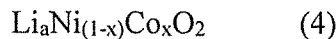
wherein M^2 is Al, V, Ti, B, Zr, Mn, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.2$, and $1.7 \leq b \leq 2.3$; or

the first and second compositions each independently comprise a composition of
Formula 3:



wherein M^3 is Al, V, Ti, B, Zr, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.1$, $0.1 \leq z \leq 0.6$, and $1.7 \leq b \leq 2.3$; or

the first and second compositions each independently comprise a composition of
Formula 4:



wherein $0.1 \leq a \leq 1.3$ and $0 < x < 0.2$ or $0.2 < x < 0.5$.

10. (Previously Presented) The particle of claim 1,

wherein the first composition comprises a composition of Formula 4 wherein $0 < x < 0.2$, and the second composition comprises a composition of Formula 4 wherein $0.2 < x < 0.5$.

11. (Previously Presented) The particle of claim 1, wherein a concentration of cobalt in the crystallites is about 0.25 to about 17 atomic percent, and a concentration of cobalt in the grain boundary is about 0.5 to about 32 atomic percent, each based on a total atomic composition of the particle.

12. (Previously Presented) The particle of claim 1, further comprising a layer on a surface of the particle, wherein the layer comprises an oxide, a phosphate, a pyrophosphate, a fluorophosphate, a carbonate, a fluoride, an oxyfluoride, or a combination thereof, of Zr, Al, Ti, Al, B, or Si, or a combination thereof.

13. (Currently Amended) A particle, comprising:
a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising
lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,
nickel in an amount of about 0.1 to about 0.79 or about 0.91 to about 0.99 mole, per mole of the first composition,
cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and
oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition;
and
a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof,
wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

14. (Canceled)

15. (Currently Amended) A method of manufacturing a particle, the method comprising:

combining a lithium compound, a cobalt compound, and a nickel compound to form a mixture;

heat treating the mixture at about 30 to about 200°C to form a dried mixture;

heat treating the dried mixture at about 200 to about 500°C for about 0.1 to about 5 hours;
then

heat treating at 600 to about 900°C for about 0.1 to about 10 hours to manufacture the particle, wherein the particle comprises a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising Li, Ni, Co, and O, wherein

the Li is present in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,

nickel is present in an amount of about 0.1 to about 0.79 mole or about 0.91 to about 0.99 mole, per mole of the first composition,

cobalt is present in an amount of 0 to about 0.5 mole, per mole of the first composition, and

oxygen is present in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and

a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof,

wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

16-20. (Canceled)

REMARKS

In view of the above amendments and remarks, Applicants believe the pending application is in condition for allowance.

Dated: October 13, 2014

Respectfully submitted,

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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 14/238,643	Filing Date 02/12/2014	☐ To be Mailed
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ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO**APPLICATION AS FILED – PART I**

(Column 1)

(Column 2)

FOR	NUMBER FILED	NUMBER EXTRA	RATE (\$)	FEE (\$)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X \$ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X \$ =	
☐ 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).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

(Column 1)

(Column 2)

(Column 3)

AMENDMENT	10/13/2014	CLAIMS REMAINING AFTER AMENDMENT	MINUS	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE (\$)	ADDITIONAL FEE (\$)
	Total (37 CFR 1.16(i))	* 14	Minus	** 20	= 0	X \$40 =	0
	Independent (37 CFR 1.16(h))	* 3	Minus	*** 3	= 0	X \$210 =	0
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
TOTAL ADD'L FEE						0	

(Column 1)

(Column 2)

(Column 3)

AMENDMENT	CLAIMS REMAINING AFTER AMENDMENT	MINUS	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE (\$)	ADDITIONAL FEE (\$)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X \$ =
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X \$ =
	☐ Application Size Fee (37 CFR 1.16(s))					
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					
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 number found in the appropriate box in column 1.

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/DONNA PRICE/

This collection of information is required by 37 CFR 1.16. 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 12 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, 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.**

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/238,643	02/12/2014	David Ofer	TIA-10102/57

CONFIRMATION NO. 1064

PUBLICATION NOTICE

25006
GIFFORD, KRASS, SPRINKLE, ANDERSON & CITKOWSKI, P.C
PO BOX 7021
TROY, MI 48007-7021



OC000000069655345

Title: POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

Publication No. US-2014-0197357-A1

Publication Date: 07/17/2014

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 Office of Public Records. The Office of Public Records can be reached by telephone at (703) 308-9726 or (800) 972-6382, by facsimile at (703) 305-8759, by mail addressed to the United States Patent and Trademark Office, Office of Public Records, 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 <http://pair.uspto.gov/>. 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 Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101



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U.S. APPLICATION NUMBER NO.	FIRST NAMED APPLICANT	ATTY. DOCKET NO.
14/238,643	David Ofer	TIA-10102/57

25006

GIFFORD, KRASS, SPRINKLE, ANDERSON & CITKOWSKI, P.C.
PO BOX 7021
TROY, MI 48007-7021

INTERNATIONAL APPLICATION NO.

PCT/US2012/048602

I.A. FILING DATE	PRIORITY DATE
07/27/2012	08/16/2011

CONFIRMATION NO. 1064
371 ACCEPTANCE LETTER



Date Mailed: 04/08/2014

NOTICE OF ACCEPTANCE OF APPLICATION UNDER 35 U.S.C 371 AND 37 CFR 1.495

The applicant is hereby advised that the United States Patent and Trademark Office, in its capacity as a Designated / Elected Office (37 CFR 1.495), has ACCEPTED the above identified international application for national patentability examination in the United States Patent and Trademark Office.

The United States Application Number assigned to the application is shown above and the relevant dates are:

02/12/2014
DATE OF RECEIPT OF 35 U.S.C. 371(c)(1),
(c)(2) and (c)(4) REQUIREMENTS

02/16/2014
DATE OF COMPLETION OF ALL
35 U.S.C. 371 REQUIREMENTS

A Filing Receipt (PTO-103X) will be issued for the present application in due course. **THE DATE APPEARING ON THE FILING RECEIPT AS THE " FILING DATE" IS THE DATE ON WHICH THE LAST OF THE 35 U.S.C. 371 (c)(1), (c)(2) and (c)(4) REQUIREMENTS HAS BEEN RECEIVED IN THE OFFICE. THIS DATE IS SHOWN ABOVE.** *The filing date of the above identified application is the international filing date of the international application (Article 11(3) and 35 U.S.C. 363).*

The following items have been received:

- Indication of Small Entity Status
- Copy of the International Application filed on 02/12/2014
- Copy of the International Search Report filed on 02/12/2014
- Preliminary Amendments filed on 02/12/2014
- Information Disclosure Statements filed on 02/12/2014
- Inventor's Oath or Declaration filed on 02/12/2014
- U.S. Basic National Fees filed on 02/12/2014
- Priority Documents filed on 02/12/2014
- Power of Attorney filed on 02/12/2014
- Application Data Sheet (37 CFR 1.76) filed on 02/12/2014

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

INDIA L EVANS

Telephone: (571) 272-9085



UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY. DOCKET NO	TOT CLAIMS	IND CLAIMS
14/238,643	02/12/2014		740	TIA-10102/57	19	3

CONFIRMATION NO. 1064

25006
GIFFORD, KRASS, SPRINKLE, ANDERSON & CITKOWSKI, P.C
PO BOX 7021
TROY, MI 48007-7021

FILING RECEIPT



Date Mailed: 04/08/2014

Receipt is acknowledged of this non-provisional 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 APPLICANT, 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 Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections 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**

Inventor(s)

David Ofer, Needham, MA;
Adrian W. Pullen, Boston, MA;
Suresh Sriamulu, Arlington, MA;

Applicant(s)

David Ofer, Needham, MA;
Adrian W. Pullen, Boston, MA;
Suresh Sriamulu, Arlington, MA;

Assignment For Published Patent Application

TIAX LLC, Lexington, MA

Power of Attorney: The patent practitioners associated with Customer Number 25006

Domestic Priority data as claimed by applicant

This application is a 371 of PCT/US2012/048602 07/27/2012
which claims benefit of 61/575,115 08/16/2011

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see <http://www.uspto.gov> for more information.) - None.

Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

If Required, Foreign Filing License Granted: 03/29/2014

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 14/238,643**

Projected Publication Date: 07/17/2014

Non-Publication Request: No

Early Publication Request: No

**** SMALL ENTITY ****

Title

POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

Preliminary Class

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

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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.

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PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number
14/238,643

APPLICATION AS FILED - PART I

(Column 1)		(Column 2)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
FOR	NUMBER FILED	NUMBER EXTRA	RATE(\$)	FEE(\$)		RATE(\$)	FEE(\$)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	140		N/A	
SEARCH FEE (37 CFR 1.16(k), (l), or (m))	N/A	N/A	N/A	240		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	360		N/A	
TOTAL CLAIMS (37 CFR 1.16(j))	19	minus 20 = *	x 40 =	0.00	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3	minus 3 = *	x 210 =	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			
			TOTAL	740		TOTAL	

* If the difference in column 1 is less than zero, enter "0" in column 2.

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
AMENDMENT A		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE(\$)	ADDITIONAL FEE(\$)		RATE(\$)	ADDITIONAL FEE(\$)
	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))							OR		
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1)		(Column 2)	(Column 3)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
AMENDMENT B		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE(\$)	ADDITIONAL FEE(\$)		RATE(\$)	ADDITIONAL FEE(\$)
	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))							OR		
	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.

MULTIPLE DEPENDENT CLAIM FEE CALCULATION SHEET Substitute for Form PTO-1360 (For use with Form PTO/SB/06)							Application Number 14238643		Filing Date	
							Applicant(s) David Ofer			
							* May be used for additional claims or amendments			
CLAIMS	AS FILED		AFTER FIRST AMENDMENT		AFTER SECOND AMENDMENT			*	*	*
	Indep	Depend	Indep	Depend	Indep	Depend				
1	1		1							
2		1		1						
3		2		1						
4		(1)		1						
5		(1)		1						
6		(1)		1						
7		(1)		1						
8		(1)		1						
9		(1)		1						
10		(1)		1						
11		(1)		1						
12		(1)		1						
13	1		1							
14		(1)	---	---						
15	1		1							
16				1						
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49										
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Total Indep	3		3		0					
Total Depend	13	↙	16	↙	0	↙				
Total Claims	16		19		0					
51										
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STATEMENT UNDER 37 CFR 3.73(b)Applicant/Patent Owner: TIAX LLCApplication No./Patent No.: 14/238,643 Filed/Issue Date: February 12, 2014Titled: POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAMETIAX LLC, a Limited Liability Company
(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that it is:

1. ☒ the assignee of the entire right, title, and interest in;
2. ☐ an assignee of less than the entire right, title, and interest in
(The extent (by percentage) of its ownership interest is _____ %); or
3. ☐ an assignee of an undivided interest in the entirety of (a complete assignment from one of the joint inventors was made)
- the patent application/patent identified above by virtue of either:

- A. ☐ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel _____, Frame _____, or for which a copy thereof is attached.

OR

- B. ☒ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as follows:

1. From: David Ofer To: TIAX LLC
The document was recorded in the United States Patent and Trademark Office at Reel 032206, Frame 0960, or for which a copy thereof is attached.
2. From: Adrian W. Pullen To: TIAX LLC
The document was recorded in the United States Patent and Trademark Office at Reel 032206, Frame 0960, or for which a copy thereof is attached.
3. From: Suresh Sriramulu To: TIAX LLC
The document was recorded in the United States Patent and Trademark Office at Reel 032206, Frame 0960, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet(s).

- ☒ As required by 37 CFR 3.73(b)(1)(i), the documentary evidence of the chain of title from the original owner to the assignee was, or concurrently is being, submitted for recordation pursuant to 37 CFR 3.11.

[NOTE: A separate copy (i.e., a true copy of the original assignment document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, to record the assignment in the records of the USPTO. See MPEP 302.08]

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

/Weston R. Gould, Ph. D./
Signature

February 14, 2014
Date

Weston R. Gould, Ph. D.
Printed or Typed Name

Attorney for Assignee
Title

Electronic Acknowledgement Receipt

EFS ID:	18206316
Application Number:	14238643
International Application Number:	
Confirmation Number:	1064
Title of Invention:	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME
First Named Inventor/Applicant Name:	David Ofer
Customer Number:	25006
Filer:	Weston Gould/Ann Andrusiak
Filer Authorized By:	Weston Gould
Attorney Docket Number:	57TIA-10102
Receipt Date:	14-FEB-2014
Filing Date:	
Time Stamp:	13:35:49
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no
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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Assignee showing of ownership per 37 CFR 3.73.	SCAN_A2_024807.pdf	73368 2a3d3313fb70479fe41b7c6d74e6539a7e0f0b4d	no	1

Warnings:

Information:

Total Files Size (in bytes):

73368

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.

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.

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A SUBMISSION UNDER 35 U.S.C. 371		Attorney Docket No. TIA-10102/57 U.S. Application No. (if known, see 37 CFR 1.5)
International Application No. PCT/US2012/048602	International Filing Date 27 July 2012	Priority Date Claimed 16 August 2011
Title of Invention POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		
First Named Inventor David Ofer et al.		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information. 1. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). NOTE: The express request under 35 U.S.C. 371(f) will not be effective unless the requirements under 35 U.S.C. 371(c)(1), (2), and (4) for payment of the basic national fee, copy of the International Application and English translation thereof (if required), and the oath or declaration of the inventor(s) have been received. 2. ☐ A copy of the International Application (35 U.S.C. 371(c)(2)) is attached hereto (not required if the International Application was previously communicated by the International Bureau or was filed in the United States Receiving Office (RO/US)). 3. An English language translation of the International Application (35 U.S.C. 371(c)(2)). a. ☐ is attached hereto. b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4). 4. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). a. ☒ is attached. b. ☐ was previously filed in the international phase under PCT Rule 4.17(iv). Items 5 to 8 below concern amendments made in the international phase. <u>PCT Article 19 and 34 amendments</u> 5. ☐ Amendments to the claims under PCT Article 19 are attached (not required if communicated by the International Bureau) (35 U.S.C. 371(c)(3)). 6. ☐ English translation of the PCT Article 19 amendment is attached (35 U.S.C. 371(c)(3)). 7. ☐ English translation of annexes (Article 19 and/or 34 amendments only) of the International Preliminary Examination Report is attached (35 U.S.C. 371(c)(5)). <u>Cancellation of amendments made in the international phase</u> 8a. ☐ Do not enter the amendment made in the international phase under PCT Article 19. 8b. ☐ Do not enter the amendment made in the international phase under PCT Article 34. NOTE: A proper amendment made in English under Article 19 or 34 will be entered in the U.S. national phase application absent a clear instruction from applicant not to enter the amendment(s). The following items 9 to 17 concern a document(s) or information included. 9. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 10. ☒ A preliminary amendment. 11. ☒ An Application Data Sheet under 37 CFR 1.76. 12. ☐ A substitute specification. NOTE: A substitute specification cannot include claims. See 37 CFR 1.125(b). 13. ☒ A power of attorney and/or change of address letter. 14. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.3 and 37 CFR 1.821–1.825. 15. ☐ Assignment papers (<i>cover sheet and document(s)</i>). Name of Assignee: 16. ☐ 37 CFR 3.73(c) Statement (<i>when there is an Assignee</i>).		

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.

U.S. APPLN. No. (if known - see 37 CFR 1.5)	INTERNATIONAL APPLICATION No. PCT/US2012/048602	ATTORNEY DOCKET No. TIA-10102/57
17. ☐ Other items or information:		
The following fees have been submitted.		CALCULATIONS
18. ☒ Basic national fee (37 CFR 1.492(a))..... \$280		\$ 280.00
19. ☒ Examination fee (37 CFR 1.492(c)) If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4)..... \$0 All other situations \$720		\$ 720.00
20. ☒ Search fee (37 CFR 1.492(b)) If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4) \$0 Search fee (37 CFR 1.445(a)(2)) has been paid on the international application to the USPTO as an International Searching Authority..... \$120 International Search Report prepared by an ISA other than the US and provided to the Office or previously communicated to the US by the IB..... \$480 All other situations \$600		\$ 480.00
TOTAL OF 18, 19, and 20 =		\$ 1,480.00
☐ Additional fee for specification and drawings filed in paper over 100 sheets (excluding sequence listing in compliance with 37 CFR 1.821(c) or (e) in an electronic medium or computer program listing in an electronic medium) (37 CFR 1.492(j)). Fee for each additional 50 sheets of paper or fraction thereof \$400		
Total Sheets	Extra Sheets	Number of each addition 50 or fraction thereof (round up to a whole number)
- 100 =	/50 =	x \$400
		\$
Surcharge of \$140.00 for furnishing any of the search fee, examination fee, or the oath or declaration after the date of commencement of the national stage (37 CFR 1.492(h)).		\$
CLAIMS	NUMBER FILED	NUMBER EXTRA
Total claims	20 - 20 =	0
Independent claims	3 - 3 =	0
MULTIPLE DEPENDENT CLAIM(S) (if applicable)		+ \$780
Processing fee of \$140.00 for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.492(i)).		\$
TOTAL OF ABOVE CALCULATIONS =		\$ 1,480.00
☐ Applicant asserts small entity status. See 37 CFR 1.27. Fees above are reduced by 1/2.		
☐ Applicant certifies micro entity status. See 37 CFR 1.29. Fees above are reduced by 3/4. Applicant must attach form PTO/SB/15A or B or equivalent.		
TOTAL NATIONAL FEE =		\$ 1,480.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property.		\$
		\$
TOTAL FEES ENCLOSED =		\$ 1,480.00
		Amount to be refunded: \$
		Amount to be charged: \$

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.

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. 07-1180 in the amount of \$ _____ to cover the above fees.
- c. ☒ The Director is hereby authorized to charge additional fees which may be required, or credit any overpayment, to Deposit Account No. 07-1180 as follows:
- i. ☒ any required fee.
- ii. ☐ any required fee except for excess claims fees required under 37 CFR 1.492(d) and (e) and multiple dependent claim fee required under 37 CFR 1.492(f).
- d. ☒ Fees are to be charged to a credit card. **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. The PTO-2038 should only be mailed or faxed to the USPTO. However, when paying the basic national fee, the PTO-2038 may NOT be faxed to the USPTO.

ADVISORY: If filing by EFS-Web, do NOT attach the PTO-2038 form as a PDF along with your EFS-Web submission. Please be advised that this is **not** recommended and by doing so your **credit card information may be displayed via PAIR**. To protect your information, it is recommended to pay fees online by using the electronic payment method.

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the International Application to pending status.

Correspondence Address

☒ The address associated with Customer Number: 25006 OR ☐ Correspondence address below

Name					
Address					
City		State		Zip Code	
Country				Telephone	
Email					

Signature	/Weston R. Gould, Ph. D./	Date	February 12, 2014
Name (Print/Type)	Weston R. Gould, Ph. D.	Registration No. (Attorney/Agent)	59,142

Under the Paperwork Reduction Act of 1995, no person are required to respond to a collection of information unless it displays a valid OMB control number

FEE TRANSMITTAL	Complete if known	
	Application Number	Not Yet Assigned
	Filing Date	
	First Named Inventor	David Ofer
	Examiner Name	Not Yet Assigned
☐ Applicant asserts small entity status. See 37 CFR 1.27	Art Unit	N/A
☐ 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	Practitioner Docket No.	TIA-10102/57
TOTAL AMOUNT OF PAYMENT	(\$) 1,480.00	

METHOD OF PAYMENT (check all that apply)

☐ Check ☒ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____
☐ Deposit Account Deposit Account Number: 07-1180 Deposit Account Name: Gifford, Krass, Sprinkle, Anderson & Citkowski, P.C.

For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)

☐ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, **except for the filing fee**
☒ Charge any additional fee(s) or underpayment of fee(s) under 37 CFR 1.16 and 1.17 ☒ Credit any overpayment of fee(s)

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.

FEE CALCULATION**1. BASIC FILING, SEARCH, AND EXAMINATION FEES** (U = undiscounted fee; S = small entity fee; M = micro entity fee)

Application Type	FILING FEES			SEARCH FEES			EXAMINATION FEES			Fees Paid (\$)
	U (\$)	S (\$)	M (\$)	U (\$)	S (\$)	M (\$)	U (\$)	S (\$)	M (\$)	
Utility	280	140*	70	600	300	150	720	360	180	
Design	180	90	45	120	60	30	460	230	115	
Plant	180	90	45	380	190	95	580	290	145	
Reissue	280	140	70	600	300	150	2,160	1,080	540	
Provisional	260	130	65	0	0	0	0	0	0	

* The \$140 small entity status filing fee for a utility application is further reduced to \$70 for a small entity status applicant who files the application via EFS-Web.

2. EXCESS CLAIM FEES

Fee Description	Undiscounted Fee (\$)	Small Entity Fee (\$)	Micro Entity Fee (\$)
Each claim over 20 (including Reissues)	80	40	20
Each independent claim over 3 (including Reissues)	420	210	105
Multiple dependent claims	780	390	195
Total Claims			
20 - 20 or HP = 0 x =			
HP = highest number of total claims paid for, if greater than 20.			
Indep. Claims			
3 - 3 or HP = 0 x =			
HP = highest number of independent claims paid for, if greater than 3.			

3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$400 (\$200 for small entity) (\$100 for micro entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

Total Sheets	Extra Sheets	Number of each additional 50 or fraction thereof	Fee (\$)	Fee Paid (\$)
- 100 =	/50 =	(round up to a whole number) x		

4. OTHER FEE(S)

Non-English specification, \$130 fee (no small or micro entity discount)

Non-electronic filing fee under 37 CFR 1.16(t) for a utility application, \$400 fee (\$200 small or micro entity)

Other (e.g., late filing surcharge):	1631 Basic National Stage fee	280.00
	1633 National Stage Examination Fee - all other ...	720.00
	1642 National Stage Search Fee - search report ...	480.00

SUBMITTED BY			
Signature	/Weston R. Gould, Ph. D./	Registration No. (Attorney/Agent)	59,142
Name (Print/Type)	Weston R. Gould, Ph. D.	Telephone	(248) 647-6000
		Date	February 12, 2014

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	TIA-10102/57
		Application Number	
Title of Invention	POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		
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.)
--------------------------	---

Applicant Information:

Applicant 1									
Applicant Authority		☒ Inventor			☐ Legal Representative under 35 U.S.C. 117			☐ Party of Interest under 35 U.S.C. 118	
Prefix	Given Name		Middle Name		Family Name			Suffix	
Mr.	David				Ofer				
Residence Information (Select One)									
☒ US Residency ☐ Non US Residency ☐ Active US Military Service									
City	Needham		State/Province	MA	Country of Residence		US		
Citizenship under 37 CFR 1.41(b)			US						
Mailing Address of Applicant:									
Address 1		37 Booth Street							
Address 2									
City	Needham			State/Province	MA				
Postal Code		02494		Country	US				
Applicant 2									
Applicant Authority		☒ Inventor			☐ Legal Representative under 35 U.S.C. 117			☐ Party of Interest under 35 U.S.C. 118	
Prefix	Given Name		Middle Name		Family Name			Suffix	
Mr.	Adrian		W.		Pullen				
Residence Information (Select One)									
☒ US Residency ☐ Non US Residency ☐ Active US Military Service									
City	Boston		State/Province	MA	Country of Residence		US		
Citizenship under 37 CFR 1.41(b)			US						
Mailing Address of Applicant:									
Address 1		35 Boylston Street, #3							
Address 2									
City	Boston			State/Province	MA				
Postal Code		02130		Country	US				
Applicant 3									
Applicant Authority		☒ Inventor			☐ Legal Representative under 35 U.S.C. 117			☐ Party of Interest under 35 U.S.C. 118	
Prefix	Given Name		Middle Name		Family Name			Suffix	
Mr.	Suresh				Sriramulu				
Residence Information (Select One)									
☒ US Residency ☐ Non US Residency ☐ Active US Military Service									
City	Arlington		State/Province	MA	Country of Residence		US		

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	TIA-10102/57
		Application Number	
Title of Invention	POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		

Citizenship under 37 CFR 1.41(b)		US	
Mailing Address of Applicant:			
Address 1	23 Virginia Road		
Address 2			
City	Arlington	State/Province	MA
Postal Code	02476	Country	US
All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the Add button.			

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	25006		
Email Address		Add Email	Remove Email

Application Information:

Title of the Invention	POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		
Attorney Docket Number	TIA-10102/57	Small Entity Status Claimed	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Suggested Class (if any)		Sub Class (if any)	
Suggested Technology Center (if any)	N/A		
Total Number of Drawing Sheets (if any)	9	Suggested Figure for Publication (if any)	

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). Enter either 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 1.9)

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	TIA-10102/57
		Application Number	
Title of Invention	POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		
Customer Number	25006		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this 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(a)(2) or CFR 1.78(a)(4), and need not otherwise be made part of the specification.

Prior Application Status		Remove	
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	a 371 of international	PCTUS2012048602	2012-07-27
Prior Application Status		Remove	
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
PCTUS2012048602	non provisional of	61575115	2011-08-16

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 benefit of foreign priority and to identify any prior foreign application for which priority is not claimed. 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(a).

	Remove		
Application Number	Country ¹	Parent Filing Date (YYYY-MM-DD)	Priority Claimed
			☐ Yes ☐ No

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.

Assignee Information:

Providing this information in the application data sheet does not substitute for compliance with any requirement of part 3 of Title 37 of the CFR to have an assignment recorded in the Office.

Assignee 1

If the Assignee is an Organization check here. ☒

Organization Name	TIAX LLC		
-------------------	----------	--	--

Mailing Address Information:

Address 1	35 Hartwell Avenue		
Address 2			
City	Lexington	State/Province	MA
Country	US	Postal Code	02421
Phone Number		Fax Number	
Email Address			

Additional Assignee Data may be generated within this form by selecting the **Add** button.

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	TIA-10102/57
		Application Number	
Title of Invention	POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME		

Signature:

A signature of the applicant or representative is required in accordance with 37 CFR 1.33 and 10.18. Please see 37 CFR 1.4(d) for the form of the signature.					
Signature	/Weston R. Gould, Ph. D./			Date (YYYY-MM-DD)	2014-02-12
First Name	Weston	Last Name	Gould, Ph. D.	Registration Number	59142

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.**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF,
AND ARTICLES COMPRISING THE SAME

the specification of which was filed on July 27, 2012 as Application No.
PCT/US2012/048602.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by an amendment, if any, specifically referred to herein.

I acknowledge the duty to disclose all information known to me that is material to patentability as defined in 37 C.F.R. § 1.56.

FOREIGN PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

☒ no such foreign applications have been filed

☐ such foreign applications have been filed as follows:

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

Application Number	Country	Date of Filing	Priority Claimed Under 35 USC 119

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

Application Number	Country	Date of Filing

CLAIM FOR BENEFIT OF EARLIER U.S. PROVISIONAL APPLICATIONS

I hereby claim priority benefits under Title 35, United States Code § 119(e), of any United States provisional patent application(s) listed below:

☐ no such U.S. provisional applications have been filed.

☒ such U.S. provisional applications have been filed as follows:

Application Number	Date of Filing	Priority Claimed Under 35 USC 119
61/575,115	August 16, 2011	☒ Yes ☐ No

CLAIM FOR BENEFIT OF EARLIER U.S./PCT APPLICATION(S)

I hereby claim the benefit under Title 35, United States Code, § 120 of the United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose all information that is material to patentability as defined in 37 C.F.R. § 1.56 which became available to me between the filing date of the prior application and the national or PCT international filing date of this application:

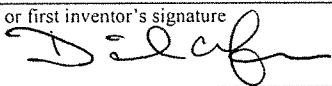
☒ no such U.S./PCT applications have been filed.

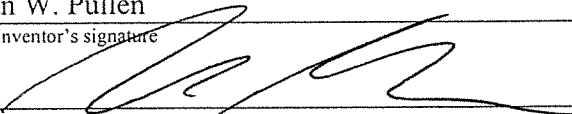
☐ such U.S./PCT applications have been filed as follows:

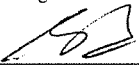
Application Number	Relationship	Parent Application	Date of Filing

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Please direct all correspondence to Weston R. Gould at the address associated with Customer Number 25006.

Full name of sole or first inventor David Ofer	
Sole or first inventor's signature 	Date
Residence Needham, MA	
Citizenship US	
Mailing Address 37 Booth Street Needham, MA 02494	

Full name of second inventor, if any Adrian W. Pullen	
Second inventor's signature 	Date 1/28/14
Residence Boston, MA	
Citizenship US	
Mailing Address 65 Boylston St., #3 Boston, MA 02130	

Full name of third inventor, if any Suresh Sriramulu	
Third inventor's signature 	Date 01/28/2014
Residence Arlington, MA	
Citizenship US	
Mailing Address 23 Virginia Road Arlington, MA 02476	

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.

POWER OF ATTORNEY TO PROSECUTE APPLICATIONS BEFORE THE USPTO

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

I hereby appoint:

☒ Practitioners associated with the Customer Number: 25006

OR

☐ Practitioner(s) named below (if more than ten patent practitioners are to be named, then a customer number must be used):

Name	Registration Number	Name	Registration Number

as attorney(s) or agent(s) to represent the undersigned before the United States Patent and Trademark Office (USPTO) in connection with any and all patent applications assigned only to the undersigned according to the USPTO assignment records or assignment documents attached to this form in accordance with 37 CFR 3.73(b).

Please change the correspondence address for the application identified in the attached statement under 37 CFR 3.73(b) to:

☐ The address associated with Customer Number:

OR

☐ Firm or Individual Name

Address

City

State

Zip

Country

Telephone

Email

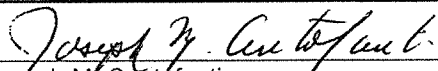
Assignee Name and Address:

TIAX LLC

A copy of this form, together with a statement under 37 CFR 3.73(b) (Form PTO/SB/96 or equivalent) is required to be filed in each application in which this form is used. The statement under 37 CFR 3.73(b) 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.

SIGNATURE of Assignee of Record

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

Signature		Date	JAN. 24, 2014
Name	Joseph M. Centofanti	Telephone	781-879-1285
Title	General Counsel, TIAX, LLC		

Docket No.: TIA-10102/57
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Utility Application of:
David Ofer et al.

Application No.: National Stage of
PCT/US2012/048602

Confirmation No.: N/A

Filed: Concurrently Herewith

Art Unit: N/A

For: POLYCRYSTALLING METAL OXIDE,
METHODS OF MANUFACTURE THEREOF,
AND ARTICLES COMPRISING THE SAME

Examiner: Not Yet Assigned

FIRST PRELIMINARY AMENDMENT UNDER 37 C.F.R. 1.115

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

Dear Madam:

INTRODUCTORY COMMENTS

Prior to examination on the merits, please amend the above-identified U.S. patent application as follows:

AMENDMENTS TO THE SPECIFICATION

Please insert the following paragraph on page 1, following the title:

This application is the U.S. national phase of PCT/US2012/048602, filed July 27, 2012, which claims priority from U.S. provisional patent application Serial No. 61/575,115, filed August 16, 2011, the contents of each of which are incorporated herein in their entirety.

AMENDMENTS TO THE CLAIMS

1. (Currently Amended) A particle, comprising:
a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising
lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,
nickel in an amount of about 0.1 to about 0.79 mole, per mole of the first composition,
cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and
oxygen; and
a grain boundary between adjacent crystallites of the plurality of crystallites and
comprising a second composition having the layered α -NaFeO₂-type structure, a cubic structure,
or a combination thereof,
wherein a concentration of cobalt in the grain boundary is greater than a concentration of
cobalt in the crystallites.
2. (Original) The particle of claim 1, wherein the grain boundary is substantially
rectilinear in cross-section.
3. (Currently Amended) The particle of ~~any of claim~~[[s]] 1 [[to 2]], wherein a
direction of a surface of the grain boundary is different than a direction of a tangent of a nearest
outer surface of the particle.
4. (Currently Amended) The particle of ~~any of claim~~[[s]] 1 [[to 3]], wherein the
particle comprises a first grain boundary and a second grain boundary, wherein the first grain
boundary and the second grain boundary are each directly on a same crystallite of the plurality of
crystallites, and wherein the first grain boundary and second grain boundary intersect at an angle
determined by a crystal structure of the first composition.
5. (Currently Amended) The particle of ~~any of claim~~[[s]] 1 [[to 4]],
having an average grain boundary length of about 50 to about 1000 nanometers,

having an average grain boundary thickness of about 1 to about 200 nanometers,
wherein the grain boundary has a length of about 50 to about 1000 nanometers, wherein
the length is parallel to a surface of an adjacent crystallite, and
wherein the grain boundary has a thickness of about 1 to about 200 nanometers, wherein
the thickness is perpendicular to the crystallite surface.

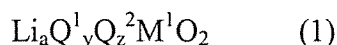
6. (Currently Amended) The particle of ~~any of claim~~[[s]] 1 [[to 5]], wherein
the second composition comprises
lithium in an amount of about 0.1 to about 1.3 moles, per mole of the second
composition,
nickel in an amount of about 0.1 to about 0.95 mole, per mole of the second composition,
cobalt in an amount of about 0.02 to about 0.99 mole, per mole of the second
composition, and
oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the second
composition.

7. (Currently Amended) The particle of ~~any of claim~~[[s]] 1 [[to 6]], wherein
the first composition may further comprise an additional metal, wherein the additional
metal of the first composition is present in an amount of about 0.01 to about 0.9 mole, per mole
of the first composition;
the second composition further comprises an additional metal, wherein the additional
metal of the second composition is present in an amount of about 0.01 to about 0.9 mole, per
mole of the second composition; and
the additional metal of the first and second compositions each independently comprise
Mg, Sr, Ca, Cu, Zn, Mn, Al, V, Ba, Zr, Ti, Cr, Fe, Mo, B, or a combination thereof.

8. (Currently Amended) The particle of ~~any of claim~~[[s]] 1 [[to 7]], wherein
the first composition comprises Mn, and the Mn is present in the first composition in an
amount of about 0.01 to about 0.6 mole, per mole of the first composition, and

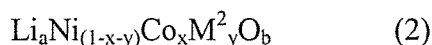
the second composition comprises Mn, and the Mn is present in the second composition in an amount of about 0.01 to about 0.6 mole, per mole of the second composition.

9. (Currently Amended) The particle of ~~any of~~ claim[[s]] 1 [[to 8]], wherein the first and second compositions each independently comprise a composition of Formula 1:



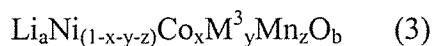
wherein Q^1 is Mg, Sr, Ca, Cu, Zn, or a combination thereof, Q^2 is Mn, Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga, or B, or a combination thereof, M^1 is Ni and Co, $0.1 \leq a \leq 1.2$, $0 < y \leq 0.2$, and $0 \leq z \leq 0.6$; or

the first and second compositions each independently comprise a composition of Formula 2



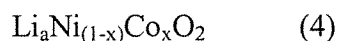
wherein M^2 is Al, V, Ti, B, Zr, Mn, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.2$, and $1.7 \leq b \leq 2.3$; or

the first and second compositions each independently comprise a composition of Formula 3:



wherein M^3 is Al, V, Ti, B, Zr, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.1$, $0.1 \leq z \leq 0.6$, and $1.7 \leq b \leq 2.3$; or

the first and second compositions each independently comprise a composition of Formula 4:



wherein $0.1 \leq a \leq 1.3$ and $0 < x < 0.2$ or $0.2 < x < 0.5$.

10. (Currently Amended) The particle of ~~any of~~ claim[[s]] 1 [[to 9]], wherein the first composition comprises a composition of Formula 4 wherein $0 < x < 0.2$, and the second composition comprises a composition of Formula 4 wherein $0.2 < x < 0.5$.

11. (Currently Amended) The particle of ~~any of claim~~[[s]] 1 [[to 10]], wherein a concentration of cobalt in the crystallites is about 0.25 to about 17 atomic percent, and a concentration of cobalt in the grain boundary is about 0.5 to about 32 atomic percent, each based on a total atomic composition of the particle.

12. (Currently Amended) The particle of ~~any of claim~~[[s]] 1 [[to 11]], further comprising a layer on a surface of the particle, wherein the layer comprises an oxide, a phosphate, a pyrophosphate, a fluorophosphate, a carbonate, a fluoride, an oxyfluoride, or a combination thereof, of Zr, Al, Ti, Al, B, or Si, or a combination thereof.

13. (Currently Amended) A particle, comprising:
a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising
lithium ~~in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,~~
nickel in an amount of about 0.1 to about 0.79 or about 0.91 to about 0.99 mole, per mole of the first composition,
~~cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and~~
~~oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition;~~
and
a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof,
wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

14. (Canceled)

15. (Currently Amended) A method of manufacturing a particle, the method comprising:

combining a lithium compound, a cobalt compound, and a nickel compound to form a mixture;

heat treating the mixture at about 30 to about 200°C to form a dried mixture;

heat treating the dried mixture at about 200 to about 500°C for about 0.1 to about 5 hours;
then

heat treating at 600 to about 900°C for about 0.1 to about 10 hours to manufacture the particle, wherein the particle comprises a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising Li, Ni, [[Co,]] and O, wherein

~~the Li is present in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,~~

~~nickel is present in an amount of about 0.1 to about 0.79 mole or about 0.91 to about 0.99 mole, per mole of the first composition,~~

~~cobalt is present in an amount of 0 to about 0.5 mole, per mole of the first composition, and~~

~~oxygen is present in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and~~

a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof,

wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

16. (New) The particle of claim 1 wherein said first composition comprises cobalt in an amount of 0.01 to about 0.5 mole, per mole of the first composition.

17. (New) The particle of claim 1 wherein
said lithium in said first composition is in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,

said nickel in said first composition is in an amount of about 0.1 to about 0.79 mole, per mole of the first composition, and

said oxygen in said first composition is in an amount of about 1.7 to about 2.3 moles, per mole of the first composition.

18. (New) The particle of claim 13 wherein said first composition comprises cobalt in an amount of 0.01 to about 0.5 mole, per mole of the first composition.

19. (New) The particle of claim 13 wherein
said lithium in said first composition is in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,

said nickel in said first composition is in an amount of about 0.1 to about 0.79 mole, per mole of the first composition, and

said oxygen in said first composition is in an amount of about 1.7 to about 2.3 moles, per mole of the first composition.

20. (New) The method of claim 15 wherein
said lithium in said first composition is in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,

said nickel in said first composition is in an amount of about 0.1 to about 0.79 mole, per mole of the first composition,

cobalt in said first composition is in an amount of 0 to about 0.5 mole, per mole of the first composition, and

said oxygen in said first composition is in an amount of about 1.7 to about 2.3 moles, per mole of the first composition.

REMARKS

In view of the above amendments and remarks, Applicants believe the pending application is in condition for allowance.

Dated: February 12, 2014

Respectfully submitted,

Electronic signature: /Weston R. Gould, Ph. D./
Weston R. Gould, Ph. D.
Registration No.: 59,142
GIFFORD, KRASS, SPRINKLE, ANDERSON
& CITKOWSKI, P.C.
2701 Troy Center Drive, Suite 330
Post Office Box 7021
Troy, Michigan 48007-7021
(248) 647-6000
(248) 647-5210 (Fax)
Attorney for Applicant

Docket No.: TIA-10102/57
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Utility Application of:
David Ofer et al.

Application No.: National Stage of
PCT/US2012/048602

Confirmation No.: N/A

Filed: Concurrently Herewith

Art Unit: N/A

For: POLYCRYSTALLING METAL OXIDE,
METHODS OF MANUFACTURE THEREOF,
AND ARTICLES COMPRISING THE SAME

Examiner: Not Yet Assigned

INFORMATION DISCLOSURE STATEMENT (IDS)

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

Dear Madam:

Pursuant to 37 C.F.R. § 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the references listed on the attached PTO/SB/08. It is respectfully requested that the information be expressly considered during the prosecution of this application, and that the references be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

This Information Disclosure Statement accompanies the new patent application submitted herewith.

In accordance with 37 C.F.R. § 1.98(a)(2)(ii), Applicant has not submitted copies of U.S. patents and U.S. patent applications. Applicant submits herewith copies of foreign patents and non-patent literature in accordance with 37 C.F.R. § 1.98(a)(2).

In accordance with 37 C.F.R. § 1.97(g), the filing of this Information Disclosure Statement shall not be construed to mean that a search has been made or that no other material information as defined in 37 C.F.R. § 1.56(a) exists. In accordance with 37 C.F.R. § 1.97(h), the filing of this Information Disclosure Statement shall not be construed to be an admission that any patent, publication or other information referred to therein is “prior art” for this invention unless specifically designated as such.

It is submitted that the Information Disclosure Statement is in compliance with 37 C.F.R. § 1.98 and the Examiner is respectfully requested to consider the listed references.

The Director is hereby authorized to charge any deficiency in the fees filed, asserted to be filed or which should have been filed herewith to our Deposit Account No. 07-1180, under Order No. TIA-10102/57.

Dated: February 12, 2014

Respectfully submitted,

Electronic signature: /Weston R. Gould, Ph. D./
Weston R. Gould, Ph. D.

Registration No.: 59,142
GIFFORD, KRASS, SPRINKLE, ANDERSON
& CITKOWSKI, P.C.

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Attorney for Applicant

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				Application Number	Not Yet Assigned
				Filing Date	Concurrently Herewith
				First Named Inventor	David Ofer
				Art Unit	N/A
				Examiner Name	Not Yet Assigned
				Attorney Docket Number	TIA-10102/57
Sheet	1	of	2		

[illegible]

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear	T ⁶
		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)				
	BA	JP-2008234872-A	10-02-2008	Sony Corp		√
	BB	KR-1020100099668	09-13-2010	Sony Corp.		√

Examiner Signature		Date Considered	
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***EXAMINER:** Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. * CITE NO.: Those application(s) which are marked with an single asterisk (*) next to the Cite No. are not supplied (under 37 CFR 1.98(a)(2)(iii)) because that application was filed after June 30, 2003 or is available in the IFW. ¹ Applicant's unique citation designation number (optional). ² See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. ³ Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). ⁴ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁵ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁶ Applicant is to place a check mark here if English language Translation is attached.

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.

Substitute for form 1449/PTO INFORMATION DISCLOSURE STATEMENT BY APPLICANT <i>(Use as many sheets as necessary)</i>				<i>Complete if Known</i>	
				Application Number	Not Yet Assigned
				Filing Date	Concurrently Herewith
				First Named Inventor	David Ofer
				Art Unit	N/A
				Examiner Name	Not Yet Assigned
				Attorney Docket Number	TIA-10102/57
Sheet	2	of	2		

[illegible]

Examiner Signature		Date Considered	
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

¹Applicant's unique citation designation number (optional). ²Applicant is to place a check mark here if English language Translation is attached.



Espacenet

Bibliographic data: JP2008234872 (A) — 2008-10-02

POSITIVE ELECTRODE ACTIVE MATERIAL AND BATTERY

No documents available for this priority number.

Inventor(s): ISHIMATSU TAKANAO; SATO TAKASHI; OKAWA TAKASHI;
 TERAUCHI MASUMI; YAMAMOTO YOSHIKATSU ± (ISHIMATSU
 TAKANAO, ; SATO TAKASHI, ; OKAWA TAKASHI, ; TERAUCHI
 MASUMI, ; YAMAMOTO YOSHIKATSU)

Applicant(s): SONY CORP ± (SONY CORP)

Classification: - international: *H01M4/36; H01M4/50; H01M4/52*
 - cooperative: Y02E60/12

Application number: JP20070069114 20070316

Priority number(s): JP20070069114 20070316

Abstract of JP2008234872 (A)

PROBLEM TO BE SOLVED: To provide a positive electrode active material and a battery having superior filling-up performance, superior low-temperature characteristics, and superior high-temperature cycle characteristics. ; SOLUTION: A positive electrode 21A includes a positive electrode active material made of a mixture of a first positive electrode active material and a second positive electrode active material at a weight ratio of 95:5 to 70:30 (first positive electrode active material: second positive electrode active material). The first positive electrode active material includes lithium composite oxide containing, for instance, Li, Co, M1, and M2 (M1 indicates a first element, and M2 indicates a second element), a first sub-component element, and a second sub-component element. The second positive electrode active material is a lithium transition metal composite oxide containing Li, Ni, Co, Mn, and A (A is at least one kind out of Mg and Al). ; COPYRIGHT: (C)2009,JPO&INPIT

(19) 日本国特許庁 (JP)

(12) 公開特許公報(A)

(11) 特許出願公開番号

特開2008-234872

(P2008-234872A)

(43) 公開日 平成20年10月2日 (2008. 10. 2)

(51) Int. Cl.

F I

テーマコード (参考)

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5 H O 5 O

H O 1 M 4/36 (2006.01)

H O 1 M 4/36 E

H O 1 M 4/50 (2006.01)

H O 1 M 4/36 B

H O 1 M 4/50 1 O 2

審査請求 未請求 請求項の数 8 O L (全 23 頁)

(21) 出願番号 特願2007-69114 (P2007-69114)

(22) 出願日 平成19年3月16日 (2007. 3. 16)

(71) 出願人 000002185

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東京都港区港南1丁目7番1号

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最終頁に続く

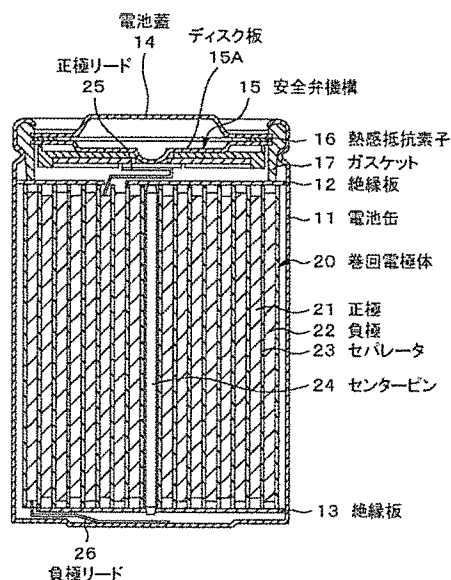
(54) 【発明の名称】 正極活物質および電池

(57) 【要約】 (修正有)

【課題】 充填性に優れており、低温特性、及び高温のサイクル特性に優れた正極活物質および電池を提供する。

【解決手段】 正極21Aは、第1の正極活物質と、第2の正極活物質とを、95:5~70:30の重量比(第1の正極活物質:第2の正極活物質)で混合した混合物よりなる正極活物質を含有する。第1の正極活物質は、例えば、Li、Co、M1、M2、(M1は第1元素、M2は第2元素を表す。)を含有するリチウム複合酸化物と、第1副成分元素と、第2副成分元素と、を含有するものである。第2の正極活物質は、Li、Ni、Co、Mn、A、(AはMg、Alのうちの少なくとも1種である。)を含有するリチウム遷移金属複合酸化物である。

【選択図】 図1



【特許請求の範囲】

【請求項1】

第1の正極活物質と、第2の正極活物質とを、95：5～70：30の重量比（第1の正極活物質：第2の正極活物質）で混合した混合物よりなる正極活物質であって、

上記第1の正極活物質は、

リチウム（Li）、コバルト（Co）、第1元素および第2元素を含むリチウムコバルト複合酸化物と、第1副成分元素および第2副成分元素と、
を含有するものであり、

上記第1元素は、アルミニウム（Al）、クロム（Cr）、バナジウム（V）、マンガン（Mn）および鉄（Fe）からなる群のうちの少なくとも1種であり、

上記第2元素は、マグネシウム（Mg）およびカルシウム（Ca）からなる群のうちの少なくとも1種であり、

上記第1副成分元素は、チタン（Ti）、ジルコニウム（Zr）およびハフニウム（Hf）からなる群のうちの少なくとも1種であり、

上記第2副成分元素は、ケイ素（Si）、ゲルマニウム（Ge）およびスズ（Sn）からなる群のうちの少なくとも1種であり、

コバルト（Co）と、上記第1元素と、上記第2元素とのモル比は、コバルト（Co）の組成をa、上記第1元素の組成をb、上記第2元素の組成をcとすると、それぞれ $0.9 \leq a < 1$ 、 $0.001 \leq b \leq 0.05$ 、 $0.001 \leq c \leq 0.05$ の範囲内であり、

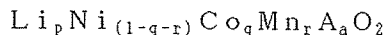
上記第1の副成分元素の含有量は、コバルト（Co）に対する割合で、 $0.01 \text{ mol} \%$ 以上 $10 \text{ mol} \%$ 以下の範囲内であり、

上記第2の副成分元素の含有量は、コバルト（Co）に対する割合で、 $0.01 \text{ mol} \%$ 以上 $10 \text{ mol} \%$ 以下の範囲内であり、

上記第2の正極活物質は、

化1で表されるリチウム遷移金属複合酸化物であること
を特徴とする正極活物質。

（化1）

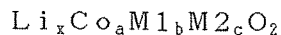


（化1において、Aはマグネシウム（Mg）、アルミニウム（Al）のうちの少なくとも1種である。aは $0 \leq a \leq 0.10$ である。p、q、rは、 $0.05 \leq p \leq 1.15$ 、 $0.4 \leq q+r \leq 0.70$ 、 $0.05 \leq r \leq 0.40$ である。）

【請求項2】

上記リチウムコバルト複合酸化物は、化2で表されること
を特徴とする請求項1記載の正極活物質。

（化2）



（化1において、M1は第1元素、M2は第2元素を表し、x、a、bおよびcはそれぞれ $0.9 \leq x \leq 1.1$ 、 $0.9 \leq a < 1$ 、 $0.001 \leq b \leq 0.05$ 、 $0.001 \leq c \leq 0.05$ 、 $a+b+c=1$ の範囲内の値である。）

【請求項3】

上記第1の正極活物質において、上記第1副成分元素および上記第2副成分元素の少なくとも一部は、化合物として、上記リチウムコバルト複合酸化物の結晶粒界に存在することを特徴とする請求項1記載の正極活物質。

【請求項4】

上記第1の正極活物質の平均粒径は、 $5 \mu\text{m} \sim 25 \mu\text{m}$ であり、

上記第2の正極活物質の平均粒径は、 $1 \mu\text{m} \sim 15 \mu\text{m}$ であり、

（第1の正極活物質の平均粒径／第2の正極活物質の平均粒径） > 1.6 であることを特徴とする請求項1記載の正極活物質。

【請求項5】

正極および負極と、電解質と、を備えた電池であって、

上記正極は、第1の正極活物質と、第2の正極活物質とを、95：5～70：30の重量比（第1の正極活物質：第2の正極活物質）で混合した混合物よりなる正極活物質を有し、

上記第1の正極活物質は、

リチウム（Li）、コバルト（Co）、第1元素および第2元素を含むリチウムコバルト複合酸化物と、第1副成分元素および第2副成分元素と、を含有するものであり、

上記第1元素は、アルミニウム（Al）、クロム（Cr）、バナジウム（V）、マンガン（Mn）および鉄（Fe）からなる群のうちの少なくとも1種であり、

上記第2元素は、マグネシウム（Mg）およびカルシウム（Ca）からなる群のうちの少なくとも1種であり、

上記第1副成分元素は、チタン（Ti）、ジルコニウム（Zr）およびハフニウム（Hf）からなる群のうちの少なくとも1種であり、

上記第2副成分元素は、ケイ素（Si）、ゲルマニウム（Ge）およびスズ（Sn）からなる群のうちの少なくとも1種であり、

コバルト（Co）と、上記第1元素と、上記第2元素とのモル比は、コバルト（Co）の組成をa、上記第1元素の組成をb、上記第2元素の組成をcとすると、それぞれ $0.9 \leq a < 1$ 、 $0.001 \leq b \leq 0.05$ 、 $0.001 \leq c \leq 0.05$ の範囲内であり、

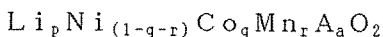
上記第1の副成分元素の含有量は、コバルト（Co）に対する割合で、 $0.01 \text{ mol} \%$ 以上 $10 \text{ mol} \%$ 以下の範囲内であり、

上記第2の副成分元素の含有量は、コバルト（Co）に対する割合で、 $0.01 \text{ mol} \%$ 以上 $10 \text{ mol} \%$ 以下の範囲内であり、

上記第2の正極活物質は、

化1で表されるリチウム遷移金属複合酸化物であること
を特徴とする電池。

（化1）

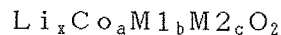


（化1において、Aはマグネシウム（Mg）、アルミニウム（Al）のうちの少なくとも1種である。aは $0 \leq a \leq 0.10$ である。p、q、rは、 $0.05 \leq p \leq 1.15$ 、 $0.4 \leq q + r \leq 0.70$ 、 $0.05 \leq r \leq 0.40$ である。）

【請求項6】

上記リチウムコバルト複合酸化物は、化2で表されること
を特徴とする請求項5記載の電池。

（化2）



（化1において、M1は第1元素、M2は第2元素を表し、x、a、bおよびcはそれぞれ $0.9 \leq x \leq 1.1$ 、 $0.9 \leq a < 1$ 、 $0.001 \leq b \leq 0.05$ 、 $0.001 \leq c \leq 0.05$ 、 $a + b + c = 1$ の範囲内の値である。）

【請求項7】

上記第1の正極活物質において、上記第1副成分元素および上記第2副成分元素の少なくとも一部は、化合物として、上記リチウムコバルト複合酸化物の結晶粒界に存在することを特徴とする請求項5記載の電池。

【請求項8】

上記第1の正極活物質の平均粒径は、 $5 \mu\text{m} \sim 25 \mu\text{m}$ であり、

上記第2の正極活物質の平均粒径は、 $1 \mu\text{m} \sim 15 \mu\text{m}$ であり、

（第1の正極活物質の平均粒径／第2の正極活物質の平均粒径） > 1.6 であることを特徴とする請求項5記載の電池。

【発明の詳細な説明】

この発明は、正極活物質および電池に関する。さらに詳しくは2種類のリチウム複合酸化物を有する正極活物質およびこれを用いた電池に関する。

【背景技術】

【0002】

近年、携帯型電子機器が次々と開発されており、その電源として二次電池が重要な位置を占めるようになってきている。特に最近では、二次電池の高容量化および軽量化が求められており、そのような要求に応える二次電池として、電極反応物質にリチウムを用いたリチウムイオン二次電池が実用化されている。

【0003】

リチウムイオン二次電池の特徴としては、他の電池と比較して酸化還元電位が高い正極と酸化還元電位の低い負極を組み合わせることで、容量が大きい、すなわちエネルギー密度が大きい電池を作製できる点にあり、現在リチウムイオン二次電池の正極活物質として、主流となっているものは、コバルト酸リチウムである。

【0004】

このコバルト酸リチウムを用いたリチウムイオン二次電池は、平均放電電位が高いという利点があるものの、サイクル特性が良くないことや低温での大出力放電時では、電圧低下が激しく、例えば、寒冷地においてパーソナルコンピュータの電源を入れた際、出力不足により起動しない問題が考えられる。また、近年では、より広い温度範囲における使用や、大電流での使用も求められており、特性に対する要求がより厳しくなっている。

【0005】

そこで、コバルト酸リチウムのコバルト(Co)を他の元素で置換したり、または他の元素を添加することにより、特性を向上させる試みが多数なされている。例えば、特許文献1には、コバルト(Co)の一部を、アルミニウム(Al)、クロム(Cr)、バナジウム(V)、マンガン(Mn)および鉄(Fe)からなる群のうちの少なくとも1種の第1元素と、マグネシウム(Mg)およびカルシウム(Ca)からなる群のうちの少なくとも1種の第2元素とで置換することにより、高温時における安定性を向上させることができる正極活物質が記載されている。また、特許文献2には、コバルト酸リチウムを合成する際に、ジルコニウム化合物を共沈させて、コバルト酸リチウムの粒子表面にジルコニウム(Zr)を存在させることにより、負荷特性、低温特性および熱安定性を向上させることができる正極活物質が記載されている。

【0006】

【特許文献1】特開2001-319652号公報

【特許文献2】特開2004-311408号公報

【発明の開示】

【発明が解決しようとする課題】

【0007】

しかしながら、特許文献1に記載の正極活物質では、高温特性は向上させることができるものの、低温特性については満足できる程度の特性を得ることはできず、サイクル特性についても、さらなる向上が求められていた。また、特許文献2に記載の正極活物質では、熱安定性を向上させることができるものの、近年要求されている程度の特性は得ることができなかった。

【0008】

したがって、この発明の目的は、充填性に優れており、低温特性および高温におけるサイクル特性に優れた正極活物質および電池を提供することにある。

【課題を解決するための手段】

【0009】

上述の課題を解決するために、第1の発明は、

第1の正極活物質と、第2の正極活物質とを、95:5~70:30の重量比(第1の正極活物質:第2の正極活物質)で混合した混合物よりなる正極活物質であって、

第1の正極活物質は

リチウム(Li)、コバルト(Co)、第1元素および第2元素を含むリチウムコバルト複合酸化物と、第1副成分元素および第2副成分元素と、を含有するものであり、

第1元素は、アルミニウム(Al)、クロム(Cr)、バナジウム(V)、マンガン(Mn)および鉄(Fe)からなる群のうちの少なくとも1種であり、

第2元素は、マグネシウム(Mg)およびカルシウム(Ca)からなる群のうちの少なくとも1種であり、

第1副成分元素は、チタン(Ti)、ジルコニウム(Zr)およびハフニウム(Hf)からなる群のうちの少なくとも1種であり、

第2副成分元素は、ケイ素(Si)、ゲルマニウム(Ge)およびスズ(Sn)からなる群のうちの少なくとも1種であり、

コバルト(Co)と、第1元素と、第2元素とのモル比は、コバルト(Co)の組成をa、第1元素の組成をb、第2元素の組成をcとすると、それぞれ $0.9 \leq a < 1$ 、 $0.001 \leq b \leq 0.05$ 、 $0.001 \leq c \leq 0.05$ の範囲内であり、

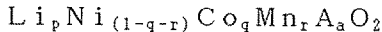
第1の副成分元素の含有量は、コバルト(Co)に対する割合で、 $0.01 \text{ mol\%}$ 以上 $10 \text{ mol\%}$ 以下の範囲内であり、

第2の副成分元素の含有量は、コバルト(Co)に対する割合で、 $0.01 \text{ mol\%}$ 以上 $10 \text{ mol\%}$ 以下の範囲内であり、

第2の正極活物質は、

化1で表されるリチウム遷移金属複合酸化物であることを特徴とする正極活物質である。

(化1)



(化1において、Aはマグネシウム(Mg)、アルミニウム(Al)のうちの少なくとも1種である。aは $0 \leq a \leq 0.10$ である。p、q、rは、 $0.05 \leq p \leq 1.15$ 、 $0.4 \leq q+r \leq 0.70$ 、 $0.05 \leq r \leq 0.40$ である。)

【0010】

第2の発明は、

正極および負極と、電解質と、を備えた電池であって、

正極は、第1の正極活物質と、第2の正極活物質とを、95:5~70:30の重量比(第1の正極活物質:第2の正極活物質)で混合した混合物よりなる正極活物質を有し、

第1の正極活物質は、

リチウム(Li)、コバルト(Co)、第1元素および第2元素を含むリチウムコバルト複合酸化物と、第1副成分元素および第2副成分元素と、を含有するものであり、

第1元素は、アルミニウム(Al)、クロム(Cr)、バナジウム(V)、マンガン(Mn)および鉄(Fe)からなる群のうちの少なくとも1種であり、

第2元素は、マグネシウム(Mg)およびカルシウム(Ca)からなる群のうちの少なくとも1種であり、

第1副成分元素は、チタン(Ti)、ジルコニウム(Zr)およびハフニウム(Hf)からなる群のうちの少なくとも1種であり、

第2副成分元素は、ケイ素(Si)、ゲルマニウム(Ge)およびスズ(Sn)からなる群のうちの少なくとも1種であり、

コバルト(Co)と、第1元素と、第2元素とのモル比は、コバルト(Co)の組成をa、第1元素の組成をb、第2元素の組成をcとすると、それぞれ $0.9 \leq a < 1$ 、 $0.001 \leq b \leq 0.05$ 、 $0.001 \leq c \leq 0.05$ の範囲内であり、

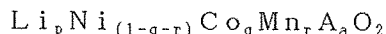
第1の副成分元素の含有量は、コバルト(Co)に対する割合で、 $0.01 \text{ mol\%}$ 以上 $10 \text{ mol\%}$ 以下の範囲内であり、

第2の副成分元素の含有量は、コバルト(Co)に対する割合で、 $0.01 \text{ mol\%}$ 以上 $10 \text{ mol\%}$ 以下の範囲内であり

第2の正極活物質は、

化1で表されるリチウム遷移金属複合酸化物であることを特徴とする電池である。

(化1)



(化1において、Aはマグネシウム(Mg)、アルミニウム(Al)のうちの少なくとも1種である。aは $0 \leq a \leq 0.10$ である。p、q、rは、 $0.05 \leq p \leq 1.15$ 、 $0.4 \leq q+r \leq 0.70$ 、 $0.05 \leq r \leq 0.40$ である。)

【0011】

この発明では、第1の正極活物質において、第1元素および第2元素を所定量含むリチウムコバルト複合酸化物を含有すると共に、第1副成分元素および第2副成分元素を所定量含有するようにしたので、結晶構造の安定性をより向上させることができる。よって、電池に用いた場合に、負荷特性および低温特性を向上させることができると共に、高温におけるサイクル特性も向上させることができる。また、第1の正極活物質と、第2の正極活物質とを所定の割合で混合するようにしたので、充填性を向上でき、電池に用いた場合に、低温特性および高温におけるサイクル特性をさらに向上させることができる。

【発明の効果】

【0012】

この発明によれば、正極活物質の充填性を向上させることができ、電池に用いた場合に、優れた低温特性および高温におけるサイクル特性を得ることができる。

【発明を実施するための最良の形態】

【0013】

以下、この発明の実施形態について図面を参照しながら説明する。なお、以下の実施形態の全図においては、同一または対応する部分には同一の符号を付す。

【0014】

この発明の一実施形態による正極活物質は、第1の正極活物質と、第2の正極活物質とを混合した混合物よりなるものである。

【0015】

第1の正極活物質は、粒子状であり、リチウム(Li)と、コバルト(Co)とを含むリチウムコバルト複合酸化物を有する。また、リチウム(Li)およびコバルト(Co)に加えて、さらに、アルミニウム(Al)、クロム(Cr)、バナジウム(V)、マンガン(Mn)および鉄(Fe)からなる群のうちの少なくとも1種の第1元素と、マグネシウム(Mg)およびカルシウム(Ca)からなる群のうちの少なくとも1種の第2元素とを含んでいる。第1元素は酸素との結合エネルギーが大きいので、第1元素を含むことによりリチウムが抜けた状態の結晶構造を強固に保持することができ、また、第2元素を含むことにより電子伝導性を向上させることができるからである。

【0016】

このリチウムコバルト複合酸化物におけるコバルト(Co)と、第1元素と、第2元素とのモル比は、コバルトの組成をa、第1元素の組成をb、第2元素の組成をcとすると、それぞれ $0.9 \leq a < 1$ 、 $0.001 \leq b \leq 0.05$ 、 $0.001 \leq c \leq 0.05$ の範囲内であることが好ましい。コバルト(Co)の含有量が多くなると添加効果が薄れてしまい、少なくなると充放電容量が低下してしまう。第1元素の含有量が多くなると結晶内でのリチウムイオンの拡散が阻害されてしまい、少なくなるとリチウム(Li)が抜けた状態の結晶構造を強固に保持する効果が低くなってしまい、第2元素の含有量が多くなると結晶構造の崩壊が促進されてしまい、少なくなると伝導性向上の効果が低くなってしまい。

【0017】

また、この正極活物質は、さらに、チタン(Ti)、ジルコニウム(Zr)およびハフニウム(Hf)からなる群のうちの少なくとも1種の第1副成分元素と、ケイ素(Si)、ゲルマニウム(Ge)およびスズ(Sn)からなる群のうちの少なくとも1種の第2副

成分元素とを含んでいる。

【0018】

第1副成分元素の少なくとも一部は、例えば酸素(O)を含有する化合物、または酸素(O)およびリチウム(Li)を含有する化合物などとして、リチウムコバルト複合酸化物の結晶粒界に存在している。例えば正極活物質が第1副成分元素としてジルコニウム(Zr)を含む場合には、第1副成分元素であるジルコニウム(Zr)の少なくとも一部は、例えば酸化ジルコニウムまたはジルコン酸リチウムなどの化合物として、リチウムコバルト複合酸化物の結晶粒界に存在している。これによりリチウムコバルト複合酸化物の結晶構造をより安定化させることができるようになっている。なお、第1副成分元素の一部はリチウムコバルト複合酸化物に固溶していてもよく、また、リチウムコバルト複合酸化物の粒子の表面に存在していてもよい。

【0019】

第1副成分元素の含有量は、リチウムコバルト複合酸化物のコバルト(Co)に対する割合(第1副成分元素/コバルト)で、0.01mol%以上10mol%以下の範囲内であることが好ましい。第1副成分元素の含有量が少ないと十分な効果を得ることができず、多いと容量が低下してしまうからである。

【0020】

また、第2副成分元素の少なくとも一部は、例えば酸素(O)を含有する化合物、または酸素(O)およびリチウム(Li)を含有する化合物などとして、リチウムコバルト複合酸化物の結晶粒界に存在している。例えば正極活物質が第2副成分元素としてスズ(Sn)を含む場合には、第2副成分元素であるスズ(Sn)の少なくとも一部は、例えば酸化スズまたはスズ酸リチウムなどの化合物として、リチウムコバルト複合酸化物の結晶粒界に存在している。これによりリチウムコバルト複合酸化物の結晶構造をより安定化させることができるようになっている。なお、第2副成分元素の一部はリチウムコバルト複合酸化物に固溶していてもよく、また、リチウムコバルト複合酸化物の粒子の表面に存在していてもよい。

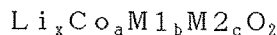
【0021】

第2副成分元素の含有量は、リチウムコバルト複合酸化物のコバルト(Co)に対する割合(第2副成分元素/コバルト)で、0.01mol%以上10mol%以下の範囲内であることが好ましい。第2副成分元素の含有量が少ないと十分な効果を得ることができず、多いと容量が低下してしまうからである。

【0022】

リチウムコバルト複合酸化物の化学式は、例えば化Iで表される。

(化I)



(化Iにおいて、M1は第1元素、M2は第2元素を表し、x、a、bおよびcはそれぞれ $0.9 \leq x \leq 1.1$ 、 $0.9 \leq a < 1$ 、 $0.001 \leq b \leq 0.05$ 、 $0.001 \leq c \leq 0.05$ 、 $a + b + c = 1$ の範囲内の値である。)

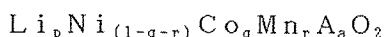
【0023】

第1の正極活物質は、例えば、硫酸コバルトなどのコバルト化合物と、第1副成分元素を含む化合物と、第2副成分元素を含む化合物とを溶解させた酸性溶液に、炭酸水素ナトリウムなどのアルカリ溶液を加えて、炭酸コバルトなどのコバルト化合物と共に第1副成分元素および第2副成分元素を共沈させたのち、この炭酸コバルトなどのコバルト化合物と、炭酸リチウムなどのリチウム化合物と、第1元素を含む化合物と、第2元素を含む化合物とを混合し、焼成することにより得ることができる。

【0024】

第2の正極活物質は、化IIで表されるリチウム遷移金属複合酸化物である。

(化II)



(化IIにおいて Aはマグネシウム(Mg) アルミニウム(Al)のうちの少なくとも

1種である。 a は $0 \leq a \leq 0.10$ である。 p 、 q 、 r は、 $0.05 \leq p \leq 1.15$ 、 $0.40 \leq q+r \leq 0.70$ 、 $0.05 \leq r \leq 0.40$ である。)

【0025】

第2の正極活物質は、化IIにおいて、 $0.40 \leq q+r \leq 0.60$ であるものがより好ましい。より高容量が得られるからである。

【0026】

第1の正極活物質と、第2の正極活物質との混合重量比は、 $95:5 \sim 70:30$ である。第2の正極活物質の割合を上記範囲より、少なくすると、第2の正極活物質を加えることによる効果が小さいからである。また、第2の正極活物質の割合を上記範囲より、多くすると、充填性が低下するからである。

【0027】

第1の正極活物質の粒径は、平均粒径で $5 \mu\text{m} \sim 25 \mu\text{m}$ が好ましい。平均粒径が $25 \mu\text{m}$ を超えると、負荷特性が著しく低下するからであり、また、 $25 \mu\text{m}$ を超えるものは製造し難いからである。第2の正極活物質の粒径は、平均粒径で $1 \mu\text{m} \sim 15 \mu\text{m}$ が好ましい。平均粒径が $15 \mu\text{m}$ を超えると、負荷特性が著しく低下するからであり、また、 $25 \mu\text{m}$ を超えるものは製造し難いからである。

【0028】

また、第1の正極活物質の平均粒径と、第2の正極活物質の平均粒径との粒径比（「第1の正極活物質の平均粒径／第2の正極活物質の平均粒径」）は、 $(\text{第1の正極活物質の平均粒径} / \text{第2の正極活物質の平均粒径}) > 1.6$ が好ましく、 $1.5 > (\text{第1の正極活物質の平均粒径} / \text{第2の正極活物質の平均粒径}) \geq 1.67$ であることがより好ましく、 $5 \geq (\text{第1の正極活物質の平均粒径} / \text{第2の正極活物質の平均粒径}) \geq 1.67$ であることが特に好ましい。第1の正極活物質と、第2の正極活物質との粒径差が小さすぎると、充填性が低下し、また、第1の正極活物質と、第2の正極活物質との粒径差が大きすぎても、充填性が低下し、電池に用いた場合に、容量が低下してしまうからである。

【0029】

この発明の一実施形態による正極活物質では、第1の正極活物質において、第1元素および第2元素を所定量含むリチウムコバルト複合酸化物を含有すると共に、第1副成分元素および第2副成分元素を所定量含有するようにしたので、結晶構造の安定性をより向上させることができる。よって、電池に用いた場合に、負荷特性および低温特性を向上させることができると共に、高温におけるサイクル特性も向上させることができる。また、第1の正極活物質と、第2の正極活物質とを所定の割合で混合するようにしたので、充填性を向上でき、電池に用いた場合に、低温特性および高温におけるサイクル特性をさらに向上させることができる。

【0030】

次に、この発明の一実施形態による正極活物質を用いた二次電池の第1の例について説明する。

【0031】

図1は、この発明の一実施形態による正極活物質を用いた二次電池の第1の例の一構成例を示す断面図である。この二次電池は、例えば、非水電解質二次電池であり、また例えば、リチウムイオン二次電池である。この二次電池では、一对の正極および負極当たりの完全充電状態における開回路電圧が例えば 4.20 V または 4.20 V を越えて設定される。 4.20 V を越えて設定される開回路電圧の範囲は、例えば 4.25 V 以上 4.60 V 以下または 4.25 V 以上 6.00 V 以下である。

【0032】

この二次電池は、いわゆる円筒型といわれるものであり、ほぼ中空円柱状の電池缶11の内部に、帯状の正極21と帯状の負極22がセパレータ23を介して巻回された巻回電極体20を有している。電池缶11は、例えばニッケル(Ni)のめっきがされた鉄(Fe)により構成されており、一端部が閉鎖され他端部が開放されている。電池缶11の内部には、巻回電極体20を挟むように巻回周面に対して垂直に一对の絶縁板12、13が

それぞれ配置されている。

【0033】

電池缶11の開放端部には、電池蓋14と、この電池蓋14の内側に設けられた安全弁機構15および熱感抵抗(PTC: Positive Temperature Coefficient)素子16が、ガスケット17を介してかしめられることにより取り付けられており、電池缶11の内部は密閉されている。電池蓋14は、例えば、電池缶11と同様の材料により構成されている。安全弁機構15は、熱感抵抗素子16を介して電池蓋14と電氣的に接続されており、内部短絡あるいは外部からの加熱などにより電池の内圧が一定以上となった場合にディスク板15Aが反転して電池蓋14と巻回電極体20との電氣的接続を切断するようになっている。熱感抵抗素子16は、温度が上昇すると抵抗値の増大により電流を制限し、大電流による異常な発熱を防止するものである。ガスケット17は、例えば、絶縁材料により構成されており、表面にはアスファルトが塗布されている。

【0034】

巻回電極体20は、例えば、センターピン24を中心に巻回されている。巻回電極体20の正極21にはアルミニウム(A1)などよりなる正極リード25が接続されており、負極22にはニッケル(Ni)などよりなる負極リード26が接続されている。正極リード25は安全弁機構15に溶接されることにより電池蓋14と電氣的に接続されており、負極リード26は電池缶11に溶接され電氣的に接続されている。

【0035】

図2は、図1に示した巻回電極体20の一部を拡大して表す断面図である。巻回電極体20は、正極21と負極22とをセパレータ23を介して積層し、巻回したものである。

【0036】

正極21は、例えば、正極集電体21Aと、この正極集電体21Aの両面に設けられた正極活物質層21Bとを有している。正極集電体21Aは、例えば、アルミニウム箔などの金属箔により構成されている。

【0037】

正極活物質層21Bは、第1の実施形態による正極活物質と、必要に応じて炭素材料などの導電剤およびポリフッ化ビニリデンあるいはポリテトラフルオロエチレンなどの結着剤とを含んでいる。これによりこの二次電池では、正極活物質の結晶構造がより安定し、負荷特性および低温特性を向上させることができると共に、高温におけるサイクル特性を向上させることができるようになっている。なお、化1に示したリチウムの組成xは、組み立て時、すなわち完全放電時のものである。

【0038】

正極活物質層21Bの体積密度は 2.0 g/cm^3 以上 4.0 g/cm^3 以下の範囲内であることが好ましい。体積密度が小さいと単位体積当たりの容量が小さくなってしまい、大きいと電解液の浸透性が低下し、負荷特性および低温特性が低下してしまうからである。

【0039】

負極22は、例えば、正極21と同様に、負極集電体22Aと、この負極集電体22Aの両面に設けられた負極活物質層22Bとを有している。負極集電体22Aは、例えば、銅箔などの金属箔により構成されている。

【0040】

負極活物質層22Bは、例えば、負極活物質として、リチウムを吸蔵および放出することが可能な負極材料のいずれか1種または2種以上を含んで構成されており、必要に応じて導電剤および結着剤を含んでもよい。

【0041】

リチウムを吸蔵および放出することが可能な負極材料としては、例えば、黒鉛、難黒鉛化性炭素あるいは易黒鉛化炭素などの炭素材料が挙げられる。炭素材料には、いずれか1種を単独で用いてもよく、2種以上を混合して用いてもよく、また、平均粒子径の異なる2種以上を混合して用いてもよい。

【0042】

リチウムを吸蔵および放出することが可能な負極材料としては、また、リチウムと合金を形成可能な金属元素または半金属元素を構成元素として含む材料が挙げられる。具体的には、リチウムと合金を形成可能な金属元素の単体、合金、あるいは化合物、またはリチウムと合金を形成可能な半金属元素の単体、合金、あるいは化合物、またはこれらの1種あるいは2種以上の相を少なくとも一部に有する材料が挙げられる。

【0043】

このような金属元素あるいは半金属元素としては、例えば、スズ(Sn)、鉛(Pb)、アルミニウム、インジウム(In)、ケイ素(Si)、亜鉛(Zn)、アンチモン(Sb)、ビスマス(Bi)、カドミウム(Cd)、マグネシウム、ホウ素(B)、ガリウム(Ga)、ゲルマニウム(Ge)、ヒ素(As)、銀(Ag)、ジルコニウム、イットリウム(Y)またはハフニウム(Hf)が挙げられる。中でも、長周期型周期表における14族の金属元素あるいは半金属元素が好ましく、特に好ましいのはケイ素あるいはスズである。ケイ素およびスズはリチウムを吸蔵および放出する能力が大きく、高いエネルギー密度を得ることができるからである。

【0044】

ケイ素(Si)の合金としては、例えば、ケイ素(Si)以外の第2の構成元素として、スズ(Sn)、ニッケル(Ni)、銅(Cu)、鉄(Fe)、コバルト(Co)、マンガン(Mn)、亜鉛(Zn)、インジウム(In)、銀(Ag)、チタン(Ti)、ゲルマニウム(Ge)、ビスマス(Bi)、アンチモン(Sb)およびクロム(Cr)からなる群のうちの少なくとも1種を含むものが挙げられる。スズ(Sn)の合金としては、例えば、スズ(Sn)以外の第2の構成元素として、ケイ素(Si)、ニッケル(Ni)、銅(Cu)、鉄(Fe)、コバルト(Co)、マンガン(Mn)、亜鉛(Zn)、インジウム(In)、銀(Ag)、チタン(Ti)、ゲルマニウム(Ge)、ビスマス(Bi)、アンチモン(Sb)およびクロム(Cr)からなる群のうちの少なくとも1種を含むものが挙げられる。

【0045】

ケイ素(Si)の化合物あるいはスズ(Sn)の化合物としては、例えば、酸素(O)あるいは炭素(C)を含むものが挙げられ、ケイ素(Si)またはスズ(Sn)に加えて、上述した第2の構成元素を含んでいてもよい。

【0046】

セバレータ23は、電気的に安定であると共に、正極活物質、負極活物質あるいは溶媒に対して化学的に安定であり、かつ電気伝導性を有していなければどのようなものを用いてもよい。例えば、高分子の不織布、多孔質フィルム、ガラスあるいはセラミックスの繊維を紙状にしたものを用いることができ、これらを複数積層して用いてもよい。特に、多孔質ポリオレフィンフィルムを用いることが好ましく、これをポリイミド、ガラスあるいはセラミックスの繊維などよりなる耐熱性の材料と複合させたものを用いてもよい。

【0047】

電解液は、電解質塩と、この電解質塩を溶解する溶媒とを含んでいる。電解質塩としては、例えば、 LiClO_4 、 LiPF_6 、 LiBF_4 、 $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ 、 $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ 、あるいは LiAsF_6 などのリチウム塩が挙げられる。電解質塩にはいずれか1種を用いてもよいが、2種以上を混合して用いてもよい。

【0048】

溶媒としては、例えば、 γ -ブチロラクトン、 γ -バレロラクトン、 δ -バレロラクトンあるいは ϵ -カプロラクトンなどのラクトン系溶媒、炭酸エチレン、炭酸プロピレン、炭酸ブチレン、炭酸ビニレン、炭酸ジメチル、炭酸エチルメチルあるいは炭酸ジエチルなどの炭酸エステル系溶媒、1,2-ジメトキシエタン、1-エトキシ-2-メトキシエタン、1,2-ジエトキシエタン、テトラヒドロフランあるいは2-メチルテトラヒドロフランなどのエーテル系溶媒、アセトニトリルなどのニトリル系溶媒、スルフォラン系溶媒、リン酸類、リン酸エステル溶媒、またはピロリドン類などの非水溶媒が挙げられる。溶

媒は、いずれか1種を単独で用いてもよく、2種以上を混合して用いてもよい。

【0049】

次に、この二次電池の製造方法の一例について説明する。正極21は、以下のようにして作製する。まず、正極活物質と、導電剤と、結着剤とを混合して正極合剤を調製し、この正極合剤をN-メチル-2-ピロリドンなどの溶剤に分散させて正極合剤スラリーとする。次いで、この正極合剤スラリーを正極集電体21Aに塗布し、溶剤を乾燥させた後、ロールプレス機などにより圧縮成型して正極活物質層21Bを形成し、正極21を得る。

【0050】

負極22は、以下のようにして作製する。まず、負極活物質と、結着剤とを混合して負極合剤を調製し、この負極合剤をN-メチル-2-ピロリドンなどの溶剤に分散させて負極合剤スラリーとする。次いで、この負極合剤スラリーを負極集電体22Aに塗布し溶剤を乾燥させたのち、ロールプレス機などにより圧縮成型して負極活物質層22Bを形成し、負極22を得る。

【0051】

次に、正極集電体21Aに正極リード25を溶接などにより取り付けると共に、負極集電体22Aに負極リード26を溶接などにより取り付ける。その後、正極21と負極22とをセパレータ23を介して巻回し、正極リード25の先端部を安全弁機構15に溶接すると共に、負極リード26の先端部を電池缶11に溶接して、巻回した正極21および負極22を一对の絶縁板12、13で挟み、電池缶11の内部に収納する。正極21および負極22を電池缶11の内部に収納したのち、電解質を電池缶11の内部に注入し、セパレータ23に含浸させる。その後、電池缶11の開口端部に電池蓋14、安全弁機構15および熱感抵抗素子16を、ガスケット17を介してかしめることにより固定する。以上により、図1に示した二次電池が作製される。

【0052】

この発明の一実施形態による正極活物質を用いた二次電池の第1の例では、充電を行うと、例えば、正極21からリチウムイオンが放出され、電解液を介して負極22に吸蔵される。一方、放電を行うと、例えば、負極22からリチウムイオンが放出され、電解液を介して正極21に吸蔵される。

【0053】

次に、この発明の一実施形態による正極活物質を用いた二次電池の第2の例について説明する。図3は、この発明の一実施形態による正極活物質を用いた二次電池の第2の例の一構成例を示す斜視図である。この二次電池は、正極リード31および負極リード32が取り付けられた電池素子30をフィルム状の外装部材41の内部に収納した構成を有している。この二次電池では、一对の正極および負極当たりの完全充電状態における開回路電圧が例えば4.20Vまたは4.20Vを越えて設定される。4.20Vを越えて設定される開回路電圧の範囲は、例えば4.25V以上4.60V以下または4.25V以上6.00V以下である。

【0054】

正極リード31および負極リード32は、それぞれ例えば短冊状であり、外装部材41の内部から外部に向かい例えば同一方向にそれぞれ導出されている。正極リード31は、例えばアルミニウムなどの金属材料により構成されており、負極リード32は、例えばニッケル(Ni)などの金属材料により構成されている。

【0055】

外装部材41は、例えば、絶縁層、金属層および最外層をこの順に積層しラミネート加工などにより貼り合わせた構造を有している。外装部材41は、例えば、絶縁層の側を内側として、各外縁部が融着あるいは接着剤により互いに密着されている。

【0056】

絶縁層は、例えば、ポリエチレン、ポリプロピレン、変性ポリエチレン、変性ポリプロピレンあるいはこれらの共重合体などのポリオレフィン樹脂により構成されている。水分透過性を低くすることができ、気密性に優れているからである。金属層は、箔状あるいは

板状のアルミニウム、ステンレス、ニッケルあるいは鉄などにより構成されている。最外層は、例えば絶縁層と同様の樹脂により構成されていてもよいし、ナイロンなどにより構成されていてもよい。破れや突き刺し等に対する強度を高くすることができるからである。外装部材41は、絶縁層、金属層および最外層以外の他の層を備えていてもよい。

【0057】

外装部材41と正極リード31および負極リード32との間には、正極リード31および負極リード32と、外装部材41の内側との密着性を向上させ、外気の侵入を防止するための密着フィルム42が挿入されている。密着フィルム42は、正極リード31および負極リード32に対して密着性を有する材料により構成され、例えば、正極リード31および負極リード32が上述した金属材料により構成される場合には、ポリエチレン、ポリプロピレン、変性ポリエチレンあるいは変性ポリプロピレンなどのポリオレフィン樹脂により構成されることが好ましい。

【0058】

図4は、図3に示した電池素子30のIV-IV線に沿った断面図である。電池素子30は、正極33と負極34とをセパレータ35および電解質36を介して積層し、巻回したものであり、最外周部は保護テープ37により保護されている。

【0059】

正極33は、例えば、正極集電体33Aと、この正極集電体33Aの両面に設けられた正極活物質層33Bとを有している。負極34は、例えば、負極集電体34Aと、この負極集電体34Aの両面に設けられた負極活物質層34Bとを有している。正極集電体33A、正極活物質層33B、負極集電体34A、負極活物質層34Bおよびセパレータ35の構成はそれぞれ、上述の第1の例における正極集電体21A、正極活物質層21B、負極集電体22A、負極活物質層22Bおよびセパレータ23と同様である。

【0060】

電解質36は、電解液と、この電解液を保持する高分子化合物を含む保持体とを含有しており、いわゆるゲル状となっている。電解液（すなわち溶媒および電解質塩など）の構成は、上述した第1の例における電解液と同様である。

【0061】

高分子化合物は、溶媒を吸収してゲル化するものであればよく、例えば、ポリフッ化ビニリデンあるいはビニリデンフルオロライドとヘキサフルオロプロピレンとの共重合体などのフッ素系高分子化合物、ポリエチレンオキシドあるいはポリエチレンオキシドを含む架橋体などのエーテル系高分子化合物、ポリアクリロニトリル、ポリプロピレンオキシドあるいはポリメチルメタクリレートを繰返し単位として含むものなどが挙げられる。高分子化合物には、いずれか1種を単独で用いてもよく、2種以上を混合して用いてもよい。

【0062】

特に、酸化還元安定性の点からは、フッ素系高分子化合物が望ましく、中でも、ビニリデンフルオロライドとヘキサフルオロプロピレンとを成分として含む共重合体が好ましい。更に、この共重合体は、モノメチルマレイン酸エステルなどの不飽和二塩基酸のモノエステル、三フッ化塩化エチレンなどのハロゲン化エチレン、炭酸ビニレンなどの不飽和化合物の環状炭酸エステル、またはエポキシ基含有アクリルビニルモノマーなどを成分として含んでいてもよい。より高い特性を得ることができるからである。

【0063】

次に、この二次電池の第2の例の製造方法の一例について説明する。まず、例えば、正極集電体33Aに正極活物質層33Bを形成し正極33を作製する。正極活物質層33Bは、例えば、正極活物質の粉末と導電剤と結着剤とを混合して正極合剤を調製したのち、この正極合剤をN-メチル-2-ピロリドンなどの溶剤に分散させてペースト状の正極合剤スラリーとし、この正極合剤スラリーを正極集電体33Aに塗布し乾燥させ、圧縮成型することにより形成する。また、例えば、正極33と同様にして、負極集電体34Aに負極活物質層34Bを形成し、負極34を作製する。次いで、正極集電体33Aに正極リード

31を取り付けると共に、負極集電体34Aに負極リード32を取り付ける。

【0064】

続いて、電解液と、高分子化合物とを、混合溶剤を用いて混合し、この混合溶液を正極活物質層33Bの上、および負極活物質層34Bの上に塗布し、混合溶剤を揮発させて、電解質36を形成する。次いで、正極33、セパレータ35、負極34、およびセパレータ35を順に積層して巻回し、最外周部に保護テープ37を接着して電池素子30を形成したのち、外装部材41の間に挟み込み、外装部材41の外周縁部を熱融着する。その際、正極リード31および負極リード32と外装部材41の間には密着フィルム42を挿入する。これにより図3、4に示した二次電池が得られる。

【0065】

また、電解質36を正極33および負極34の上に形成したのちに巻回するのではなく、正極33および負極34をセパレータ35を介して巻回し、外装部材41の間に挟み込んだのち、電解液と高分子化合物のモノマーとを含む電解質組成物を注入し、外装部材41の内部でモノマーを重合させるようにしてもよい。

【0066】

この二次電池では、充電を行うと、例えば、正極33からリチウムイオンが放出され、電解質36を介して負極34に吸蔵される。一方、放電を行うと、例えば、負極34からリチウムイオンが放出され、電解質36を介して正極33に吸蔵される。

【0067】

次に、この発明の一実施形態による正極活物質を用いた二次電池の第3の例について説明する。この二次電池の第3の例は、二次電池の第2の例において、ゲル状の電解質36に代えて電解液を用いるものである。この場合、電解液はセパレータ35に含浸される。電解液としては、上述の第1の例と同様のものを用いることができる。

【0068】

このような構成を有する二次電池は、例えば以下のようにして作製することができる。ゲル状の電解質36の形成を省略する以外は、上述の第2の例と同様にして正極33および負極34を巻回して電池素子30を作製し、この電池素子30を外装部材41の間に挟み込んだのち、電解液を注入して外装部材41を密閉する。

【実施例】

【0069】

以下、実施例によりこの発明を具体的に説明するが、この発明はこれらの実施例のみに限定されるものではない。

【0070】

<実施例1-1>

第1の正極活物質を以下に説明するようにして作製した。まず、硫酸コバルトと硫酸ジルコニウムと硫酸スズを純水に溶解し、炭酸水素ナトリウム溶液を加えて、炭酸コバルトと共にジルコニウムおよびスズを共沈させた。その際、硫酸コバルトと硫酸ジルコニウムと硫酸スズとの混合比を調整して、コバルト(Co)に対するジルコニウム(Zr)の割合を0.01mol%とし、コバルト(Co)に対するスズ(Sn)の割合を0.01mol%とした。

【0071】

次に、ジルコニウム(Zr)およびスズ(Sn)を共沈させた炭酸コバルトと、炭酸リチウムと、水酸化アルミニウムと、炭酸マグネシウムとを混合し、焼成した。以上により、第1の正極活物質を得た。その際、リチウム：コバルト：アルミニウム：マグネシウムのモル比、すなわち化Iにおけるx：a：b：cが0.962：0.98：0.01：0.01となるように混合した。

【0072】

得られた第1の正極活物質について、原子吸光分析法により定量分析を行ったところ、ほぼ目的とする組成の物質が得られていることが確認された。また、粒径をレーザ回折法により測定したところ、平均粒径は5μmであった。

【0073】

第2の正極活物質は、以下に説明するようにして、作製した。まず、硝酸ニッケルと、硝酸コバルトと、硝酸マンガンとを純水に溶解し、ニッケル(Ni)、コバルト(Co)、マンガン(Mn)のモル比(Ni:Co:Mn)が0.50:0.20:0.30となるように混合し、十分に攪拌しながらアンモニア水を滴下して複合水酸化物を得た。次に、これを水酸化リチウムと混合し、酸素気流中、900℃で10時間焼成した後に粉碎し、これにより第2の正極活物質を得た。

【0074】

得られた第2の正極活物質粉末を原子吸光スペクトルにより分析したところ、 $\text{LiNi}_{0.50}\text{Co}_{0.20}\text{Mn}_{0.30}\text{O}_2$ の組成が確認された。また、レーザ回折法により粒径を測定したところ、平均粒径は1μmであった。

【0075】

次に、上述のようにして作製した第1の正極活物質と、第2の正極活物質とを、重量比(第1の正極活物質:第2の正極活物質)で、95:5となるように混合して、実施例1-1の正極活物質を得た。

【0076】

<実施例1-2>

第1の正極活物質と、第2の正極活物質とを重量比で85:15となるように混合した点以外は、実施例1-1と同様にして、実施例1-2の正極活物質を得た。

【0077】

<実施例1-3>

第1の正極活物質と、第2の正極活物質とを重量比で70:30となるように混合した点以外は、実施例1-1と同様にして、実施例1-3の正極活物質を得た。

【0078】

<実施例2-1>

製造条件を変えて、第1の正極活物質の平均粒径が15μmになるようにした。製造条件を変えて、第2の正極活物質の平均粒径が5μmになるようにした。以上の点以外は、実施例1-1と同様にして、実施例2-1の正極活物質を得た。

【0079】

<実施例2-2>

第1の正極活物質と、第2の正極活物質とを重量比で85:15となるように混合した点以外は、実施例2-1と同様にして、実施例2-2の正極活物質を得た。

【0080】

<実施例2-3>

第1の正極活物質と、第2の正極活物質とを重量比で70:30となるように混合した点以外は、実施例2-1と同様にして、実施例2-3の正極活物質を得た。

【0081】

<実施例3-1>

製造条件を変えて、第1の正極活物質の平均粒径が25μmになるようにした。製造条件を変えて、第2の正極活物質の平均粒径が5μmになるようにした。以上の点以外は、実施例1-1と同様にして、実施例3-1の正極活物質を得た。

【0082】

<実施例3-2>

第1の正極活物質と、第2の正極活物質とを重量比で85:15となるように混合した点以外は、実施例3-1と同様にして、実施例3-2の正極活物質を得た。

【0083】

<実施例3-3>

第1の正極活物質と、第2の正極活物質とを重量比で70:30となるように混合した点以外は、実施例3-3の正極活物質を得た。

【0084】

<実施例4-1>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。以上の点以外は、実施例1-1と同様にして、実施例4-1の正極活物質を得た。

【0085】

<実施例4-2>

第1の正極活物質と、第2の正極活物質とを重量比で85:15となるように混合した点以外は、実施例4-1と同様にして、実施例4-2の正極活物質を得た。

【0086】

<実施例4-3>

第1の正極活物質と、第2の正極活物質とを重量比で70:30となるように混合した点以外は、実施例4-1と同様にして、実施例4-3の正極活物質を得た。

【0087】

<比較例1-1>

第2の正極活物質を加えないようにした点以外は、実施例1-1と同様にして、比較例1-1の正極活物質を得た。

【0088】

<比較例1-2>

製造条件を変えて、第1の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした点以外は、比較例1-1と同様にして、比較例1-2の正極活物質を得た。

【0089】

<比較例1-3>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした点以外は、比較例1-1と同様にして、比較例1-3の正極活物質を得た。

【0090】

<比較例2-1>

第1の正極活物質と、第2の正極活物質とを重量比で60:40となるように混合した点以外は、実施例1-1と同様にして、比較例2-1の正極活物質を得た。

【0091】

<比較例2-2>

製造条件を変えて、第1の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $5\mu\text{m}$ になるようにした。以上の点以外は、比較例2-1と同様にして、比較例2-2の正極活物質を得た。

【0092】

<比較例2-3>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $5\mu\text{m}$ になるようにした。以上の点以外は、比較例2-1と同様にして、比較例2-3の正極活物質を得た。

【0093】

<比較例2-4>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。以上の点以外は、比較例2-1と同様にして、比較例2-4の正極活物質を得た。

【0094】

<比較例3-1>

製造条件を変えて、第1の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。第1の正極活物質と、第2の正極活物質とを重量比で85:15となるように混合した。以上の点以外は、実施例1-1と同様にして、比較例3-1の正極活物質を得た。

【0095】

<比較例3-2>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした点以外は、比較例3-1と同様にして、比較例3-2の正極活物質を得た。

【0096】

<比較例4-1>

製造条件を変えて、第2の正極活物質の平均粒径が $5\mu\text{m}$ になるようにした。第1の正極活物質と、第2の正極活物質とを重量比で85:15となるように混合した。以上の点以外は、実施例1-1と同様にして、比較例4-1の正極活物質を得た。

【0097】

<比較例4-2>

製造条件を変えて、第2の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした点以外は、比較例4-1と同様にして、比較例4-2の正極活物質を得た。

【0098】

<比較例4-3>

製造条件を変えて、第1の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。以上の点以外は、比較例4-1と同様にして、比較例4-3の正極活物質を得た。

【0099】

<比較例5-1>

製造条件を変えて、第1の正極活物質において、コバルトに対するジルコニウムの割合を0m o 1%とし、コバルトに対するスズの割合を0m o 1%とした。第1の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $5\mu\text{m}$ になるようにした。以上の点以外は、実施例1-1と同様にして、比較例5-1の正極活物質を得た。

【0100】

<比較例5-2>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした点以外は、比較例5-1と同様にして、比較例5-2の正極活物質を得た。

【0101】

<比較例5-3>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。以上の点以外は、比較例5-1と同様にして、比較例5-3の正極活物質を得た。

【0102】

<比較例6-1>

第1の正極活物質と、第2の正極活物質とを重量比で98:2となるように混合するようにした点以外は、実施例1-1と同様にして、比較例6-1の正極活物質を得た。

【0103】

<比較例6-2>

製造条件を変えて、第1の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $5\mu\text{m}$ になるようにした。以上の点以外は、比較例6-1と同様にして、比較例6-2の正極活物質を得た。

【0104】

<比較例6-3>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $5\mu\text{m}$ になるようにした。以上の点以外は、比較例6-1と同様にして、比較例6-3の正極活物質を得た。

【0105】

<比較例6-4>

製造条件を変えて、第1の正極活物質の平均粒径が $25\mu\text{m}$ になるようにした。製造条件を変えて、第2の正極活物質の平均粒径が $15\mu\text{m}$ になるようにした。以上の点以外は

、比較例6-1と同様にして、比較例6-4の正極活物質を得た。

【0106】

次に、実施例1-1～実施例4-3および比較例1-1～比較例6-4の正極活物質について、充填性を評価するため、15φの金型に正極活物質試料1mgを入れ、2tの圧力を加えて錠剤にし、この錠剤について体積密度を算出した。

【0107】

また、実施例1-1～実施例4-3、比較例1-1～比較例6-4の正極活物質を用いて、以下に説明するようにして、電池を作製して、容量、低温特性、50℃サイクル特性の評価を行った。

【0108】

まず、正極活物質92質量%と、結着剤である粉末状ポリフッ化ビニリデン3質量%と、導電剤である粉末状黒鉛5質量%とを、溶剤であるN-メチル-2-ピロリドンを用いて混練し、正極合剤スラリーを作製した。次いで、正極合剤スラリーをアルミニウム箔よりなる正極集電体33Aの両面に均一に塗布し、乾燥させたのち、減圧状態において乾燥させた。続いて、ロールプレス機で圧縮成型して正極活物質層33Bを形成し、正極33を作製した。そののち、正極33の端部にアルミニウムリボンよりなる正極リード31を溶接した。

【0109】

また、負極活物質であるメソフェーズ系球状黒鉛90質量%と、結着剤である粉末状ポリフッ化ビニリデン10質量%とを、溶剤であるN-メチル-2-ピロリドンを用いて混練し、負極合剤スラリーを作製した。次いで、負極合剤スラリーを銅箔よりなる負極集電体34Aの両面に均一に塗布し、乾燥させたのち、減圧状態において乾燥させた。続いて、ロールプレス機で圧縮成型して負極活物質層34Bを形成し、負極34を作製した。そののち、負極34の端部にニッケルリボンよりなる負極リード32を溶接した。

【0110】

次に、炭酸エチレン(EC)を12.5重量%と、炭酸エチルメチル(EMC)を12.5重量%と、電解質塩であるLiPF₆を5重量%とを混合して可塑剤を調整した。これに対して分子量が600000であるブロック共重合ポリ(ビニリデンフルオライド-*c*o-ヘキサフルオロプロピレン)を10重量%と、炭酸ジエチルを60重量%とを混合して溶解させた。次に、これを正極33および負極34の両面に均一に塗布して含浸させた。そして、常温で8時間放置することによって炭酸ジエチルを気化させて除去し、ゲル状の電解質36を作製した。

【0111】

次に、上述したようにしてゲル状の電解質36が形成された正極33および負極34と、多孔質ポリエチレンフィルムよりなるセパレータ35とを、負極34、セパレータ35、正極33、セパレータ35の順に積層してから、この積層体を平板の芯に巻き付け多数巻回した後、最外周部に保護テープ37を接着して電池素子30を作製した。

【0112】

最後に、このようにして作製した電池素子30を、アルミニウム箔をポリオレフィンフィルムで挟んだアルミラミネートフィルムよりなる外装部材41の間に挟み込み、外装部材41の外周縁部を熱融着した。その際、正極リード31および負極リード32と外装部材41との間には密着フィルム42を挿入した。以上により、目的とする二次電池を作製した。

【0113】

上述のようにして得られた各実施例および各比較例の二次電池について充放電試験を行い、放電容量(容量)、低温特性および50℃におけるサイクル特性を評価した。

【0114】

23℃において上限電圧4.2V、電流1Cで充電時間の総計が3時間に達するまで定電流定電圧充電を行ったのち、23℃において電流0.2C、終止電圧3Vで定電流放電を行った時の放電容量を測定した。

【0115】

低温特性は、23℃において電流0.5C、終止電圧3Vで定電流放電を行った時の放電容量と、-20℃において電流0.5C、終止電圧3Vで定電流放電を行った時の放電容量とから、式1により求めた。その際、充電は、23℃において上限電圧4.2V、電流1Cで充電時間の総計が3時間に達するまで定電流定電圧充電を行った。なお、0.5Cは理論容量を2時間で放電しきる電流値である。

(式1)

$$\text{低温特性 (\%)} = (-20^{\circ}\text{Cでの放電容量} / 23^{\circ}\text{Cでの放電容量}) \times 100 (\%)$$

【0116】

50℃におけるサイクル特性は、50℃において上限電圧4.2V、電流1Cで充電時間の総計が3時間に達するまで定電流定電圧充電を行ったのち、50℃において電流1C、終止電圧3Vで定電流放電を行い、1サイクル目の放電容量と、300サイクル目の放電容量とから、式2により求めた。

(式2)

サイクル特性 (%)

$$= (300\text{サイクル目の放電容量} / 1\text{サイクル目の放電容量}) \times 100 (\%)$$

【0117】

体積密度の算出結果、並びに容量、低温特性および50℃サイクル特性の測定結果を表1に示す。

【0118】

【表1】

	第1の正極活物質		第2の正極活物質		* 1 粒径比	配合比 (重量比)	充填性 (体積密度) [g/cm ³]	* 2 容量 [%]	低温 特性 [%]	50℃ サイクル特性 [%]
	Zr, Sn 添加	平均粒径 [μ m]	平均粒径 [μ m]							
実施例1-1	有	5	1		5	95:5	3.6	100.0	85	91
実施例1-2	有	5	1		5	85:15	3.62	100.6	87	92
実施例1-3	有	5	1		5	70:30	3.6	100.0	89	92
実施例2-1	有	15	5		3	95:5	3.67	101.9	83	90
実施例2-2	有	15	5		3	85:15	3.69	102.5	85	92
実施例2-3	有	15	5		3	70:30	3.66	101.7	87	93
実施例3-1	有	25	5		5	95:5	3.72	103.3	83	92
実施例3-2	有	25	5		5	85:15	3.75	104.2	85	93
実施例3-3	有	25	5		5	70:30	3.71	103.1	87	94
実施例4-1	有	25	15		1.67	95:5	3.71	103.1	82	90
実施例4-2	有	25	15		1.67	85:15	3.73	103.6	83	91
実施例4-3	有	25	15		1.67	70:30	3.7	102.8	84	91
比較例1-1	有	5	—		—	100:0	3.52	97.8	84	89
比較例1-2	有	15	—		—	100:0	3.56	98.9	82	88
比較例1-3	有	25	—		—	100:0	3.59	99.7	80	87
比較例2-1	有	5	1		5	60:40	3.51	97.5	89	92
比較例2-2	有	15	5		3	60:40	3.54	98.3	83	93
比較例2-3	有	25	5		5	60:40	3.52	97.8	87	94
比較例2-4	有	25	15		1.67	60:40	3.55	98.6	78	91
比較例3-1	有	15	1		15	85:15	3.56	98.9	83	88
比較例3-2	有	25	1		25	85:15	3.59	99.7	82	87
比較例4-1	有	5	5		1	85:15	3.51	97.5	87	92
比較例4-2	有	5	15		0.33	85:15	3.53	98.1	86	92
比較例4-3	有	15	15		1	85:15	3.54	98.3	87	92
比較例5-1	なし	15	5		3	85:15	3.69	102.5	75	80
比較例5-2	なし	25	5		5	85:15	3.75	104.2	75	82
比較例5-3	なし	25	15		1.67	85:15	3.73	103.6	73	81
比較例6-1	有	5	1		5	98:2	3.54	97.8	84	89
比較例6-2	有	15	5		3	98:2	3.57	98.9	82	89
比較例6-3	有	25	5		5	98:2	3.6	99.8	81	88
比較例6-4	有	25	15		1.67	98:2	3.6	99.9	80	87

* 1 粒径比=(第1の正極活物質の平均粒径/第2の正極活物質の平均粒径)

* 2 容量:実施例1-1の容量を100.0%として換算した値

【0119】

表1に示すように、実施例1-1～実施例4-3の正極活物質では、充填性が優れており、電池に用いた場合に、高容量であり、且つ低温特性および50℃サイクル特性が優れていた。

【0120】

比較例1-1～比較例1-3では、第2の正極活物質を加えていないので、実施例と比べると、充填性が低下し、低温特性も若干低下した。

【0121】

また、比較例2-1～比較例2-4では、第2の正極活物質の混合割合が多いので、実施例と比べると、充填性が低下した。

【0122】

さらに、比較例3-1～比較例3-2では、第1の正極活物質と第2の正極活物質と

低下した。

【0123】

さらに、比較例4-1～比較例4-3では、第2の正極活物質の粒径が、第1の正極活物質の粒径に比べて、大きいまたは同じであるので、実施例と比べると、充填性が低下した。

【0124】

さらに、比較例5-1～比較例5-3では、第1の正極活物質を、ジルコニウム(Zr)およびスズ(Sn)を含まないものにしたので、実施例と比べると、低温特性、50℃サイクル特性が低下した。

【0125】

さらに、比較例6-1～比較例6-4では、第2の正極活物質の混合割合が少ないので、実施例と比べると、充填性、低温特性、50℃サイクル特性が若干低下した。

【0126】

以上、この発明の実施形態および実施例について具体的に説明したが、この発明は、上述の実施形態および実施例に限定されるものではなく、この発明の技術的思想に基づく各種の変形が可能である。

【0127】

例えば、上述の実施形態および実施例において挙げた数値はあくまでも例に過ぎず、必要に応じてこれと異なる数値を用いてもよい。

【0128】

また、上述の実施形態および実施例の各構成は、本発明の主旨を逸脱しない限り、互いに組み合わせることが可能である。

【0129】

また、上述の実施形態および実施例では、電解質36として電解液またはゲル状の電解質を用いる場合について説明したが、他の電解質を用いるようにしてもよい。他の電解質としては、イオン伝導性を有する固体電解質、固体電解質と電解液とを混合したもの、あるいは固体電解質とゲル状の電解質とを混合したものが挙げられる。

【0130】

なお、固体電解質には、例えば、イオン伝導性を有する高分子化合物に電解質塩を分散させた高分子固体電解質、またはイオン伝導性ガラスあるいはイオン性結晶などよりなる無機固体電解質を用いることができる。高分子固体電解質の高分子化合物としては、例えば、ポリエチレンオキシサイドあるいはポリエチレンオキシサイドを含む架橋体などのエーテル系高分子化合物、ポリメタクリレートなどのエステル系高分子化合物、アクリレート系高分子化合物を単独あるいは混合して、または共重合させて用いることができる。また、無機固体電解質としては、窒化リチウムあるいはリン酸リチウムなどを含むものを用いることができる。

【0131】

また、上述の実施形態および実施例では、電池素子が巻回されている場合について説明したが、正極と負極とをセパレータおよび電解質を介して積層したカード型の電池素子を備える場合、または、2以上の正極と負極とをセパレータおよび電解質を介して交互に積層した積層型の電池素子を備える場合、または、正極と負極とをセパレータおよび電解質層を介して積層しつつ折りにした電池素子を備える場合についても、本発明を同様に適用することができる。

【0132】

さらに、上述の実施形態および実施例では、円筒型およびフィルム状の外装部材41を用いる場合について説明したが、この発明は、例えば角型、コイン型あるいはボタン型の二次電池にも適用することができる。その場合も、同様の効果を得ることができる。加えて、二次電池に限らず一次電池にも適用することができる。

【図面の簡単な説明】

【0133】

【図1】この発明の一実施形態による正極活物質を用いた二次電池の第1の例の一構成例を示す斜視図である。

【図2】図1に示した巻回電極体の断面図である。

【図3】この発明の一実施形態による正極活物質を用いた二次電池の第2の例の一構成例を示す斜視図である。

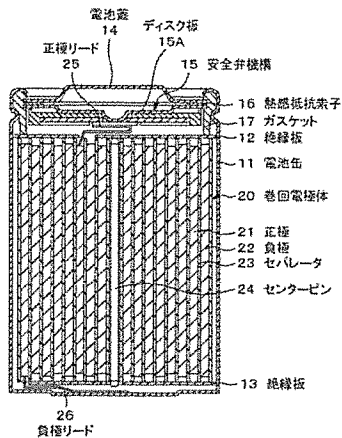
【図4】図3に示した電池素子のI V-I V線に沿った断面図である。

【符号の説明】

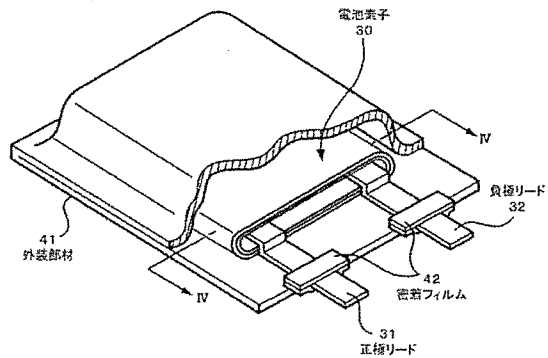
【0134】

11・・・電池缶、12、13・・・絶縁板、14・・・電池蓋、15・・・安全弁機構、16・・・熱感抵抗素子、17・・・ガスケット、20・・・巻回電極体、21、33・・・正極、21A、33A・・・正極集電体、21B、33B・・・正極活物質層、22、34・・・負極、22A、34A・・・負極集電体、22B、34B・・・負極活物質層、23、35・・・セパレータ、24・・・センターピン、25、31・・・正極リード、26、32・・・負極リード、30・・・電池素子、36・・・電解質、37・・・保護テープ、41・・・外装部材、42・・・密着フィルム

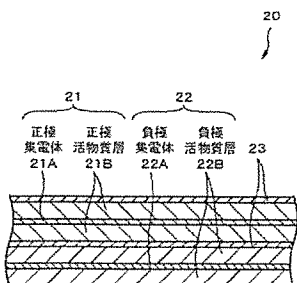
【図1】



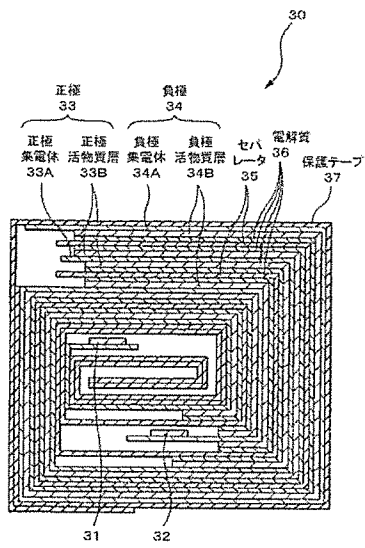
【図3】



【図2】



【図4】



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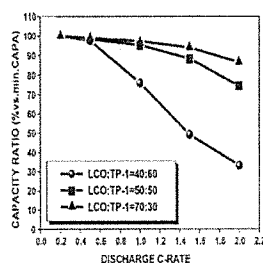
(54) **ANODIC MATERIAL HAVING A HIGH ENERGY DENSITY, CAPABLE OF OBTAINING HIGH CAPACITY AND DISPLAYING HIGH CYCLIC STABILITY, AND A SECONDARY LITHIUM BATTERY INCLUDING THE SAME**

(57) Abstract:

PURPOSE: An anodic material is provided to obtain a high energy density and excellent capacity, to be used for manufacturing a secondary lithium battery having a superior rate property, and to improve the performance of the secondary lithium battery.

CONSTITUTION: An anodic material is a mixture of oxide powder(a), which is marked by chemical formula 1 of $\text{Li}_x(\text{Co}_y\text{A}_m\text{D}_z)\text{O}_t$, and oxide powder(b). The oxide powder (b) is selected from oxide powder(b1), which is marked by chemical formula 2 of, or oxide powder(b2). The oxide powder(a) and the oxide powder(b) are mixed in a ratio of 50 : 50 - 90 : 10. The oxide powder(b2) includes mixed transition metal of Ni, Mn, and Co.

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Legal Status

No.	Receipt/Delivery No.	Receipt/Delivery Date	Document Title (KOR.)	Status (KOR.)
1	1-1-2010-0135216-14	2010.03.03	[Patent Application] Patent Application ([특허출원]특허출원서)	Accepted (수리)
2	9-1-9999-9999999-89	2011.05.11	Request for Prior Art Search (선행기술조사 의뢰서)	Accepted (수리)
3	9-1-2011-0046435-39	2011.05.26	Report of Prior Art Search (선행기술조사 보고서)	Accepted (수리)
4	1-1-2011-0669186-02	2011.08.29	[Amendment to Patent Application, etc.] Amendment ([출원서등 보정]보정서)	Accepted (수리)
5	9-5-2011-0603411-03	2011.10.20	Notification of reason for refusal (의견제출통지서)	Completion of Transmission (발송처리완료)
6	1-1-2011-0977116-18	2011.12.08	[Amendment to Description, etc.] Amendment ([명세서등 보정]보정서)	Regarded as an acceptance of amendment (보정승인간주)
7	1-1-2011-0977096-82	2011.12.08	[Opinion according to the Notification of Reasons for Refusal] Written Opinion(Written Reply, Written Substantiation) ([거절이유 등 통지에 따른 의견]의견(답변, 소명)서)	Accepted (수리)
8	9-5-2012-0317750-13	2012.05.31	Decision to grant (등록결정서)	Completion of Transmission (발송처리완료)

고에너지밀도의 양극 재료 및 이를 포함하는 리튬 이차전지

Cathode Materials Having High Energy Density and Lithium Secondary Battery Containing the Same

(51) Int. CL H01M 4/485(2010.01) H01M 10/0525(2010.01)
H01M 2/02(2006.01)

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(71) Applicant LG CHEM. LTD.

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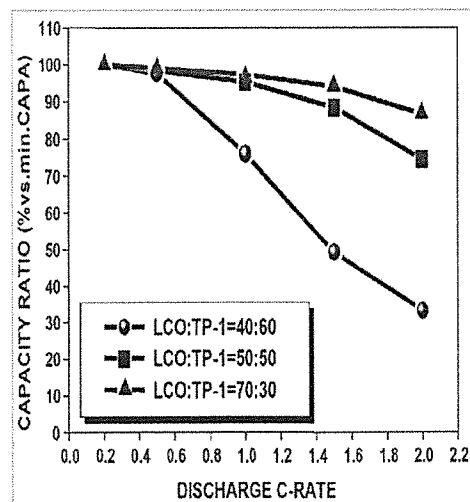
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Number of examination claims 21



Zoom Q

the invention relates to the mixture selected from the group consisting of the oxide powder (b2) of the oxide powder (b) more than the oxide powder (a), defined in this specification and the oxide powder (b1) defined in this specification and one kind. And the mixing ratio (oxide powder of two oxide powders (a): the anode material which is the oxide powder (b)) is 50: 50 through 90: 10 is provided. The anode material according to the present invention has the advantage that can implement 50% this harrow oxide powder (a) and high capacity battery the oxide powder (b) the high energy density is exhibited by mixing and using having the predetermined composition expression which can be the high-capacity and it can exhibit the high cyclic stability and can exhibit the excellent storage-stable and high temperature safety.

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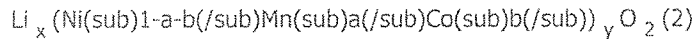
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1	[특허출원]특허출원서 ([Patent Application] Patent Application)	2010.03.03	수리 (Accepted)	112010013521614
2	선행기술조사의뢰서 (Request for Prior Art Search)	2011.05.11	수리 (Accepted)	919999999999989
3	선행기술조사보고서 (Report of Prior Art Search)	2011.05.26	수리 (Accepted)	912011004643539
4	[출원서등 보정]보정서 ([Amendment to Patent Application, etc.] Amendment)	2011.08.29	수리 (Accepted)	112011066918602
5	의견제출통지서 (Notification of reason for refusal)	2011.10.20	발송처리완료 (Completion of Transmission)	952011060341103
6	[거절이유 등 통지에 따른 의견] 의견(답변, 소명)서 ([Opinion according to the Notification of Reasons for Refusal] Written Opinion(Written Reply, Written Substantiation))	2011.12.08	수리 (Accepted)	112011097709682
7	[명세서등 보정]보정서 ([Amendment to Description, etc.] Amendment)	2011.12.08	보정승인간주 (Regarded as an acceptance of amendment)	112011097711618
8	등록결정서 (Decision to grant)	2012.05.31	발송처리완료 (Completion of Transmission)	952012031775013

Claim

No.	Content
	the mixing ratio (oxide powder of two oxide powders it below is the mixture selected from the group consisting of the oxide powder (b2) of the oxide powder (b) more than the oxide powder (a), defined and the oxide powder (b1) which it below defines and one kind (a): the oxide powder :



, which is at least one kind selected to be the anode material :

[oxide powder (a)]

following equation (1) which is the oxide powder (b)) is 50: 50 through 90: 10 from group comprising D is the ti, zr, hf, V, nb, ta: Cr, and the mo, W, mn, tc, re, fe, ru, os, co, rh, ir, ni, pd, pt, cu, au, ag, zn, cd, hg, B, al, ga, in, Ti, C, si, ge, sn, pb, N, P, as, sb it is at least one kind selected from the Ca and bi and is expressed as

1 [oxide powder (b1)]

following equation (2) in the above formula. Oxide powder satisfying the condition of the following equation 3 and 4 $0.05 \leq a \leq 0.4$, $0.1 \leq b \leq 0.4$, $0.4 \leq 1-a-b \leq 0.7$, $0.95 \leq x \leq 1.05$, $1.9 \leq x+y \leq 2.3$, and [oxide powder (b2)]

Ni, and the mixing transition metal of the Co and Mn are included: the m (Ni) / m (Mn) in

$$1.1003 \leq m(\text{Ni}) / m(\text{Mn}) \leq 1.5 \quad (3)$$

$$0.4003 \leq m(\text{Ni}^{2+}) / m(\text{Mn}^{4+}) \leq 1 \quad (4)$$

the equation may be the $m(\text{Ni}^{2+}) / m(\text{Mn}^{4+})$ is the mole ratio of the Mn^{4+} comparison Ni^{2+} it is the mole ratio of the manganese comparison nickel.

2 The anode material of claim 1, wherein the mixing ratio of oxide powders is 50: 50 through 70: 30.

3 The anode material of claim 1, wherein the oxide powder (a) is the LiCoO_2 powder.

4 As for claim 1, the anode material wherein the oxide powder (b1) interconnects MO layers the part Ni ion is inserted that originate from the lithium ion among mixing transition metal oxide layer ('MO layer') is the MO layer in the occlusion of the occlusion and lithium ion and emission layer ('reversible lithium layer') it is emitted.

5 As for claim 4, the anode material in which the Ni^{2+} and Ni^{3+} coexist in the MO layer and the part Ni^{2+} reversibles which is inserted into the lithium layer among that.

6 The anode material of claim 5, wherein the molar fraction of the Ni^{2+} reversibling is inserted into the lithium layer in the oxide powder (b1) and is combined are the standard which is the whole transition metal of the oxide powder (b1) 0.03 ~ 0.07.

7 The anode material of claim 1, wherein the m (Ni) / m (Mn) in the oxide powder (b2) is $1.2 \leq m(\text{Ni}) / m(\text{Mn}) \leq 1.4$.

8 As for claim 1, the anode material wherein the average oxidation number of the whole transition metal except for the lithium in the oxide powder (b2) is 3.0 excess to 3.5 or less.

As for claim 1, the anode material consisting of the nickel (2) of the content wherein the nickel in the oxide

- 9 powder (b2) corresponds to the nickel (1), of the manganese content comparison overshoot and manganese content.
- 10 The anode material having the average oxidation number of claim 1, wherein the nickel in the oxide powder (b2) is above the +2 edge.
- 11 The anode material of claim 9, wherein the nickel (1) of the per content overshoot between above net is the Ni^{3+} .
- 12 As for claim 9, the anode material wherein the total average oxidation number of the nickel (2) of the content corresponding to manganese and manganese content are 3.0 excess to 3.5 or less.
- 13 As for claim 9, the anode material wherein the nickel (2) of the content corresponding to the manganese content comprises the Ni^{2+} and Ni^{3+} .
- 14 As for claim 9, the anode material wherein the rate of the Ni^{3+} among the nickel (2) of the content corresponding to the manganese content is 11 ~ 60%.
- 15 The anode material of claim 1, wherein the rate of the site which the Ni ($\text{Ni}(\text{sup})2+(\text{sup})$) occupies in the oxide powder (b2) in the Li whole site is 5 mol% under.
- 16 The anode material of claim 1, wherein the oxide powder (a) is the particle in which it is the particle of the single phase (monolithic) structure ; and the oxide powder (b) comprises the aggregate of the minute particles. Of the condensed phase (agglomerated) structure.
- 17 The anode material of claim 1, wherein the D50 of the oxide powder (a) is the D50 of the oxide powder (b) is 8 μm or less it is 15 μm or greater.
- 18 The anode material of claim 17, wherein the D50 of the oxide powder (a) is the D50 of the oxide powder (b) is 4 through 7 μm it is 20 through 30 μm .
- 19 As for claim 18, the anode material consisting of the aggregate of the minute particles wherein 90% or greater of the oxide powder (b) has the size of 1 through 4 μm .
- 20 The lithium secondary battery including the anode material according to any one among claim n to claim n.
- 21 The lithium secondary battery which is the pouched type battery installed at the pouch-type sheet case with the state where the electrode assembly is sealed up of claim 20, wherein the lithium secondary battery comprises the polymer resin layer and the metallic layer.

Designated States

Kind	Country
:: Empty ::	

Prior Art Document(s)

JP2002100357 A KR1020100070181 A

(* the document(s) cited by patent examiners)



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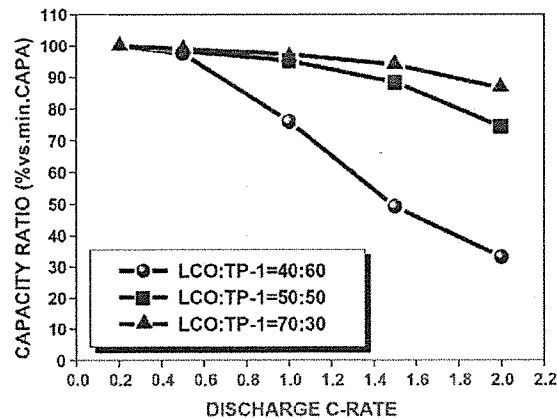
심사관 : 박상호

(54) 발명의 명칭 고에너지밀도의 양극 재료 및 이를 포함하는 리튬 이차전지

(57) 요약

본 발명은 본 명세서에서 정의하는 산화물 분말(a)와, 본 명세서에서 정의하는 산화물 분말(b1) 및 산화물 분말(b2)로 이루어진 군에서 선택되는 1종 이상의 산화물 분말(b)의 혼합물로서, 두 산화물 분말들의 혼합비(산화물 분말(a): 산화물 분말(b))가 50: 50 내지 90: 10인 양극 재료를 제공한다. 본 발명에 따른 양극 재료는 고용량이고 높은 사이클 안정성을 발휘할 수 있으며, 우수한 저장 안정성 및 고온 안전성을 발휘할 수 있는 소정의 조성비를 갖는 산화물 분말(b)를 50% 이하로 산화물 분말(a)와 혼합 사용함으로써 높은 에너지밀도를 발휘하면서도 고용량 전지를 구현할 수 있다는 장점이 있다.

대표도 - 도3



(72) 발명자

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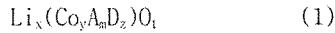
특허청구의 범위

청구항 1

하기에서 정의한 산화물 분말(a)과, 하기에서 정의한 산화물 분말(b1) 및 산화물 분말(b2)로 이루어진 군에서 선택되는 1종 이상의 산화물 분말(b)의 혼합물로서, 두 산화물 분말들의 혼합비(산화물 분말(a): 산화물 분말(b))가 50: 50 내지 90: 10인 것을 특징으로 하는 양극 재료:

[산화물 분말(a)]

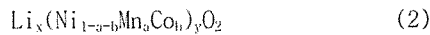
하기 식(1)로 표현되는 산화물 분말:



상기 식에서, $0.8 \leq x \leq 1.2$, $0 \leq z \leq 0.3$, $1.8 \leq t \leq 4.2$, $(0.8-m-z) \leq y \leq (2.2-m-z)$, $0 \leq m \leq 0.3$ 이고, A는 Mg 및 Ca으로부터 선택되는 1종 이상이며, D는 Ti, Zr, Hf, V, Nb, Ta; Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Au, Ag, Zn, Cd, Hg, B, Al, Ga, In, Tl, C, Si, Ge, Sn, Pb, N, P, As, Sb 및 Bi로 이루어진 군으로부터 선택되는 1종 이상이고;

[산화물 분말(b1)]

하기 식(2)로 표현되는 산화물 분말:



상기 식에서, $0.05 \leq a \leq 0.4$, $0.1 \leq b \leq 0.4$, $0.4 \leq 1-a-b \leq 0.7$, $0.95 \leq x \leq 1.05$, $1.9 \leq x+y \leq 2.3$ 이며;

[산화물 분말(b2)]

Ni, Mn 및 Co의 혼합 전이금속을 포함하며 리튬을 제외한 전체 전이금속의 평균 산화수가 +3가 보다 크고, 하기 식 3 및 4의 조건을 만족하는 산화물 분말:

$$1.1 < m(\text{Ni})/m(\text{Mn}) < 1.5 \quad (3)$$

$$0.4 < m(\text{Ni}^{2+})/m(\text{Mn}^{4+}) < 1 \quad (4)$$

상기 식에서, $m(\text{Ni})/m(\text{Mn})$ 는 망간 대비 니켈의 몰비이고, $m(\text{Ni}^{2+})/m(\text{Mn}^{4+})$ 는 Mn^{4+} 대비 Ni^{2+} 의 몰비이다.

청구항 2

제 1 항에 있어서, 상기 산화물 분말들의 혼합비는 50: 50 내지 70: 30 인 것을 특징으로 하는 양극 재료.

청구항 3

제 1 항에 있어서, 상기 산화물 분말(a)는 LiCoO_2 분말인 것을 특징으로 하는 양극 재료.

청구항 4

제 1 항에 있어서, 상기 산화물 분말(b1)은 혼합 전이금속 산화물 층('MO층')들 사이로 리튬 이온이 흡장 및 방출되며, 상기 리튬 이온의 흡장 및 방출 층('가역적 리튬층')에는 MO층으로부터 유래된 일부 Ni 이온이 삽입되어 MO층들을 상호 결합하고 있는 것을 특징으로 하는 양극 재료.

청구항 5

제 4 항에 있어서, 상기 MO층에는 Ni^{2+} 와 Ni^{3+} 가 공존하고 있고, 그 중 일부 Ni^{2+} 가 가역적 리튬층에 삽입되어 있는 것을 특징으로 하는 양극 재료.

청구항 6

제 5 항에 있어서, 상기 산화물 분말(b1)에서 가역적 리튬층에 삽입되어 결합되는 Ni^{2+} 의 몰분율은 산화물 분말(b1)의 전체 전이금속일 기준으로 0.03 ~ 0.07인 것을 특징으로 하는 양극 재료.

청구항 7

제 1 항에 있어서, 산화물 분말(b2)에서 상기 $m(Ni)/m(Mn)$ 은 $1.2 \leq m(Ni)/m(Mn) \leq 1.4$ 인 것을 특징으로 하는 양극 재료.

청구항 8

제 1 항에 있어서, 산화물 분말(b2)에서 상기 리튬을 제외한 전체 전이금속의 평균 산화수가 3.0 초과 내지 3.5 이하인 것을 특징으로 하는 양극 재료.

청구항 9

제 1 항에 있어서, 산화물 분말(b2)에서 상기 니켈은 망간 함량 대비 초과량의 니켈(1)과, 망간 함량에 대응하는 함량의 니켈(2)로 이루어져 있는 것을 특징으로 하는 양극 재료.

청구항 10

제 1 항에 있어서, 산화물 분말(b2)에서 상기 니켈은 +2가보다 큰 평균 산화수를 가지는 것을 특징으로 하는 양극 재료.

청구항 11

제 9 항에 있어서, 상기 망간 함량 대비 초과량의 니켈(1)은 Ni^{3+} 인 것을 특징으로 하는 양극 재료.

청구항 12

제 9 항에 있어서, 망간 및 상기 망간 함량에 대응하는 함량의 니켈(2)의 전체 평균 산화수가 3.0 초과 내지 3.5 이하인 것을 특징으로 하는 양극 재료.

청구항 13

제 9 항에 있어서, 상기 망간 함량에 대응하는 함량의 니켈(2)은 Ni^{2+} 및 Ni^{3+} 로 이루어진 것을 특징으로 하는 양극 재료.

청구항 14

제 9 항에 있어서, 상기 망간 함량에 대응하는 함량의 니켈(2) 중 Ni^{3+} 의 비율이 11 ~ 60%인 것을 특징으로 하는 양극 재료.

청구항 15

제 1 항에 있어서, 상기 산화물 분말(b2)에서 Li 전체 사이트에서 $Ni(Ni^{2+})$ 이 점유하고 있는 사이트의 비율은 5 mol% 미만인 것을 특징으로 하는 양극 재료.

청구항 16

제 1 항에 있어서, 상기 산화물 분말(a)은 단일상(monolithic) 구조의 입자이고, 상기 산화물 분말(b)은 미소 입자들의 응집체로 이루어진 응집상(agglomerated) 구조의 입자인 것을 특징으로 하는 양극 재료.

청구항 17

제 1 항에 있어서, 상기 산화물 분말(a)의 D50은 15 μm 이상이고 상기 산화물 분말(b)의 D50은 8 μm 이하인 것을 특징으로 하는 양극 재료.

청구항 18

제 17 항에 있어서, 상기 산화물 분말(a)의 D50은 20 내지 30 μm 이고, 상기 산화물 분말(b)의 D50은 4 내지 7 μm 인 것을 특징으로 하는 양극 재료.

청구항 19

제 18 항에 있어서, 상기 산화물 분말(b)의 90% 이상은 1 내지 4 μm 의 크기를 가진 미소 입자들의 응집체로 이루어진 것을 특징으로 하는 양극 재료.

청구항 20

제 1 항 내지 제 19 항 중 어느 하나에 따른 양극 재료를 포함하는 리튬 이차전지.

청구항 21

제 20 항에 있어서, 상기 리튬 이차전지는 고분자 수지층과 금속층을 포함하는 파우치형 시트 케이스에 전극 조립체가 밀봉된 상태로 내장되어 있는 파우치형 전지인 리튬 이차전지.

명세서

기술분야

- 001] 본 발명은 고에너지 밀도의 양극 재료 및 이를 포함하는 리튬 이차전지에 관한 것으로, 더욱 상세하게는 특정한 조성의 산화물 분말(a)과 특정한 조성의 산화물 분말(b)의 혼합물로서, 두 산화물 분말들의 혼합비(산화물 분말(a): 산화물 분말(b))가 50: 50 내지 90: 10 인 양극 재료에 관한 것이다.

배경기술

- 002] 최근, 충방전이 가능한 이차전지는 와이어리스 모바일 기기의 에너지원으로 광범위하게 사용되고 있다. 그 중, 리튬 이차전지는 높은 에너지 밀도, 방전 전압, 출력 안정성 등의 이점으로 인해 많이 사용되고 있다.
- 003] 리튬 이차전지는 양극 재료로 LiCoO_2 등의 금속 산화물과 음극 재료로 탄소 재료를 사용하며, 음극과 양극 사이에 폴리올레핀계 다공성 분리막을 넣고, LiPF_6 등의 리튬염을 가진 비수성 전해액을 함침시켜 제조된다. 리튬 이차전지의 양극 재료로는 LiCoO_2 이 많이 사용되고 있지만, 상대적으로 고가이고, 충방전 전류량이 약 150 mAh/g 정도로 낮으며, 4.3 V 이상의 전압에서는 결정구조가 불안정하고, 전해액과 반응을 일으켜 발화의 위험성을 갖고 있는 등 여러 가지 문제점을 갖고 있다. 더욱이, LiCoO_2 은 그것의 제조 공정상에서 일부 변수(parameter)의 변화에도 매우 큰 물성 변화를 나타내는 단점을 가지고 있다. 특히, 고전위에서 사이클 특성과 고온 저장 특성은 공정 변수의 일부 변화로 인해 크게 변하는 경향이 있다.
- 004] 이와 관련하여, 고전위에서 작동할 수 있도록 LiCoO_2 의 외면을 금속(알루미늄 등)으로 코팅하는 기술, LiCoO_2 를 열처리하거나 다른 물질과 혼합 시키는 기술 등이 제시되기도 하였으나, 이러한 양극 재료로 구성된 이차전지는 고전위에서 취약한 안전성을 나타내거나, 양산 공정에서의 적용에 한계가 있다.
- 005] 최근에는, 이차전지가 화석 연료를 사용하는 기존의 가솔린 차량, 디젤 차량 등의 대기오염 등을 해결하기 위한 방안으로 제시되고 있는 전기자동차(EV), 하이브리드 전기자동차(HEV) 등의 동력원으로서도 주목받고 있음에 따라, 그것의 사용량이 더욱 증가할 것으로 예상되고 있으므로, 상기와 같은 문제점들뿐만 아니라, 고전위 상태에서 전지의 안전성과 고온 저장 특성에 대한 문제점이 부각되고 있다.
- 006] LiCoO_2 의 이러한 문제점을 해결하기 위한 방안들 중의 하나로서, 둘 이상의 서로 다른 리튬 전이금속 산화물들의 혼합물을 양극 재료로 사용하는 기술들이 제시되었는 바, 이들은 각각의 리튬 전이금속 산화물 단독으로 양극 재료를 구성할 때의 단점을 보완한다.
- 007] 그러나, 종래의 혼합물 형태의 양극 재료는 두 성분의 단순한 조합 이상의 상승 효과를 기대하기 어렵다는 한계를 가지고 있다.

발명의 내용

0008] 따라서, 본 발명은 상기와 같은 종래기술의 문제점과 과거로부터 요청되어온 기술적 과제를 해결하는 것을 목적으로 한다.

0009] 본 발명의 목적은 높은 에너지 밀도를 가지면서도 용량 특성이 우수한 양극 재료를 제공하는 것이다.

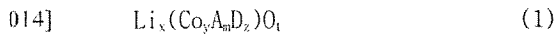
010] 본 발명의 또 다른 목적은 높은 에너지 밀도를 갖는 양극 재료를 사용함으로써 우수한 레이트 특성을 발휘할 수 있는 리튬 이차전지를 제공하는 것이다.

과제의 해결 수단

011] 이러한 목적을 달성하기 위한 본 발명에 따른 양극 재료는, 하기에서 정의한 산화물 분말(a)과, 하기에서 정의한 산화물 분말(b1) 및 산화물 분말(b2)로 이루어진 군에서 선택되는 1종 이상의 산화물 분말(b)의 혼합물로서, 두 산화물 분말들의 혼합비(산화물 분말(a): 산화물 분말(b))가 50: 50 내지 90: 10로 구성되어 있다.

012] [산화물 분말(a)]

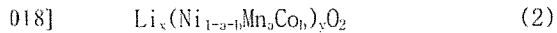
013] 하기 식(1)로 표현되는 산화물 분말:



015] 상기 식에서, $0.8 \leq x \leq 1.2$, $D \leq z \leq 0.3$, $1.8 \leq t \leq 4.2$, $(0.8-m-z) \leq y \leq (2.2-m-z)$, $0 \leq m \leq 0.3$ 이고, A는 Mg 및 Ca 으로부터 선택되는 1종 이상이며, D는 Ti, Zr, Hf, V, Nb, Ta; Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Au, Ag, Zn, Cd, Hg, B, Al, Ga, In, Tl, C, Si, Ge, Sn, Pb, N, P, As, Sb 및 Bi로 이루어진 군 으로부터 선택되는 1종 이상이고;

016] [산화물 분말(b1)]

017] 하기 식(2)로 표현되는 산화물 분말:



019] 상기 식에서, $0.05 \leq a \leq 0.4$, $0.1 \leq b \leq 0.4$, $0.4 \leq 1-a-b \leq 0.7$, $0.95 \leq x \leq 1.05$, $1.9 \leq x+y \leq 2.3$ 이며;

020] [산화물 분말(b2)]

021] Ni, Mn 및 Co의 혼합 전이금속을 포함하며 리튬을 제외한 전체 전이금속의 평균 산화수가 +3가 보다 크고, 하기 식 3 및 4의 조건을 만족하는 산화물 분말:

022]
$$1.1 < m(\text{Ni})/m(\text{Mn}) < 1.5 \quad (3)$$

023]
$$0.4 < m(\text{Ni}^{2+})/m(\text{Mn}^{4+}) < 1 \quad (4)$$

024] 상기 식에서, $m(\text{Ni})/m(\text{Mn})$ 는 망간 대비 니켈의 몰비이고, $m(\text{Ni}^{2+})/m(\text{Mn}^{4+})$ 는 Mn^{4+} 대비 Ni^{2+} 의 몰비이다.

025] 본 발명에 따른 양극 재료는 2 종의 리튬 전이금속 산화물 분말의 혼합물로서, 산화물 분말(a)와 산화물 분말(b)가 50: 50 내지 90: 10로 혼합됨으로써 높은 에너지 밀도를 발휘하면서도 용량 특성이 우수하다는 장점이 있다. 더욱 바람직한 혼합비는 50: 50 내지 70: 30이다.

026] 본 출원의 발명자들은 다양한 실험을 거듭한 끝에, 산화물 분말(a)와의 혼합 사용시 산화물 분말(b)의 혼합비가 50% 이하로 포함되는 경우, C-Rate에서 방전 용량 유지율이 매우 우수하고 소망하는 레이트 특성을 발휘할 수 있음을 확인하였다. 구체적으로, 본 발명에 따른 양극 재료를 사용하는 경우 단위 부피당 에너지 밀도(VED)가 478 Wh/l 이상이고, 단위 무게당 에너지 밀도(GED)가 201 Wh/g 이상인 리튬 이차전지를 제조할 수 있다.

027] 반면, 산화물 분말(b)의 혼합비가 50%를 초과하는 경우에는 방전용량이 현저히 감소되고 특히 C-Rate가 높아 질수록 이러한 감소율이 크게 나타나는 문제가 있고, 10% 미만이면 고용량 특성을 발휘할 수 없다는 문제가 있다.

028] 상기 산화물 분말들은 성능향상을 위해 Al_2O_3 등으로 표면이 코팅될 수도 있고, 또는 Al_2O_3 등이 함께 혼합될 수도 있음은 물론이다.

- 029] 상기 식 1의 바람직한 예로는 LiCoO_2 를 들 수 있지만, 이것으로 한정되는 것은 아니다.
- 030] 상기 산화물 분말(b)에서 산화물 분말(b1)은 조성이 상기 식(2)로 정의되는 특정 조건(도 1 참조)을 만족시킴으로써 고용량이고 높은 사이클 안정성을 발휘할 수 있으며, 우수한 저장 안정성 및 고온 안전성을 발휘할 수 있다. 이하에서는 산화물 분말(b1)에 대해 상술한다.
- 031] 상기 Ni의 전체 몰분율(1-a-b)은 망간 및 코발트에 비해 상대적으로 니켈 과잉의 조성으로서 0.4 ~ 0.7 이다. 니켈의 함량이 0.4 미만인 경우에는 높은 용량을 기대하기 어렵고, 반대로 0.7을 초과하는 경우에는 안전성이 크게 저하되는 문제가 있다.
- 032] 상기 코발트의 함량(b)은 0.1 ~ 0.4인 바, $b > 0.4$ 으로 코발트의 함량이 지나치게 높은 경우, 코발트의 높은 함량으로 인해 원료 물질의 비용이 전체적으로 증가하고 가역 용량이 다소 감소한다. 반면에, 코발트의 함량이 지나치게 낮은 경우($b < 0.1$)에는 충분한 레이트 특성과 전지의 높은 분말 밀도를 동시에 달성하기 어렵다.
- 033] 상기 리튬의 함량이 지나치게 높은 경우, 즉, $x > 1.05$ 인 경우, 특히 $T = 60^\circ\text{C}$ 에서 고전압($U = 4.35 \text{ V}$)으로 사이클 동안에 안전성이 낮아질 수 있으므로 문제가 있다. 반면에, 리튬의 함량이 지나치게 낮으면, 즉, $x < 0.95$ 인 경우에는 낮은 레이트 특성을 나타내고, 가역 용량이 감소될 수 있다.
- 034] 하나의 바람직한 예에서, 상기 산화물 분말(b1)은 혼합 전이금속 산화물 층('MO층')들 사이로 리튬 이온이 흡장 및 방출되며, 상기 리튬 이온의 흡장 및 방출 층('가역적 리튬층')에는 MO층으로부터 유래된 일부 Ni 이온이 삽입되어 MO층들을 상호 결합하고 있는 구조일 수 있다.
- 035] 이하, 본 명세서에서는 경우에 따라, 가역적 리튬층에 삽입되어 결합되는 Ni를 '삽입된 Ni'로 표현하기도 한다.
- 036] 구체적으로 본 출원의 발명자들은 도 2에서와 같이, MO층의 일부 니켈이 가역적 리튬층으로 내려와 고정되는 경우, 리튬의 흡장 및 방출이 방해될 것이라는 종래의 통념과는 달리, 오히려 결정구조가 안정화되어 리튬의 흡장 및 방출에 의해 결정구조가 붕괴되는 문제점을 방지할 수 있음을 확인하였다.
- 037] 이에 따라, 산소 탈리에 의한 추가적인 구조 붕괴가 일어나지 않고 더 이상의 Ni^{2+} 의 발생을 방지함으로써 수명특성과 안전성이 동시에 향상되는 바, 전지 용량 및 사이클 특성이 크게 향상될 수 있고, 소망하는 수준의 레이트 특성을 발휘할 수 있다. 이러한 본 발명의 개념은 종래의 관념을 완전히 뒤엎는 획기적인 것이라 할 수 있다.
- 038] 상기 산화물 분말(b1)에서 MO층에는 바람직하게는 Ni^{2+} 와 Ni^{3+} 가 공존하고 있고, 그 중 일부 Ni^{2+} 가 가역적 리튬층에 삽입되어 있는 구조일 수 있다. 즉, 가역적 리튬층에 삽입된 Ni 이온은 바람직하게는 Ni^{2+} 일 수 있다.
- 039] 이러한 Ni^{2+} 는 리튬 이온(Li^+)과 크기가 매우 유사하므로, 가역적 리튬층에 삽입되어 결정 구조의 형태를 변형시키지 않으면서 충전시 리튬 이온이 탈리되었을 때 MO층의 반발력에 의한 구조 붕괴를 지지하는 역할을 수행할 수 있다.
- 040] 또한, 상기 삽입된 Ni^{2+} 는 MO층들 간에 삽입되어 이들을 지지하는 역할을 수행하는 바 소망하는 충전 안정성 및 사이클 안정성의 향상을 발휘할 수 있도록, 적어도 MO층 사이를 안정적으로 지지할 수 있는 정도로 함유되는 것이 바람직하다. 이와 동시에, 가역적 리튬층에서 리튬 이온의 흡장 및 방출에 방해가 되지 않을 정도로 삽입됨으로써 레이트 특성을 저하시키지 않을 필요가 있다. 즉, 가역적 리튬층에 삽입된 Ni^{2+} 의 몰분율이 너무 높으면 양이온 혼합이 증가하여 국부적으로 전기화학적으로 반응이 없는 암염구조(rock salt structure)가 형성되므로 충전 및 방전을 방해할 뿐만 아니라 이에 따라 방전 용량이 감소될 수 있다.
- 041] 이러한 점을 종합적으로 고려할 때, 상기 가역적 리튬층에 삽입되어 결합되는 Ni^{2+} 의 몰분율은 바람직하게는 산화물(b1)의 전이금속 전체량을 기준으로 0.03 ~ 0.07 일 수 있다.
- 042] 한편, 상기 전이금속(M)에 대한 Li의 비(Li/M)가 낮아질수록 MO층에 삽입된 Ni의 양이 점점 증가하게 되는 바, 너무 많은 양이 가역적 리튬층으로 내려올 경우, 충전 및 방전 과정에서 Li^+ 의 용출이 발생할 수 있다. 이로 인해 용량이 감소되거나 레이트 특성이 저하되는 문제점이 있다. 반대로, Li/M의 비가 너무 높은 경우, MO층에

으므로 바람직하지 않다. 더욱이, 지나치게 높은 Li/M의 값에서는 미반응 Li_2CO_3 의 양이 많아지는 바, 즉, 불순물이 다량 생성되므로 내화학성 및 고온 안정성이 저하될 수 있다. 따라서, 하나의 바람직한 예에서, 상기 LiNiMO_2 에서 Li: M의 비율은 0.95 ~ 1.04: 1 일 수 있다.

043] 하나의 바람직한 예에서, 상기 산화물(b-1)는 불순물로서 수용성 염기, 특히 Li_2CO_3 가 실질적으로 포함되어 있지 않다.

044] 일반적으로 니켈계 리튬 혼합 전이금속 산화물에는 리튬 산화물, 황산 리튬, 탄산 리튬 등의 수용성 염기가 다량 포함되어 있는 바, 이러한 수용성 염기는 첫째, LiNiMO_2 에 존재하는 Li_2CO_3 , LiOH 등과 같은 염기일 수 있고, 둘째, LiNiMO_2 표면에서의 이온교환(H^+ (물) $\leftrightarrow$ Li^+ (표면, 벌크의 외면))에 의해 생성된 염기일 수 있다. 후자의 경우는 통상 무시할 수 있는 수준이다.

045] 상기 첫 번째 수용성 염기는 주로 소결시의 미반응 리튬 원료로 인해 형성된다. 이는, 종래 니켈계 리튬 혼합 전이금속 산화물의 층상 결정 구조의 붕괴를 방지하기 위해 상대적으로 많은 양의 리튬을 첨가하고 저온에서 소결하였는 바, 코발트계 산화물에 비해 상대적으로 많은 입계를 가지게 되고, 소결시 리튬 이온이 충분하게 반응하지 못하기 때문이다.

046] 반면에, 산화물(b1)에는, 앞서 설명한 바와 같이, 층상 결정구조가 안정적으로 유지되므로, 공기 분위기에서 상대적으로 고온의 소결 공정을 수행할 수 있어서, 상대적으로 적은 결정 입계를 갖는다. 또한, 미반응 리튬이 입자 표면에 잔류하는 것이 방지됨으로써, 입자 표면에 탄산 리튬, 황산 리튬 등의 리튬염이 실질적으로 존재하지 않는다. 또한, 산화물(b1)의 제조시 리튬 소스를 과잉 첨가할 필요가 없으므로, 분말 내 잔류하는 미반응 리튬 소스로 인해 불순물들이 형성되는 문제점을 근본적으로 방지할 수 있다.

047] 이에 따라, 수용성 염기가 존재하는 경우에 발생할 수 있는 많은 문제점들, 특히 고온에서 전해액의 분해 반응을 촉진하여 가스를 발생시킴으로써 전지의 안전성을 해치는 문제를 해결할 수 있다. 따라서, 우수한 저장 안정성 및 고온 안정성이 우수하며 저렴한 비용으로 대량생산이 가능하다는 장점이 있다.

048] 한편, 상기 산화물 분말(b) 중 산화물 분말(b2)는 우수한 층상 결정구조에 의해 현저히 향상된 고율 충방전 특성을 제공한다. 이하에서는 산화물 분말(b2)에 대해 상술한다.

049] 상기 층상 결정구조의 바람직한 예로는 $\alpha\text{-NaFeO}_2$ 층상 결정구조를 들 수 있다.

050] 종래에는 Ni^{2+} 와 Mn^{4+} 를 동량으로 포함함으로써 전이금속 이온의 산화수를 평균 +3가 상태로 만들어야 층상 구조가 잘 이루어질 수 있는 것으로 알려져 있었다. 그러나, Ni^{2+} 의 경우 Li^+ 와 거의 유사한 크기를 가짐으로써 리튬층으로 이동하여 압입 구조를 형성할 확률이 높으며, 이에 따라 전기화학적 성능이 퇴화된다는 문제가 있었다.

051] 이에, 본 출원의 발명자들은 안정적인 층상 결정구조를 가지면서도 용량 및 레이트 특성이 우수한 양극 활물질을 제조하기 위해 심도있는 연구를 수행한 결과, 안정적인 층상 결정구조는 Ni^{2+} 및 Mn^{4+} 에 기인된다고 보다, 리튬의 이온 크기와 전이금속 이온의 크기의 차이에 더욱 의존적임을 발견하였다.

052] 구체적으로, 층상 결정구조를 가지는 리튬 복합 전이금속 산화물의 경우, 가역적 리튬층과 MO층을 차지하는 이온의 크기 차이, 즉, 리튬 이온과 전이금속 이온의 크기 차이가 클수록 두 층이 적절하게 분리되어 잘 발달될 수 있다는 것을 확인하였다.

053] 이와 관련하여, 이온의 크기 차이를 크게 하기 위해 MO층에 이온 반경이 작은 금속 원소를 사용하는 방안을 고려할 수 있으나, 이 경우 층상 구조는 잘 만들 수 있지만 전자를 이동시킬 수 있는 금속 이온의 수가 작아지기 때문에 상대적으로 용량이 감소된다는 한계가 있었다.

054] 이에, 본 출원의 발명자들은 용량의 퇴화 없이 우수한 층상 결정구조를 달성하기 위해 노력한 결과, 상기 이온의 크기 차이는 산소 이온과 결합하는 거리 또는 결합력 등으로 나타낼 수 있으며, 양이온의 특성을 갖는 금속의 경우 산화수가 높아질수록 작은 이온 반경을 갖는 바, 전이금속의 산화수를 높임으로써 MO층과 가역적 리튬층의 차이를 크게 할 수 있을 것으로 판단하였고, 많은 실험들을 통해 이를 확인하였다.

추는 것이 필요한 것으로 인식해 오던 당업계의 통념을 뒤엎는 것이다.

056] 한편, 종래와 같이 Ni과 Mn의 함량을 실질적으로 동량으로 맞추는 경우, Mn^{4+} 이온이 Ni^{2+} 이온의 형성을 유도하고 이에 따라 Mn이 다량 포함된 화합물에서 다량의 Ni^{2+} 가 리튬층에 위치하게 되어 바람직하지 못하다.

057] 이에, 본원의 발명자들은 전이금속의 산화수를 높이는 방법으로서, 리튬층으로 쉽게 유입될 수 있는 Ni^{2+} 의 양을 줄여 전체적인 산화수, 즉, 평균 산화수를 +3가 이상으로 만들어주는 것이 가장 효과적일 것으로 판단하였다. 또한, Ni^{2+} 에 비해 크기가 작은 Ni^{3+} 의 양이 높아짐에 따라, 이온의 크기 차이가 더욱 커질 수 있다고 판단하였다.

058] 따라서, 상기 산화물 분말(b2)는 망간에 비해 니켈을 상대적으로 다량 포함하고(식(3) 참조), Mn^{4+} 에 비해 Ni^{2+} 를 상대적으로 소량 포함(식(4) 참조)하는 것으로 구성되어 있다. 구체적으로, 산화물 분말(b2)는 리튬 니켈-망간-코발트 산화물로서 (i) 리튬을 제외한 전체 전이금속인 니켈-망간-코발트의 평균 산화수가 +3가 보다 크고, (ii) 망간에 비해 니켈이 상대적으로 다량 포함되며, (iii) Mn^{4+} 에 비해 Ni^{2+} 가 상대적으로 소량 포함되는 점에 특징이 있다.

059] 이러한 리튬 니켈-망간-코발트 산화물은 전이금속의 평균 산화수가 +3가 보다 크게 유지됨으로써, 상기 산화물의 안정적인 결정구조에 기반하여, 가역적 리튬층에 존재하는 전이금속의 양을 현저하게 감소시킬 수 있으며, 이에 따라 리튬 이온의 이동도 및 레이트 특성을 향상시킬 수 있음은 물론, 용량의 향상도 가져올 수 있다는 장점이 있다.

060] 상기 특징(i)과 관련하여, 산화물 분말(b2)는 리튬을 제외한 전이금속의 평균 산화수가 +3가 보다 크므로, 평균 산화수가 +3가인 경우에 비해 전이금속 이온의 전반적인 크기가 작아지게 되고, 이에 따라 리튬 이온과의 크기 차이가 커지게 되어 층간 분리가 잘 이루어지므로, 안정적인 층상 결정구조를 형성할 수 있다.

061] 다만, 전이금속의 평균 산화수가 지나치게 커지게 되면 리튬 이온을 이동시킬 수 있는 전하의 양이 줄어들게 되어 용량이 감소되는 문제가 있으므로, 전이금속의 평균 산화수는 3.0 초과 내지 3.5 이하인 것이 바람직하고, 더욱 바람직하게는 3.01 내지 3.3이며, 특히 바람직하게는 3.1 내지 3.3이다.

062] 이 경우, 망간 및 망간의 함량에 대응하는 함량의 니켈의 전체 평균 산화수가 3.0 초과 내지 3.5 이하일 수 있고, 바람직하게는 3.1 내지 3.3일 수 있다.

063] 본 발명에서 상기 '리튬을 제외한 전이금속의 평균 산화수'는, 예를 들어, 리튬 이온의 일부가 전이금속의 사이트에 포함되어 있는 경우라도 리튬 이온의 평균 산화수를 고려하지 않는다는 것을 의미한다.

064] 상기와 같은 전이금속의 평균 산화수의 조절은, 예를 들어, 리튬 전이금속 산화물을 제조하는 과정에서 전이금속 전구체의 전이금속의 비율 및 리튬 전구체의 반응량을 조절함으로써 달성될 수 있다.

065] 상기 특징(ii)와 관련하여, 산화물 분말(b2)는 하기 식(3)에서와 같이, 망간 대비 니켈의 몰비가 1.1 보다 크고 1.5 보다 작은 것으로 이루어져 있다.

$$066] \quad 1.1 < m(Ni)/m(Mn) < 1.5 \quad (3)$$

067] 이와 같이, 니켈이 망간에 비해 상대적으로 다량 포함되는 경우에는, 적어도 니켈 중 망간의 함량을 초과하는 함량만큼 Ni^{3+} 이 되고, 상대적으로 이온의 크기가 작아지게 된다. 따라서, 리튬 이온의 크기와 전이금속 이온의 평균 크기 차이가 커지게 되고, Ni^{2+} 가 리튬층으로 삽입되는 것을 최소화할 수 있어서 층상 결정구조의 안정성을 높일 수 있다.

068] 다만, $m(Ni)/m(Mn)$ 가 1.5보다 커지게 되면, Mn 함량 감소로 인해 상대적으로 안전성이 나빠지고 활물질의 제조비용이 상승하게 되므로, 바람직하지 않다. 더욱 바람직한 예에서, 상기 $m(Ni)/m(Mn)$ 는 1.2 ~ 1.4일 수 있다.

069] 이와 반대로, 니켈의 함량보다 망간의 함량이 많을 경우에도 전이금속의 평균 산화수가 +3가 이상이면 층상 결정구조가 형성되기는 하지만, 상대적으로 충방전에 기여하지 않는 +4가 이온의 증가로 인해 용량이 감소할 수 있다.

라히드록시 프랑(franc), 2-메틸 테트라하이드로푸란, 디메틸술폰, 1,3-디옥소런, 포름아미드, 디메틸포름아미드, 디옥소런, 아세트니트릴, 니트로메탄, 포름산 메틸, 초산메틸, 인산 트리에스테르, 트리메톡시 메탄, 디옥소런 유도체, 설포란, 메틸 설포란, 1,3-디메틸-2-이미다졸리디논, 프로필렌 카르보네이트 유도체, 테트라하이드로푸란 유도체, 에테르, 피로피온산 메틸, 프로피온산 에틸 등의 비양자성 유기용매가 유기용매가 적어도 1종 이상 사용될 수 있다.

- 097] 바람직하게는 환형 카보네이트계 용매와 선형 카보네이트계 용매를 1종 이상 혼합하여 사용할 수 있다.
- 098] 또한, 바람직하게는 에틸렌 카르보네이트 또는 에틸렌 카르보네이트와 에틸메틸카보네이트와 같은 선형 카보네이트의 혼합 용매를 사용할 수 있다.
- 099] 상기 리튬염은 상기 비수계 전해액에 용해되기 좋은 물질로서, 예를 들어, LiCl, LiBr, LiI, LiClO₄, LiBF₄, LiB₁₀Cl₁₀, LiPF₆, LiCF₃SO₃, LiCF₃CO₂, LiAsF₆, LiSbF₆, LiAlCl₄, CH₃SO₃Li, CF₃SO₃Li, (CF₃SO₂)₂NLi, 클로로 보란 리튬, 저급 지방족 카르본산 리튬, 4 페닐 붕산 리튬, 이미드 등이 적어도 1종 이상 사용될 수 있다.
- 100] 경우에 따라서는 유기 고체 전해질, 무기 고체 전해질 등이 사용될 수도 있다.
- 101] 상기 유기 고체 전해질로는, 예를 들어, 폴리에틸렌 유도체, 폴리에틸렌 옥사이드 유도체, 폴리프로필렌 옥사이드 유도체, 인산 에스테르 폴리머, 폴리 에지테이션 리신(agitation lysine), 폴리에스테르 술파이드, 폴리비닐 알코올, 폴리 불화 비닐리덴, 이온성 해리기를 포함하는 중합체 등이 사용될 수 있다.
- 102] 상기 무기 고체 전해질로는, 예를 들어, Li₃N, LiI, Li₃NLi₂, Li₃N-LiI-LiOH, LiSiO₄, LiSiO₄-LiI-LiOH, Li₂SiS₃, Li₄SiO₄, Li₄SiO₄-LiI-LiOH, Li₃PO₄-Li₂S-SiS₂ 등의 Li의 질화물, 할로겐화물, 황산염 등이 사용될 수 있다.
- 103] 또한, 비수계 전해액에는 충방전 특성, 난연성 등의 개선을 목적으로, 예를 들어, 피리딘, 트리에틸포스파이트, 트리에탄올아민, 환상 에테르, 에틸렌 디아민, n-글라이머(glyme), 헥사 인산 트리 아미드, 니트로벤젠 유도체, 유허, 퀴논 이민 염료, N-치환 옥사졸리디논, N,N-치환 이미다졸리딘, 에틸렌 글리콜 디알킬 에테르, 암모늄염, 피롤, 2-메톡시 에탄올, 삼염화 알루미늄 등이 적어도 1종 이상 첨가될 수도 있다. 경우에 따라서는, 불연성을 부여하기 위하여, 사염화탄소, 삼불화에틸렌 등의 할로겐 함유 용매를 더 포함시킬 수도 있고, 고온 보존 특성을 향상시키기 위하여 이산화탄산 가스를 더 포함시킬 수도 있다.
- 104] 하나의 바람직한 예에서, 상기 이차전지는 수지층과 금속층을 포함하는 라미네이트 시트의 파우치형 케이스에 전극조립체가 밀봉된 파우치 전지일 수 있다.
- 105] 상기 라미네이트 시트는, 예를 들어, 내부 수지층, 차단성 금속층 및 외부 수지층을 포함하는 구조로 이루어질 수 있다. 상기 외부 수지층은 외부 환경으로부터 우수한 내성을 가져야 하므로, 소정 이상의 인장강도와 내후성을 가지는 것이 필요하다. 그러한 측면에서 외부 수지층의 고분자 수지로는 폴리에틸렌 테레프탈레이트(PET)와 연신 나일론 필름이 바람직하게 사용될 수 있다. 상기 차단성 금속층은 가스, 습기 등 이물질의 유입 내지 누출을 방지하는 기능 이외에 전지케이스의 강도를 향상시키는 기능을 발휘할 수 있도록, 바람직하게는 알루미늄이 사용될 수 있다. 상기 내부 수지층의 고분자 수지로는 열융착성(열접착성)을 가지고, 전해액의 침입을 억제하기 위해 흡습성이 낮으며, 전해액에 의해 팽창하거나 침식되지 않는 폴리올레핀(polyolefin)계 수지가 바람직하게 사용될 수 있으며, 더욱 바람직하게는 무연신 폴리프로필렌(CPP)이 사용될 수 있다.

발명의 효과

- 106] 이상의 설명과 같이, 본 발명에 따른 양극 재료는 특정한 조성의 산화물(a) 및 (b)를 혼합 사용하고, 이들의 혼합비를 특정한 범위로 조절함으로써 높은 에너지 밀도를 발휘하면서도 고용량인 이차전지를 제조할 수 있다. 특히, 상기 산화물(b)는 안정적인 층상 구조를 가지므로 충방전시 결정구조의 안정성이 향상되어, 이러한 양극 재료를 포함하는 전지는 고용량이고 높은 사이클 안정성을 발휘할 수 있는 물질이므로 전반적인 전지 성능을 향상시킬 수 있다는 장점이 있다.

도면의 간단한 설명

- 107] 도 1은 본 발명의 하나의 실시예에 따른 산화물(b) 결정구조의 모식도이다;

도 3은 본 발명의 실험예 1에 따른 방전 용량 비율을 측정한 그래프이다.

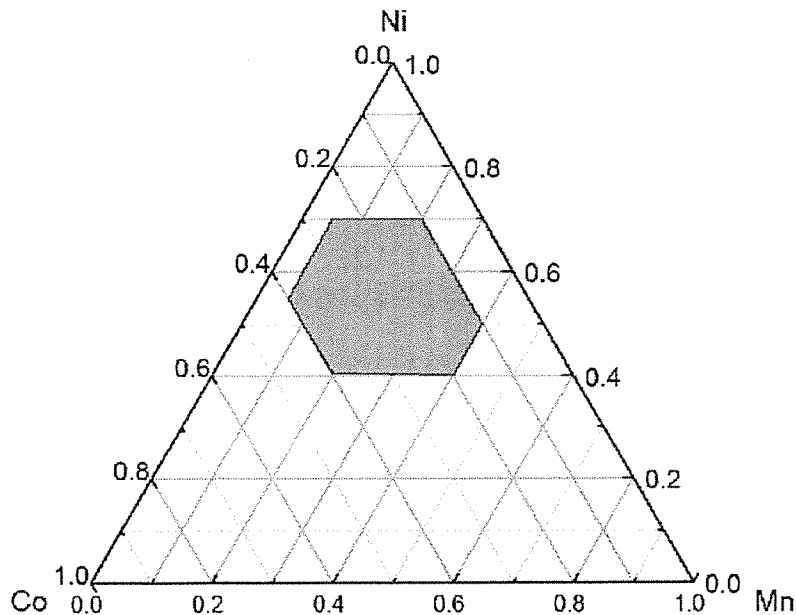
발명을 실시하기 위한 구체적인 내용

- 108] 이하에서는 실시예를 참조하여 본 발명을 더욱 상술하지만, 본 발명의 범주가 그것에 의해 한정되는 것은 아니다.
- 109] [제조예 1] 산화물 분말(b)의 제조
- 110] 혼합 전이금속 전구체로서 혼합 수산화물 MOOH ($M = \text{Ni}_{4/15}(\text{Mn}_{1/2}\text{Ni}_{1/2})_{8/15}\text{Co}_{0.2}$)을 사용하였고, 상기 혼합 수산화물과 Li_2CO_3 를 화학양론적 비율($\text{Li:M} = 1.02:1$)로 혼합하고, 혼합물을 공기 중에서 920°C 에서 10 시간 동안 소결하여, $\text{LiNi}_{0.53}\text{Co}_{0.2}\text{Mn}_{0.27}\text{O}_2$ 을 제조하였다. 이 때, 2차 입자들은 전혀 붕괴되지 않고 고스란히 유지되었다.
- 111] X-ray 분석으로 모든 샘플들이 잘 발달된 층상 결정 구조를 가지고 있음을 확인하였다. 또한, 단위 셀 체적은 소결 온도의 증가와 함께 현저하게 변화하지 않았는 바, 이는 현저한 산소 결핍 및 양이온 혼합의 현저한 증가가 나타나지 않고, 본질적으로 리튬 증발이 일어나지 않았음을 의미한다.
- 112] $\text{LiNi}_{0.53}\text{Co}_{0.2}\text{Mn}_{0.27}\text{O}_2$ 은 3.9 ~ 4.5% 정도로 니켈이 가역적 리튬층에 삽입되어 있고, 적정한 양의 Ni^{2+} 가 리튬 층에 삽입되어 구조적 안정성을 얻을 수 있다는 것을 확인하였다.
- 113] [실시예 1]
- 114] 단일상 구조로서 대략 15 ~ 20 μm 의 D50를 가진 LiCoO_2 와, 제조예 1에서 얻은 약 1 ~ 2 μm 의 미소 입자들의 응집체인 약 5 ~ 8 μm 의 D50를 가진 $\text{LiNi}_{0.53}\text{Co}_{0.2}\text{Mn}_{0.27}\text{O}_2$ 를 50:50의 비율로 혼합하여 혼합 양극 재료를 제조하였다.
- 115] 상기 제조된 혼합 양극 재료를 도전체인 Super P 및 바인더인 폴리비닐리덴 플루오라이드(polyvinylidene fluoride)를 중량비 92:4:4으로 혼합한 후, NMP(N-methyl pyrrolidone)를 첨가하여 슬러리를 제조하였다. 이러한 양극 슬러리를 알루미늄 집전체에 도포한 후 120°C 의 진공오븐에서 건조하여 양극을 제조하였다.
- 116] 또한, 음극으로는 MCMB(mesocarbon microbead)를 활물질로 사용하고 도전체로는 super P 및 바인더로는 PVdF를 각각 사용하여 92:2:6의 비율(중량비)로 혼합하고 NMP에 분산시킨 후 구리 호일에 코팅하여 음극을 제조하였다.
- 117] 이렇게 제조된 음극과 양극 사이에 폴리프로필렌으로 제조된 다공성 분리막을 사용하여 전극조립체를 제조하였다. 상기 전극조립체를 파우치형 케이스에 넣고 전극리드를 연결한 후, 1 M의 LiPF_6 이 녹아있는 부피비 1:1의 에틸렌카보네이트(EC)와 디메틸카보네이트(DMC) 용액을 전해질로 주입한 다음, 밀봉하여 리튬 이차전지를 조립하였다.
- 118] [실시예 2]
- 119] 혼합물에서 LiCoO_2 와 $\text{LiNi}_{0.53}\text{Co}_{0.2}\text{Mn}_{0.27}\text{O}_2$ 의 중량비가 70: 30인 것을 제외하고는 실시예 1과 동일한 방법으로 혼합 양극 재료 및 리튬 이차전지를 제조하였다.
- 120] [비교예 1]
- 121] 혼합물에서 LiCoO_2 와 $\text{LiNi}_{0.53}\text{Co}_{0.2}\text{Mn}_{0.27}\text{O}_2$ 의 중량비가 40: 60인 것을 제외하고는 실시예 1과 동일한 방법으로 혼합 양극 재료 및 리튬 이차전지를 제조하였다.

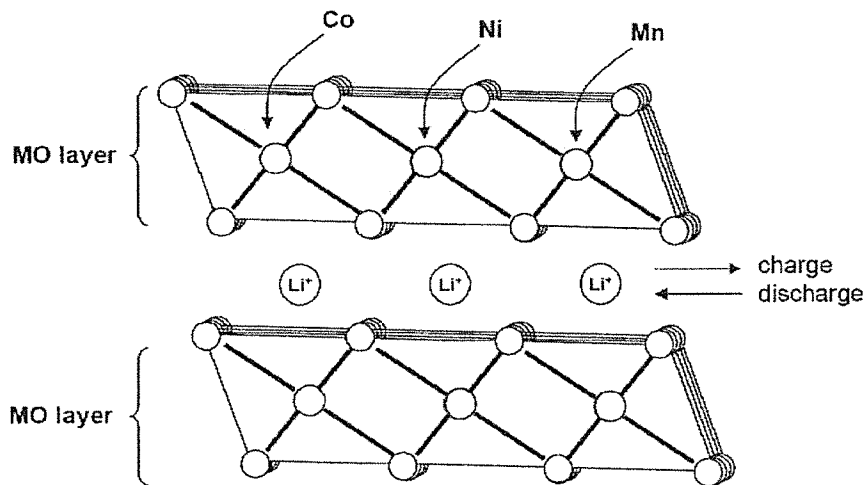
- 123] 혼합물에서 $\text{LiNi}_{0.53}\text{Co}_{0.2}\text{Mn}_{0.27}\text{O}_2$ 대신에 $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ 를 사용하였다는 점을 제외하고는 실시예 1과 동일한 방법으로 혼합 양극 재료 및 리튬 이차전지를 제조하였다.
- 124] [실험예 1]
- 125] 상기 실시예 1 및 2에서 제작된 전지와 비교예 1에서 각각 제작된 전지들을 0.2, 0.5, 1, 1.5 및 2 C rate로 방전용량(1 C rate 충전)을 측정하고, 5 C rate 용량 대비 각 C-rate에서의 방전용량의 비율을 계산하여, 이를 도 3에 나타내었다.
- 126] 도 3에서 보는 바와 같이, 비교예 1에 따른 전지는 C-rate가 높아질수록 방전용량이 급격히 저하되는 반면에, 본 발명에 따른 실시예 1과 2의 전지는 C-rate 특성이 매우 우수하고, 특히 산화물(b)의 함량이 30%인 실시예 2의 경우 C-rate 특성이 2C rate에서도 90% 이상의 높은 방전용량을 나타내는 것을 확인할 수 있다. 또한, 이러한 C-rate 특성의 향상은 1C의 낮은 C-rate에서도 발현되고 있고, 실시예 1 및 2의 전지에서 각각 C-rate가 높아질수록 방전 특성의 향상 정도가 훨씬 더 높아졌음을 알 수 있다.
- 127] 이상 검토한 바와 같이, 단순히 리튬 코발트 산화물과 리튬 니켈망간코발트 산화물을 혼합 사용하는 것만으로는 소망하는 레이트 특성을 발휘할 수 없고, 소정의 조성식을 갖는 물질을 특정한 혼합비로서 혼합하는 경우 상승효과를 발휘함을 확인할 수 있다.
- 128] 본 발명이 속한 분야에서 통상의 지식을 가진 자라면, 상기 내용을 바탕으로 본 발명의 범주내에서 다양한 응용 및 변형을 행하는 것이 가능할 것이다.

도면

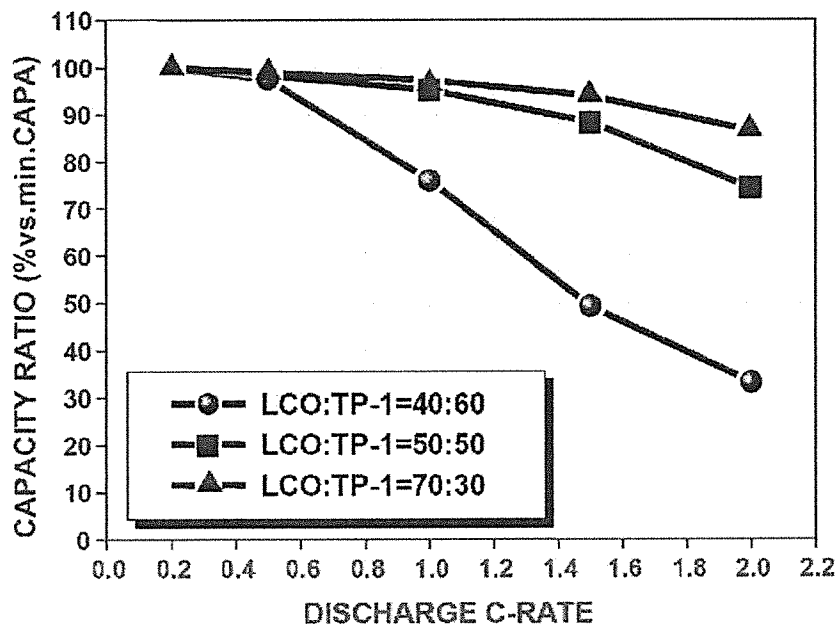
도면



도면2



도면3



Electronic Patent Application Fee Transmittal

Application Number:

Filing Date:

Title of Invention:

POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF,
AND ARTICLES COMPRISING THE SAME

First Named Inventor/Applicant Name:

David Ofer

Filer:

Weston Gould/Ann Andrusiak

Attorney Docket Number:

57TIA-10102

Filed as Small Entity

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Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Basic National Stage Fee	2631	1	140	140
Natl Stage Search Fee - Report provided	2642	1	240	240
Natl Stage Exam Fee - all other cases	2633	1	360	360

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 (\$)				740

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First Named Inventor/Applicant Name:	David Ofer
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Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part (if appl.)	Pages (if appl.)
			POSCO Future M v. TIA X LLC		
			POSCO Future M EX1005		

1		SCAN_A2_024701.pdf	1612958 273ef42f6cf93cd045f09848fd4a608c6549b257	yes	26
	Multipart Description/PDF files in .zip description				
	Document Description		Start	End	
	Transmittal of New Application		1	3	
	Transmittal Letter		4	4	
	Application Data Sheet		5	8	
	Oath or Declaration filed		9	12	
	Power of Attorney		13	13	
	Preliminary Amendment		14	22	
	Transmittal Letter		23	24	
	Information Disclosure Statement (IDS) Form (SB08)		25	26	
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2	Foreign Reference	JP2008234872.pdf	2033597 bff01ea1bb10c21c7336bd7281d71348d5a2fc81	no	24
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Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	33340 88ccb4d5b9af40477ab1d2e796b186721c89dbf3	no	2
Warnings:					
Information:					

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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.

Supplemental Application Data Sheet

Application Information

Application number::	<u>14/238,643</u>
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Subject Matter::	Utility
Suggested Group Art Unit::	N/A
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Sequence submission?::	None
Computer Readable Form (CRF)?::	No
Title::	POLYCRYSTALLING METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME
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Request for Non-Publication?::	No
Total Drawing Sheets::	9
Small Entity?::	<u>Yes</u>
Petition included?::	No
Secrecy Order in Parent Appl.?::	No

Applicant Information

Applicant Authority Type::	Inventor
----------------------------	----------

Primary Citizenship Country:: US
Status:: Full Capacity
Given Name:: David
Family Name:: Ofer
City of Residence:: Needham
State or Province of Residence:: MA
Country of Residence:: US
Street of mailing address:: 37 Booth Street
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State or Province of mailing address:: MA
Postal or Zip Code of mailing address:: 02494

Applicant Authority Type:: Inventor
Primary Citizenship Country:: US
Status:: Full Capacity
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Middle Name:: W.
Family Name:: Pullen
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State or Province of mailing address::	MA
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State or Province of Residence::	MA
Country of Residence::	US
Street of mailing address::	23 Virginia Road
City of mailing address::	Arlington
State or Province of mailing address::	MA
Postal or Zip Code of mailing address::	02476

Correspondence Information

Correspondence Customer Number::	25006
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Representative Information

Representative Customer Number::	25006
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Domestic Priority Information

Application::	Continuity Type::	Parent Application::	Parent Filing Date::
This Application	National Stage of	PCT/US2012/048602	07/27/12
PCT/US2012/048602	An application claiming the benefit under 35 USC 119(e)	61/575,115	08/16/11

Foreign Priority Information**Assignee Information**

Assignee name:: TIAX LLC

Signature:

A signature of the applicant or representative is required in accordance with 37 CFR 1.33 and 10.18. Please see 37 CFR 1.4(d) for the form of the signature.			
Signature	/Weston R. Gould, Ph. D./	Date	February 12, 2014
Name (Print/Type)	Weston R. Gould, Ph. D.	Registration No. (Attorney/Agent)	59,142

Electronic Acknowledgement Receipt

EFS ID:	18190211
Application Number:	14238643
International Application Number:	
Confirmation Number:	1064
Title of Invention:	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME
First Named Inventor/Applicant Name:	David Ofer
Customer Number:	25006
Filer:	Weston Gould/Ann Andrusiak
Filer Authorized By:	Weston Gould
Attorney Docket Number:	57TIA-10102
Receipt Date:	12-FEB-2014
Filing Date:	
Time Stamp:	16:42:10
Application Type:	U.S. National Stage under 35 USC 371

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	Application Data Sheet	SCAN_A2_024703.pdf	115805 9a2f6c83d684fb26faf4a6a6d1cbf8c618e5e331	no	4

Warnings:

Information:

POSCO Future M v. TIAX LLC

POSCO Future M EX1005

Page 167

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115805

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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.

VIII-3-1	Declaration: Entitlement to claim priority Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application specified below, where the applicant is not the applicant who filed the earlier application or where the applicant's name has changed since the filing of the earlier application (Rules 4.17(iii) and 51bis.1(a)(iii)) Name	In relation to this international application TIAX LLC is entitled to claim priority of earlier application No. 61/575,115 by virtue of the following:
VIII-3-1(i)		TIAX LLC is entitled as employer of the inventor, OFER, David
VIII-3-1(i)		TIAX LLC is entitled as employer of the inventor, PULLEN, Adrian W.
VIII-3-1(i)		TIAX LLC is entitled as employer of the inventor, SRIRAMULU, Suresh

482705

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 15, 2012

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 61/575,115

FILING DATE: August 16, 2011

RELATED PCT APPLICATION NUMBER: PCT/US12/48602

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS US61/575,115



Certified by

David J. Kappas

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

U.S. PTO
61/575115
08/16/2011

PTO/SB/16 (12-08)

Approved for use through 06/30/2010. OMB 0651-0032

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET – Page 1 of 2

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EO 052 288 914 US

081611

INVENTOR(S)		
Given Name (first and middle (if any))	Family Name or Surname	Residence (City and either State or Foreign Country)
David	Ofer	Needham, MA
Adrian Wesley	Pullen	Jamaica Plain, MA

Additional inventors are being named on the _____ n/a _____ separately numbered sheets attached hereto.

TITLE OF THE INVENTION (500 characters max):

COBALT ENRICHMENT AT GRAIN BOUNDARIES OF POLYCRYSTALLINE LAYERED METAL OXIDES

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

☐ The address corresponding to Customer Number: _____

OR

☒ Firm or Individual Name **TIAX LLC % Nadine Andon**

Address **35 Hartwell Avenue**

City **Lexington** State **MA** Zip **02421-3102**

Country **USA** Telephone **781/879-1283** Email **andon.n@tiaxllc.com**

ENCLOSED APPLICATION PARTS (check all that apply)

☒ Application Data Sheet. See 37 CFR 1.76 ☐ CD(s). Number of CDs _____

☐ Drawing(s) Number of Sheets _____ ☐ Other (specify) _____

☒ Specification (e.g. description of the invention) Number of Pages **6**

Fees Due: Filing Fee of \$220 (\$110 for small entity). If the specification and drawings exceed 100 sheets of paper, an application size fee is also due, which is \$270 (\$135 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).

METHOD OF PAYMENT OF THE FILING FEE AND APPLICATION SIZE FEE FOR THIS PROVISIONAL APPLICATION FOR PATENT

☒ Applicant claims small entity status. See 37 CFR 1.27. **\$110.00**

☐ A check or money order made payable to the Director of the United States Patent and Trademark Office is enclosed to cover the filing fee and application size fee (if applicable).

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☒ The Director is hereby authorized to charge the filing fee and application size fee (if applicable) or credit any overpayment to Deposit Account Number: **121675**

TOTAL FEE AMOUNT (\$)

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The PTO did not receive the following
Noted Item(s) app data sheet

PTO/SB/16 (12-08)
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PROVISIONAL APPLICATION COVER SHEET
Page 2 of 2

PTO/SB/16 (12-08)

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SIGNATURE

Joseph M. Centofanti

Date

AUG. 16, 2011

TYPED or PRINTED NAME

Joseph M. Centofanti

REGISTRATION NO. _____

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TELEPHONE

781/879-1285

Docket Number: _____

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET – Page 1 of 2

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Express Mail Label No. EO 052 288 914 US

INVENTOR(S)		
Given Name (first and middle (if any))	Family Name or Surname	Residence (City and either State or Foreign Country)
David	Ofer	Needham, MA
Adrian Wesley	Pullen	Jamaica Plain, MA

Additional inventors are being named on the _____ n/a _____ separately numbered sheets attached hereto.

TITLE OF THE INVENTION (500 characters max):

 COBALT ENRICHMENT AT GRAIN BOUNDARIES OF POLYCRYSTALLINE LAYERED METAL OXIDES

Direct all correspondence to: CORRESPONDENCE ADDRESS
☐ The address corresponding to Customer Number:
 OR
☒ Firm or Individual Name **TIAX LLC % Nadine Andon**
 Address **35 Hartwell Avenue**

City Lexington	State MA	Zip 02421-3102
Country USA	Telephone 781/879-1283	Email andon.n@tiaxllc.com

ENCLOSED APPLICATION PARTS (check all that apply)

☒ Application Data Sheet. See 37 CFR 1.76 ☐ Drawing(s) Number of Sheets _____ ☒ Specification (e.g. description of the invention) Number of Pages 6	☐ CD(s). Number of CDs _____ ☐ Other (specify) _____
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PROVISIONAL APPLICATION COVER SHEET
Page 2 of 2

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.



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SIGNATURE

Joseph M. Centofanti

Date

AUG 16, 2011

TYPED or PRINTED NAME

Joseph M. Centofanti

REGISTRATION NO. _____

(if appropriate)

TELEPHONE

781/879-1285

Docket Number: _____

Cobalt Enrichment at Grain Boundaries of Polycrystalline Layered Metal Oxides

David Ofer and Adrian Pullen

TIAX LLC, 35 Hartwell Avenue, Lexington, MA 02421

Abstract:

This invention concerns polycrystalline layered-structure lithiated metal oxides of composition $\text{Li}_{1+x}\text{MO}_{2+y}$ and articles formed therefrom, where $-0.1 \leq X \leq 0.3$, $-0.3 \leq Y \leq 0.3$, M is about 25-97 % Ni, 3-50 % Co, 0-60 % Mn, and 0-10 % additional elements which may comprise one or more of Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga and B, said polycrystalline layered-structure lithiated metal oxides having enrichment of Co in the grain boundary regions between primary crystallites, i.e., concentration of Co is higher in the grain boundary regions than in the bulk of the primary crystallite.

These compositions with Co-enriched grain boundaries between primary crystallites exhibit dramatically enhanced electrochemical cycling stability as lithium is de-intercalated from and re-intercalated into the crystal lattice.

Background/Prior Art

Layered structure lithium nickelate (LiNiO_2)-based materials have been sought after for Lithium-ion battery cathodes because they generally have lower cost, higher capacity and higher rate capability than the historically predominant LiCoO_2 cathode material. However, pure LiNiO_2 materials exhibit poor electrochemical stability and cycling performance. It has been found that by substituting varying amounts of other metals for some or much of the Ni in M of LiMO_2 -based compositions, some of the capacity and cost benefits of LiNiO_2 materials can be obtained with much improved electrochemical cycling stability, and accordingly a wide variety of Ni-containing layered-structure $\text{Li}_{1+x}\text{MO}_{2+y}$ materials with various compositions of metals M have been developed. In particular, Co incorporation is found to enhance electrochemical cycling stability, and is readily achieved because of the favorable solid-state solution interaction of LiCoO_2 with LiNiO_2 . However, Co is generally considerably more costly than Ni or Mn, the other principal transition metals used in formulating LiMO_2 -based layered structure materials, and Co incorporation in LiNiO_2 generally results in some diminution of the latter material's high capacity and rate capability. Therefore it is desirable to use only as much Co as is required to confer the needed stability to a Ni-based LiMO_2 material.

Ni-based layered materials of the LiMO_2 type are dense polycrystalline agglomerates of submicron-sized primary crystallites. It has been shown that in polycrystalline Ni-containing LiMO_2 -based materials having 2D $\alpha\text{-NaFeO}_2$ -type layered structure, electrochemical cycling induces the 2D layers of transition metal atoms at the crystallite grain boundaries (edges) to reorganize into a NiO-type rock salt structure and/or to be reduced in oxidation state. These transformations are also associated with the appearance of cracks between adjacent crystallites. The resulting NiO-type phases and cracks in

grain boundaries between crystallites can be expected to significantly degrade the electrochemical performance of these materials. This work has also shown that whereas Ni atoms at the grain boundaries undergo reduction in oxidation state as part of these transformations, Co atoms in the grain boundary regions do not, suggesting that it is primarily the Ni atoms that are mobile and that drive the structural rearrangements in the grain boundary regions.

The above observations indicate that Co substitution enhances electrochemical cycling by stabilizing the grain boundaries of polycrystalline Ni-based layered LiMO_2 . Therefore Co-substituted Ni-based LiMO_2 materials with Co preferentially concentrated in the intercrystallite grain boundary regions can obtain enhanced cycling stability while having lower Co levels in the bulk crystallites and minimal overall cobalt content compared to Ni-base LiMO_2 materials with uniformly distributed Co. Materials with such Co-enriched grain boundaries obtain the stabilizing benefits of Co substitution while minimizing the detrimental impacts of Co substitution on capacity, rate capability and cost.

Co-enriched grain boundary materials are explicitly distinguished from “core/shell” materials in which Ni-based LiMO_2 secondary particles are coated with a Co-based material. In these structures, only the secondary particle is coated with Co-based LiMO_2 , ostensibly to reduce the interaction between Ni and electrolyte. Such core/shell materials do not have stabilizing intercrystallite Co enrichment within the bulk of the secondary particle.

TIAX Invention

The object of this invention is to provide for enhanced discharge capacity and electrochemical cycling stability in lithium-ion batteries of a polycrystalline Ni-containing LiMO_2 -based material having 2D $\alpha\text{-NaFeO}_2$ -type layered structure, where M represents multiple elements. This objective is achieved by enriching the grain boundary regions of such polycrystalline materials with Co. Selective enrichment of the grain boundaries with Co minimizes the overall amount of Co that must be incorporated in such materials in order to enhance their electrochemical cycling. The benefits of minimizing a material's overall Co content are reduced cost together with enhanced capacity and rate capability. At the same time, such Co-enrich grain boundary materials have more Co concentrated in the grain boundaries, with attendant benefits to cycling stability, than do many materials having much higher overall Co content uniformly distributed in the bulk.

The polycrystalline material of this present invention can have the composition $\text{Li}_x\text{Q}_y\text{MO}_2$, wherein,

x is in the range $-0.1 \leq x \leq 1.2$

y is in the range $-0.00 \leq y \leq 0.2$

Q represents one or more elements selected from the list: Mg, Sr, Ca, Cu, Zn, etc., and is predominantly associated with the lithium-site of the crystal structure

M represents one or more elements selected from the list: Ni, Co, Mn, Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga and B. M can comprise 25-97 % Ni, 3-50 % Co, 0-60 % Mn, and 0-10 % additional elements selected from the list Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga and B.

The inter-crystallite region of this polycrystalline material has a higher concentration of Cobalt than the bulk.

Example 1

A sample of polycrystalline 2D α -NaFeO₂-type layered structure having overall composition $\text{Li}_{0.932}\text{Mg}_{0.023}\text{Ni}_{0.905}\text{Co}_{0.072}\text{O}_{1.955}$ with Co-enriched grain boundaries was prepared, and thinly sectioned (100-150 nm thick) particles of the material were analyzed by scanning transmission electron microscopy (STEM) with energy dispersive x-ray analysis (EDX). Figure 1 shows a low resolution image of an approximately 11 micron diameter secondary particle, and shows the secondary particle to be composed of densely agglomerated primary particles or crystallites.

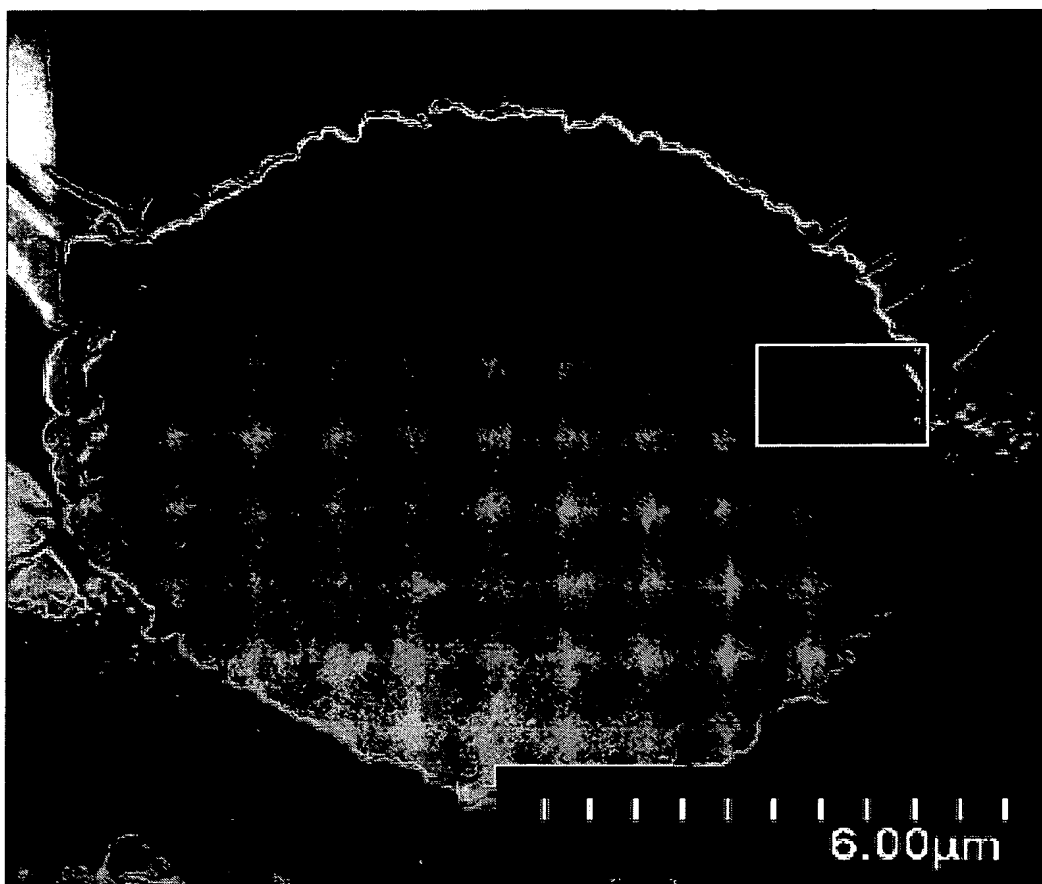


Figure 1. Cross section of $\text{Li}_{0.932}\text{Mg}_{0.023}\text{Ni}_{0.905}\text{Co}_{0.072}\text{O}_{1.955}$ particle.

The white box in Figure 1 shows an area of the cross-sectioned particle that was analyzed by high resolution STEM with EDX. Figure 2 shows the higher magnification STEM image of the selected area, together with the overall EDX spectrum for the imaged area.

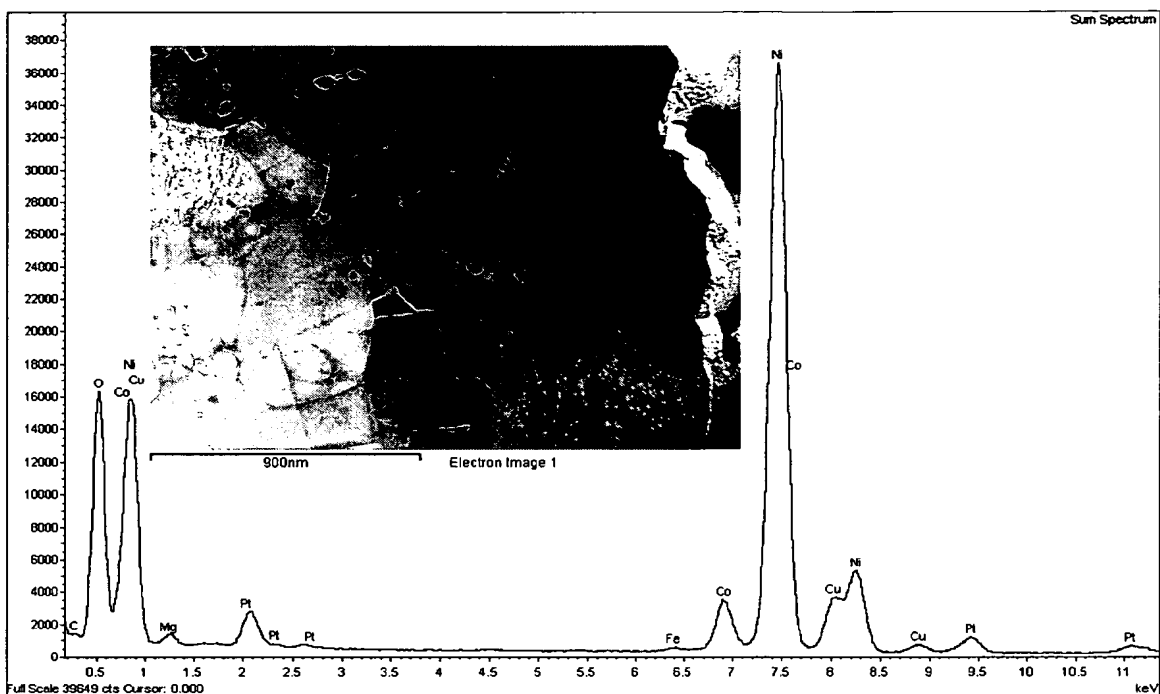


Figure 2. STEM image (inset photograph)_and overall EDX analysis of selected area in $\text{Li}_{0.932}\text{Mg}_{0.023}\text{Ni}_{0.905}\text{Co}_{0.072}\text{O}_{1.955}$ particle cross-section.

The image in Figure 2 further reveals the polycrystalline nature of the material. Integration of the EDX spectrum gives Co/Ni ratio of 0.079, in agreement with the overall material composition. However, high resolution EDX mapping of the same area, shown in Figure 3, reveals that, whereas Ni is uniformly distributed within the crystallites, Co is concentrated at the grain boundaries of the crystallites.

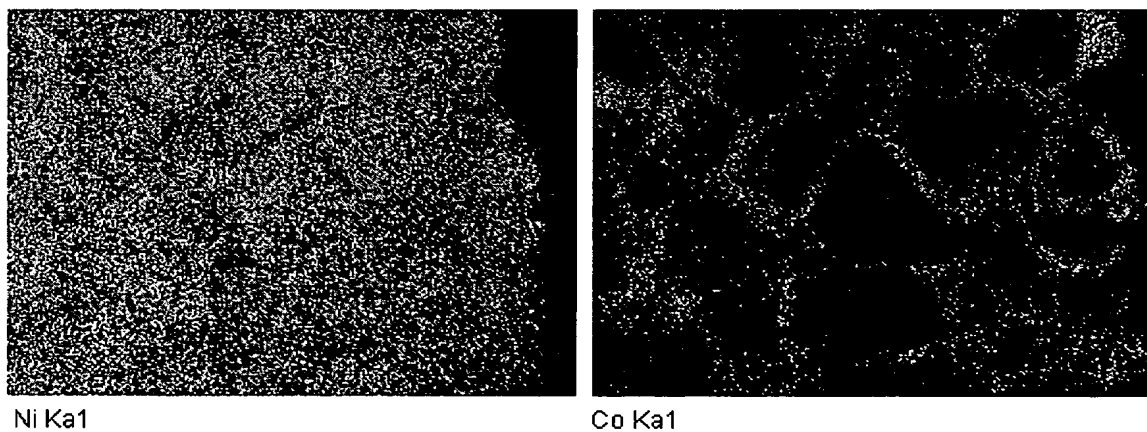


Figure 3. High resolution EDX mapping of Ni (left) and Co (right) for the cross-section STEM image shown in Figure 2.

Example 2

Two samples of polycrystalline 2D α -NaFeO₂-type layered structure having overall composition $\text{Li}_{(0.899)}\text{Mg}_{(0.022)}\text{Ni}_{(0.87)}\text{Co}_{(0.105)}\text{O}_{(1.89)}$ were made, one with Co-enriched grain boundaries and one with a uniform distribution of Cobalt. The materials were blended with PVDF binder and conductive carbon in a slurry of NMP solvent and coated onto an aluminum foil current collector. Cathode electrodes were then punched out of the foil and combined with lithium foil anodes, glass fiber separators and carbonate based electrolytes in a coin cell format for electrochemical testing. The cells were cycled through a series of charge and discharge cycles at a range of current rates and the total electrochemical discharge capacity at each rate recorded. The results of these tests are shown in the table below. The material with grain boundary Co enrichment has higher overall capacity at all rates than the uniform Co distribution material, and also has higher rate capability as indicated by Ratio of 5C to C/5.

Table 1: Half Cell results for two types of 12% Co in LiNiO₂ type of material

Cathode Type	Discharge Capacity (mAh/g)			Ratio 5C to C/5
	C/20	C/5	5C	
Co Enriched grain boundaries	214	201	168	84%
Uniform Co distribution	207	196	144	73%

Claims:

1. A polycrystalline layered metal oxide with composition $\text{Li}_{1+x}\text{MO}_{2+y}$, where - $0.1 \leq X \leq 0.3$, $-0.3 \leq Y \leq 0.3$, and M stands for one or more elements. M can comprise 25-97 % Ni, 3-50 % Co, 0-60 % Mn, and 0-10 % additional elements selected from the list Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga and B. These additional elements can reside either in the transition metal layer or in the lithium layer of the polycrystalline material with the α -NaFeO₂-type layered structure.
2. The polycrystalline material of Claim 1, having Cobalt enrichment in the regions between two crystals, that is Cobalt enrichment in the grain boundary regions. Cobalt enrichment at the primary particle grain boundaries can be measured by a high resolution analytical technique.



"grain boundary" provisional
Nadine Andon to: Elaine McLaughlin
Cc: Joe Centofanti

08/15/2011 11:28 AM

Elaine,

Please make the following minor edits to the attached document:

- ✓ 1. Page One: remove lines 1, 2, 3 and 4 (i.e., "confidential" ; the May date; "not to be disclosed,..."). The first line on the first page should be the title of the invention.
2. All pages: remove lines 1 and 2 (i.e., "confidential..." "not to be disclosed...")
- ✓ 3. Last page: remove the word, "draft", before the word, "claims".

Please prepare the necessary paperwork to file this document as a provisional application for Joe's signature. The inventors are:

1. David Ofer of Needham, MA
2. Adrian Pullen of Jamaica Plain, MA

The invention was **not** reduced to practice in any Government contract.

Please let me know the date this application is filed.

Thanks,
Nadine



Cobalt Enrichment Provisional Aug10_2010.doc

DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:	PCT/US2012/048602
International filing date:	27 July 2012 (27.07.2012)
Document type:	Certified copy of priority document
Document details:	Country/Office: US
	Number: 61/575,115
	Filing date: 16 August 2011 (16.08.2011)
Date of receipt at the International Bureau:	16 August 2012 (16.08.2012)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-bis)

PCT REQUESTOriginal (for **SUBMISSION**)

0	For receiving Office use only	
0-1	International Application No.	PCT/US12/46602
0-2	International Filing Date	27 JULY 2012 (27/07/12)
0-3	Name of receiving Office and "PCT International Application"	PCT INTERNATIONAL APPLICATION RO/US
0-4	Form PCT/RO/101 PCT Request	
0-4-1	Prepared Using	PCT-SAFE [EASY/EFS-Web mode] Version 3.51.055.231 MT/FOP 20120701/0.20.5.19
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	United States Patent and Trademark Office (USPTO) (RO/US)
0-7	Applicant's or agent's file reference	TIA0012PCT
I	Title of Invention	POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME
II	Applicant	
II-1	This person is	Applicant only
II-2	Applicant for	All designated States except US
II-4	Name	TIAX LLC
II-5	Address	35 Hartwell Avenue Lexington, Massachusetts 02421 United States of America
II-6	State of nationality	US
II-7	State of residence	US
III-1	Applicant and/or inventor	
III-1-1	This person is	Applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	OFER, David
III-1-5	Address	37 Booth Street Needham, Massachusetts 02494 United States of America
III-1-6	State of nationality	US
III-1-7	State of residence	US

PCT REQUESTOriginal (for **SUBMISSION**)

III-2	Applicant and/or inventor	
III-2-1	This person is	Applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	PULLEN, Adrian W.
III-2-5	Address	65 Boylston St., #3 Boston, Massachusetts 02130 United States of America
III-2-6	State of nationality	US
III-2-7	State of residence	US
III-3	Applicant and/or inventor	
III-3-1	This person is	Applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	SRIRAMULU, Suresh
III-3-5	Address	23 Virginia Road Arlington, Massachusetts 02476 United States of America
III-3-6	State of nationality	US
III-3-7	State of residence	US
IV-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/ has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	Agent
IV-1-1	Name (LAST, First)	EHRlich, Grant M.
IV-1-2	Address	CANTOR COLBURN LLP 20 Church Street 22nd Floor Hartford, Connecticut 06103 United States of America
IV-1-3	Telephone No.	860-286-2929
IV-1-4	Facsimile No.	860-286-0115
IV-1-5	e-mail	global-ip@cantorcolburn.com
IV-1-5(a))	E-mail authorization The receiving Office, the International Searching Authority, the International Bureau and the International Preliminary Examining Authority are authorized to use this e-mail address, if the Office or Authority so wishes, to send notifications issued in respect of this international application:	exclusively in electronic form (no paper notifications will be sent)
IV-1-6	Agent's registration No.	56185

PCT REQUESTOriginal (for **SUBMISSION**)

V	DESIGNATIONS	
V-1	The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.	
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	16 August 2011 (16.08.2011)
VI-1-2	Number	61/575,115
VI-1-3	Country	US
VI-2	Priority document request The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	VI-1
VI-3	Incorporation by reference : where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.	
VII-1	International Searching Authority Chosen	Korean Intellectual Property Office (ISA/KR)
VIII	Declarations	Number of declarations
VIII-1	Declaration as to the identity of the inventor	—
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	1
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	1
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	—
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	—

PCT REQUESTOriginal (for **SUBMISSION**)

IX	Check list	Number of sheets	Electronic file(s) attached
IX-1	Request (including declaration sheets)	6	✓
IX-2	Description	23	—
IX-3	Claims	4	—
IX-4	Abstract	1	✓
IX-5	Drawings	9	—
IX-7	TOTAL	43	
Accompanying Items		Paper document(s) attached	Electronic file(s) attached
IX-8	Fee calculation sheet	✓	—
IX-20	Figure of the drawings which should accompany the abstract	1	
IX-21	Language of filing of the international application	English	
X-1	Signature of applicant, agent or common representative	/Grant M. Ehrlich, Reg. No. 56,185/	
X-1-1	Name (LAST, First)	EHRlich, Grant M.	
X-1-2	Name of signatory		
X-1-3	Capacity (if such capacity is not obvious from reading the request)		

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	27 JULY 2012 (27/07/12)
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/KR
10-6	Transmittal of search copy delayed until search fee is paid	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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VIII-2-1	Declaration: Entitlement to apply for and be granted a patent Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent (Rules 4.17(ii) and 51bis.1(a)(ii)), in a case where the declaration under Rule 4.17(iv) is not appropriate: Name (LAST, First)	In relation to this international application TIAX LLC is entitled to apply for and be granted a patent by virtue of the following:
VIII-2-1(i)		TIAX LLC is entitled as employer of the inventor, OFER, David
VIII-2-1(i)		TIAX LLC is entitled as employer of the inventor, PULLEN, Adrian W.
VIII-2-1(i)		TIAX LLC is entitled as employer of the inventor, SRIRAMULU, Suresh



- (51) **International Patent Classification:**
C01G 49/00 (2006.01) *C01D 1/00* (2006.01)
C01G 51/00 (2006.01) *H01M 10/05* (2010.01)
- (21) **International Application Number:** PCT/US2012/048602
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- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/575,115 16 August 2011 (16.08.2011) US
- (71) **Applicant (for all designated States except US):** **TIAX LLC** [US/US]; 35 Hartwell Avenue, Lexington, Massachusetts 02421 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** **OFER, David** [US/US]; 37 Booth Street, Needham, Massachusetts 02494 (US). **PULLEN, Adrian W.** [US/US]; 65 Boylston St., #3, Boston, Massachusetts 02130 (US). **SRIRAMULU, Suresh** [US/US]; 23 Virginia Road, Arlington, Massachusetts 02476 (US).
- (74) **Agent:** **EHRlich, Grant M.**; Cantor Colburn LLP, 20 Church Street, 22nd Floor, Hartford, Connecticut 06103 (US).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(54) **Title:** POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

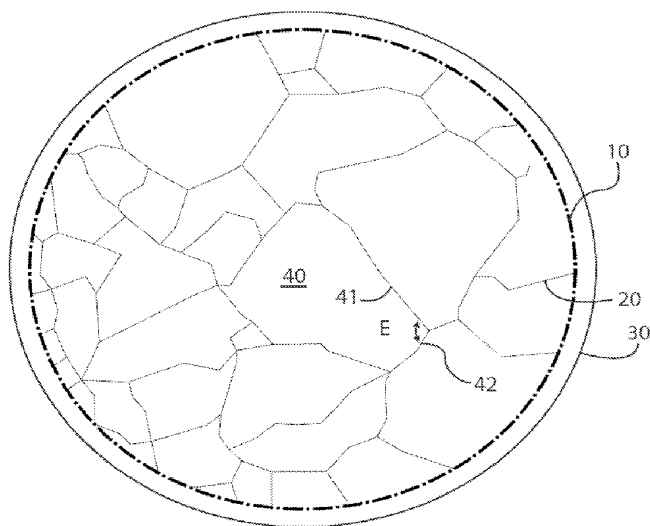


FIG. 1

(57) **Abstract:** A particle, including: a plurality of crystallites including a first composition having a layered α -NaFeO₂-type structure and including lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel in an amount of about 0.1 to about 0.79 mole, per mole of the first composition, cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and including a second composition having the layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

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(71) Applicant (for all designated States except US): **TIAX LLC** [US/US]; 35 Hartwell Avenue, Lexington, Massachusetts 02421 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **OFER, David** [US/US]; 37 Booth Street, Needham, Massachusetts 02494 (US). **PULLEN, Adrian W.** [US/US]; 65 Boylston St., #3, Boston, Massachusetts 02130 (US). **SRIRAMULU, Suresh** [US/US]; 23 Virginia Road, Arlington, Massachusetts 02476 (US).

(74) Agent: **EHRlich, Grant M.**; Cantor Colburn LLP, 20 Church Street, 22nd Floor, Hartford, Connecticut 06103 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

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(54) Title: POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

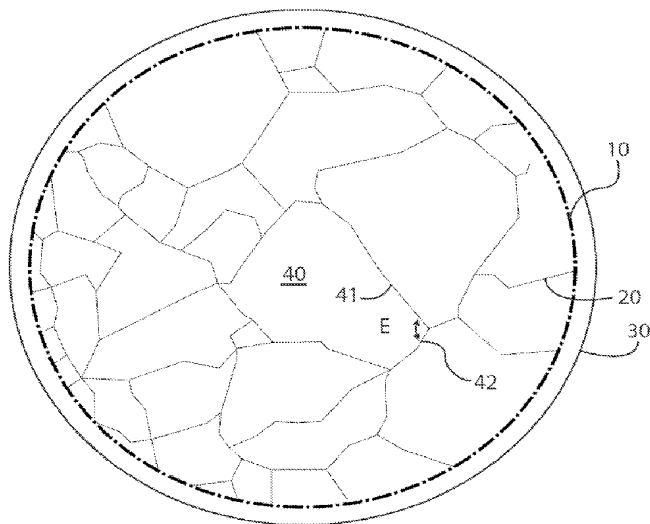


FIG. 1

(57) Abstract: A particle, including: a plurality of crystallites including a first composition having a layered α -NaFeO₂-type structure and including lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel in an amount of about 0.1 to about 0.79 mole, per mole of the first composition, cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and including a second composition having the layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

WO 2013/025328 A2

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

POLYCRYSTALLINE METAL OXIDE, METHODS OF MANUFACTURE THEREOF,
AND ARTICLES COMPRISING THE SAME

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority to U.S. Provisional Application No. 61/575,115, filed on August 16, 2011, the content of which in its entirety is incorporated herein by reference.

BACKGROUND

(1) Field

[0001] Disclosed is a polycrystalline metal oxide, methods of manufacture thereof, and articles comprising the same.

(2) Description of the Related Art

[0002] Lithium nickel oxide (LiNiO_2) materials having a layered structure are desirable as lithium battery cathode materials because they generally provide lower cost, higher capacity, and higher rate capability than lithium cobalt oxide. However, pure LiNiO_2 materials exhibit poor electrochemical stability and cycling performance. It has been found that by substituting varying amounts of other metals for some or much of the Ni in LiNiO_2 , some of the capacity and cost benefits of LiNiO_2 can be obtained with improved electrochemical cycling stability.

[0003] Accordingly, a wide variety of layered-structure lithium nickel oxides, wherein a portion of the Ni has been substituted by another metal, have been developed. In particular, cobalt (Co) incorporation is found to enhance electrochemical cycling stability, and is readily achieved because of the favorable solid-state solution interaction of lithium cobalt oxide (LiCoO_2) with LiNiO_2 . However, Co is more costly than nickel (Ni), and Co incorporation in LiNiO_2 generally results in some diminution of the high capacity and rate capability provided by LiNiO_2 . Therefore it would be desirable to use only as much Co as is required to confer sufficient stability to a LiNiO_2 to provide a lower cost material that provides more of the desirable properties of LiNiO_2 . Thus there remains a need for a lower cost lithium battery cathode material that provides the desirable properties of LiNiO_2 at lower cost.

SUMMARY

[0004] A particle, including: a plurality of crystallites including a first composition having a layered $\alpha\text{-NaFeO}_2$ -type structure and including lithium in an amount of about 0.1 to

about 1.3 moles, per mole of the first composition, nickel in an amount of about 0.1 to about 0.79 mole, per mole of the first composition, cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and including a second composition having the layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

[0005] Also disclosed is a particle, including: a plurality of crystallites including a first composition having a layered α -NaFeO₂-type structure and including lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel in an amount of about 0.91 to about 0.99 mole, per mole of the first composition, cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and including a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

[0006] Also disclosed is a lithium-ion battery including at least one of the foregoing particles.

[0007] Also disclosed is a method of manufacturing a particle, the method including: combining a lithium compound, a cobalt compound, and a nickel compound to form a mixture; heat treating the mixture at about 30 to about 200°C to form a dried mixture; heat treating the dried mixture at about 200 to about 500°C for about 0.1 to about 5 hours; then heat treating at 600 to about 900°C for about 0.1 to about 10 hours to manufacture the particle, wherein the particle includes a plurality of crystallites including a first composition having a layered α -NaFeO₂-type structure and including Li, Ni, Co, and O, wherein the Li is present in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel is present in an amount of about 0.1 to about 0.79 mole or about 0.91 to about 0.99 mole, per mole of the first composition, cobalt is present in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen is present in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and including a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof, wherein a

concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The above and other aspects, advantages and features of this disclosure will become more apparent by describing in further detail exemplary embodiments thereof with reference to the accompanying drawings, in which:

[0009] FIG. 1 is a schematic perspective view of an embodiment of a cross-section of a secondary particle;

[0010] FIG. 2 is a schematic illustration of an embodiment of a battery;

[0011] FIG. 3 is a scanning electron micrograph (SEM) of a thin cross-section of a secondary particle prepared in Example 2;

[0012] FIG. 4 is an enlarged view of the secondary particle of FIG. 3 showing the location of EDX spot analyses;

[0013] FIG. 5 is a further enlarged view of the secondary particle of FIG. 3 showing the location of EDX spot analyses;

[0014] FIG. 6 is a graph of atomic percent of non-lithium atoms versus position showing the concentration of O, Mg, Co, and Ni for each of the EDX spot analyses indicated in FIG. 5;

[0015] FIG. 7 is a graph of the concentration of cobalt (atomic percent) versus position for each of the EDX spot analyses indicated in FIG. 5;

[0016] FIG. 8 is a graph of cathode specific capacity (milliampere hours per gram) versus cycle number and shows cycling capacity results for lithium-ion cells assembled with the cathode materials of Example 2 and Example 3;

[0017] FIG. 9 is a scanning transmission electron micrograph (STEM) of a thin cross-section of a secondary particle prepared in Example 6;

[0018] FIG. 10 is an enlarged view of area A indicated in FIG. 9;

[0019] Fig. 11 is a graph of intensity (counts) versus energy (kiloelectron volts, keV) showing the results of energy dispersive X-ray (EDX) analysis of area A indicated in FIG. 9;

[0020] FIG. 12 is a Ni EDX map of area A indicated in FIG. 9; and

[0021] FIG. 13 is a Co EDX map of area A indicated in FIG. 9.

DETAILED DESCRIPTION

[0022] The inventors have discovered that lithium nickel oxides having the layered α -NaFeO₂-type structure and having cobalt enriched grain boundaries are surprisingly stabilized. The lithium nickel oxide is in the form of a secondary particle comprising a plurality of crystallites (i.e., primary particles), wherein the cobalt enriched grain boundaries are between adjacent crystallites. Such materials may be readily manufactured by treating a lithium nickel oxide with a cobalt compound and optionally a lithium compound. The lithium nickel oxides having cobalt enriched grain boundaries have excellent electrochemical properties, including improved cycling stability and improved capacity. Because cobalt is preferentially provided in the grain boundaries, where it is understood to be most effective at stabilizing the lithium nickel oxide, less cobalt is required to provide a lithium nickel oxide having suitable stability than if cobalt is provided uniformly or at a location other than the grain boundaries. Thus a lower cost material is now available that provides more of the desirable properties of LiNiO₂ with less cobalt.

[0023] The invention now will be described more fully hereinafter with reference to the accompanying drawings, in which various embodiments are shown. This invention may, however, be embodied in many different forms, and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like reference numerals refer to like elements throughout.

[0024] It will be understood that when an element is referred to as being “on” another element, it can be directly on the other element or intervening elements may be present therebetween. In contrast, when an element is referred to as being “directly on” another element, there are no intervening elements present.

[0025] It will be understood that, although the terms “first,” “second,” “third” etc. may be used herein to describe various elements, components, regions, layers, and/or sections, these elements, components, regions, layers, and/or sections should not be limited by these terms. These terms are only used to distinguish one element, component, region, layer, or section from another element, component, region, layer, or section. Thus, “a first element,” “component,” “region,” “layer,” or “section” discussed below could be termed a second element, component, region, layer, or section without departing from the teachings herein.

[0026] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. As used herein, the singular forms “a,”

“an,” and “the” are intended to include the plural forms, including “at least one,” unless the content clearly indicates otherwise. “Or” means “and/or.” As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items. It will be further understood that the terms “comprises” and/or “comprising,” or “includes” and/or “including” when used in this specification, specify the presence of stated features, regions, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, regions, integers, steps, operations, elements, components, and/or groups thereof. The term “or a combination thereof” means a combination including at least one of the foregoing elements.

[0027] Spatially relative terms, such as “beneath,” “below,” “lower,” “above,” “upper” and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. It will be understood that the spatially relative terms are intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. For example, if the device in the figures is turned over, elements described as “below” or “beneath” other elements or features would then be oriented “above” the other elements or features. Thus, the exemplary term “below” can encompass both an orientation of above and below. The device may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly.

[0028] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the present disclosure, and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[0029] Exemplary embodiments are described herein with reference to cross section illustrations that are schematic illustrations of idealized embodiments. As such, variations from the shapes of the illustrations as a result, for example, of manufacturing techniques, are to be expected. Thus, embodiments described herein should not be construed as limited to the particular shapes of regions as illustrated herein but are to include deviations in shapes that result, for example, from manufacturing. For example, a region illustrated or described as flat may have rough and/or nonlinear features. Moreover, sharp angles that are illustrated may be rounded. Thus, the regions illustrated in the figures are schematic in nature and their

shapes are not intended to illustrate the precise shape of a region and are not intended to limit the scope of the present claims.

[0030] As shown in FIG. 1, disclosed is a particle comprising a crystallite 10 comprising a first composition, and grain boundary 20 comprising a second composition, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallite. The particle comprises a plurality of crystallites, and is referred to as a secondary particle. Optionally, a layer 30 may be disposed on an outer surface of the secondary particle to provide a coated secondary particle.

[0031] The first composition of crystallite 10 has a layered α -NaFeO₂-type structure. In compositions having the layered α -NaFeO₂-type structure, hexagonal metal oxide layers are separated by planes of the alkali metal. The metal oxide layers form metal centered oxygen octahedra which are separated by alkali metal ions, and the metal oxide layers are laterally offset to provide a three-layer structure. In this structure, the alkali metal atoms occupy the so called “3a” sites in the structure ($x=0$, $y=0$, and $z=0$), the metal atoms occupy the “3b” sites ($x=0$, $y=0$, and $z=0.5$), and the oxygen atoms occupy the “6c” sites ($x=0$, $y=0$, and $z=0.25$). The coordinates of the atoms and the cell parameters can vary according to the composition. Compositions having this structure type may have cell parameters in which a is about 2.75 to about 2.95 angstroms (Å), and c is about 13.9 to about 14.6 Å.

[0032] In an embodiment, the first composition comprises lithium in an amount of about 0.1 to about 1.3 moles, specifically about 0.2 to about 1.2 moles, more specifically about 0.3 to about 1.1 moles, per mole of the first composition; nickel in an amount of about 0.1 to about 0.79 mole, specifically about 0.2 to about 0.7 mole, more specifically about 0.3 to about 0.6 mole, per mole of the first composition; cobalt in an amount of 0 to about 0.5 mole, specifically about 0.01 to about 0.5 mole, more specifically about 0.05 to about 0.4 mole, or about 0.1 to about 0.3 mole, per mole of the first composition; and oxygen in an amount of about 1.7 to about 2.3 moles, specifically about 1.8 to about 2.2 moles, more specifically about 1.9 to about 2.1 moles, per mole of the first composition. For example, the first composition can comprise lithium in an amount of about 0.1 to about 1.3 mole, nickel in an amount of about 0.5 to about 0.75 mole, cobalt in an amount of about 0.05 to about 0.1 mole, and oxygen in an amount of about 1.9 to about 2.1 moles, each per mole of the first composition. An embodiment in which cobalt is contained in an amount of about 0.01 to about 0.1 mole, specifically 0.05 mole, per mole of the first composition, is specifically mentioned.

[0033] In another embodiment, the first composition comprises lithium in an amount of about 0.1 to about 1.3 moles, specifically about 0.2 to about 1.2 moles, more specifically about 0.3 to about 1.1 moles, per mole of the first composition; nickel in an amount of about 0.91 to about 0.99 mole, specifically about 0.92 to about 0.98 mole, more specifically about 0.93 to about 0.97 mole, per mole of the first composition; cobalt in an amount of 0 to about 0.5 mole, specifically about 0.01 to about 0.5 mole, more specifically about 0.05 to about 0.4 mole, or about 0.1 to about 0.3 mole, per mole of the first composition; and oxygen in an amount of about 1.7 to about 2.3 moles, specifically about 1.8 to about 2.2 moles, more specifically about 1.9 to about 2.1 moles, per mole of the first composition. For example, the first composition can comprise lithium in an amount of about 0.1 to about 1.3 mole, nickel in an amount of about 0.91 to about 0.95 mole, cobalt in an amount of about 0.05 to about 0.1 mole, and oxygen in an amount of about 1.9 to about 2.1 moles, each per mole of the first composition. An embodiment in which cobalt is contained in an amount of about 0.01 to about 0.1 mole, specifically 0.08 mole, per mole of the first composition, is specifically mentioned.

[0034] In yet another embodiment, the secondary particle may comprise a first crystallite comprising lithium in an amount of about 0.1 to about 1.3 moles, nickel in an amount of about 0.1 to about 0.79 mole, cobalt in an amount of about 0.01 to about 0.5 mole, and oxygen in an amount of about 1.7 to about 2.3 moles, each per mole of the first composition of the first crystallite; and a second crystallite wherein the first composition comprises lithium in an amount of about 0.1 to about 1.3 moles, nickel in an amount of about 0.91 to about 0.99 mole, cobalt in an amount of about 0.01 to about 0.5 mole, and oxygen in an amount of about 1.7 to about 2.3 moles, each per mole of the first composition of the second crystallite.

[0035] The first composition may further comprise an additional metal, and the additional metal of the first composition may be present in an amount of about 0.01 to about 0.9 mole, specifically about 0.05 to about 0.8 mole, more specifically about 0.1 to about 0.7 mole, per mole of the first composition. In an embodiment, the additional metal may be present in an amount of about 0.01 to about 0.2 mole, specifically about 0.02 to about 0.18 mole, more specifically about 0.04 to about 0.16 mole, per mole of the first composition.

[0036] The additional metal may comprise Mg, Sr, Ca, Cu, Zn, Mn, Al, V, Ba, Zr, Ti, Cr, Fe, Mo, B, or a combination thereof. In an embodiment, the additional metal comprises Mg, Al, V, Ti, B, Zr, or Mn, or a combination thereof. In another embodiment, the additional

metal consists of Mg, Al, V, Ti, B, Zr, or Mn. An embodiment in which the additional metal is Mn or Mg is specifically mentioned.

[0037] Each crystallite may have any suitable shape, which can be the same or different within each secondary particle. Further, the shape of each crystallite can be the same or different in different secondary particles. Because of its crystalline nature, the crystallite may be faceted, the crystallite may have a plurality of flat surfaces, and a shape of the crystallite may approximate a geometric shape. The crystallite may have a rectilinear shape, and when viewed in cross-section, a portion of or an entirety of the crystallite may be rectilinear. The crystallite may be square, hexagonal, rectangular, triangular, or a combination thereof. A length, a width, and a thickness of the crystallite may be selected independently, and each of the length, width, and thickness of the crystallite may be about 5 to about 1000 nanometers (nm), specifically about 10 to about 900 nm, more specifically about 20 to about 800 nm.

[0038] The grain boundary is between adjacent crystallites, is on a surface of the crystallite, and comprises the second composition. The second composition has the layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof. As noted above, a concentration of cobalt in the grain boundaries is greater than a concentration of cobalt in the crystallites. An embodiment in which the grain boundaries have the layered α -NaFeO₂-type structure is specifically mentioned.

[0039] The shape of the grain boundary is defined by the shape of the crystallite adjacent the grain boundary. The shape of the grain boundary may approximate a geometric shape. The grain boundary may have a rectilinear shape, and when viewed in cross-section the grain boundary may be rectilinear. The grain boundary may be square, hexagonal, rectangular, triangular, or a combination thereof.

[0040] A direction of a surface of the grain boundary corresponds to a direction of a surface of the adjacent crystallite. Also, as shown in Fig. 1, the surface of the grain boundary and the surface of the crystallite may have any of a variety of orientations relative to an outer surface of the secondary particle. Thus the direction of the surface of the crystallite and the direction of the surface of the grain boundary may be parallel and be different than a direction of a nearest outer surface of the secondary particle. In an embodiment, a direction of a tangent of the nearest outer surface of the particle is different than the direction of the surface of the grain boundary and the direction of the surface of the adjacent particle.

[0041] As is also shown in Fig. 1, the grain boundaries may intersect to form an angle therebetween. In an embodiment, disposed on adjacent faces of a crystallite 40 is a first grain

boundary 41 and second grain boundary 42. The first grain boundary 41 and the second grain boundary 42 intersect at an angle E. The angle E may be defined by the shape of the crystallite on which the first grain boundary 41 and the second grain boundary 42 are disposed. Generally, a shape of a crystallite is influenced by a crystal structure of the crystallite. While not wanting to be bound by theory, it is understood that because the crystal structure of the first composition governs the shape of the crystallite, the angle between the first and second grain boundaries is influenced by the crystal structure of the first composition. The first and second grain boundaries may intersect at any angle, specifically an angle of about 10 to about 170 degrees, specifically about 20 to about 160 degrees, more specifically about 30 to about 150 degrees, so long as the angle is consistent with the crystal structure of the first composition, which has the layered α -NaFeO₂-type structure.

[0042] The dimensions of the grain boundary are not particularly limited. A length and a width of the grain boundary may each independently be about 50 to about 1000 nm, specifically about 60 to about 900 nm, more specifically about 70 to about 800 nm. The length and width of the grain boundaries are perpendicular to each other and are parallel to the surface of the adjacent crystallite. A thickness of the grain boundary may be about 1 to about 200 nm, specifically about 5 to about 180 nm, more specifically about 10 to about 160 nm. The thickness of the grain boundary is perpendicular to the length and the width of the grain boundary and may be perpendicular to the surface of the adjacent crystallite.

[0043] An average grain boundary length and an average grain boundary width of the plurality of grain boundaries may each independently be about 50 to about 1000 nm, specifically about 60 to about 900 nm, more specifically about 70 to about 800 nm. Also, an average grain boundary thickness of the plurality of grain boundaries may be about 1 to about 200 nm, specifically about 5 to about 180 nm, more specifically about 10 to about 160 nm.

[0044] In an embodiment, the second composition of the grain boundaries comprises lithium in an amount of about 0.1 to about 1.3 moles, specifically about 0.2 to about 1.2 moles, more specifically about 0.3 to about 1.1 moles, per mole of the second composition; nickel in an amount of about 0.1 to about 0.95 mole, specifically about 0.2 to about 0.90 mole, more specifically about 0.3 to about 0.85 mole, per mole of the second composition; cobalt in an amount of about 0.02 to about 0.99 mole, specifically about 0.04 to about 0.90 mole, more specifically about 0.06 to about 0.80 mole, per mole of the second composition; and oxygen in an amount of about 1.7 to about 2.3 moles, specifically about 1.8 to about 2.2 moles, more specifically about 1.9 to about 2.1 moles per mole of the second composition. An embodiment in which the second composition comprises nickel in an amount of about 0.1

to about 0.79 mole, per mole of the second composition, and cobalt in an amount of about 0.02 to about 0.5 mole, per mole of the second composition, is specifically mentioned.

[0045] The second composition may further comprise an additional metal, and the additional metal of the second composition may be present in an amount of about 0.01 to about 0.9 mole, specifically about 0.05 to about 0.8 mole, more specifically about 0.1 to about 0.7 mole, per mole of the second composition. In an embodiment, the additional metal of the second composition may be present in an amount of about 0.01 to about 0.2 mole, specifically about 0.02 to about 0.18 mole, more specifically about 0.04 to about 0.16 mole, per mole of the second composition.

[0046] The additional metal of the second composition may comprise Mg, Sr, Ca, Cu, Zn, Mn, Al, V, Ba, Zr, Ti, Cr, Fe, Mo, B, or a combination thereof. In an embodiment, the additional metal of the second composition comprises Mg, Al, V, Ti, B, Zr, or Mn, or a combination thereof. In another embodiment, the additional metal of the second composition consists of Mg, Al, V, Ti, B, Zr, or Mn. An embodiment in which the additional metal of the second composition is Mn or Mg is specifically mentioned. In an embodiment, the additional metal of the first composition and the additional metal of the second composition are each Mg. An embodiment in which the first composition further comprises Mn, and the Mn is present in the first composition in an amount of about 0.01 to about 0.6 mole, specifically about 0.02 to about 0.5 mole, per mole of the first composition, and the second composition comprises Mn, and the Mn is present in the second composition in an amount of about 0.01 to about 0.6 mole, specifically about 0.02 to about 0.5 mole, per mole of the second composition, is also specifically mentioned.

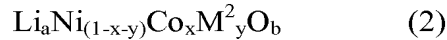
[0047] In an embodiment, the first and second compositions may each independently comprise a composition of Formula 1:



wherein Q^1 is Mg, Sr, Ca, Cu, Zn, or a combination thereof, Q^2 is Mn, Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga, B, or a combination thereof, M^1 is Ni and Co, $0.1 \leq a \leq 1.2$, $0 < y \leq 0.2$, and $0 \leq z \leq 0.6$, with the proviso that the concentration of cobalt in the second composition is greater than the concentration of cobalt in the first composition. An embodiment in which Q^1 consists of Mg, Sr, Ca, Cu, or Zn, and an embodiment wherein Q^1 is Mg, are each specifically mentioned. Also mentioned is an embodiment in which Q^2 comprises Mn, Al, Mg, Ca, B, or a combination thereof. An embodiment in which Q^2 consists of Mg, and another embodiment in which Q^2 consists of Mn, are each specifically

mentioned. In Formula 1, a and y may be independently selected so long as Formula 1 is satisfied, and, a may satisfy $0.2 \leq a \leq 1.1$, specifically $0.3 \leq a \leq 1$, and y of Formula 1 may satisfy $0.01 < y \leq 0.15$, specifically $0.05 < y \leq 0.1$.

[0048] In an embodiment, the first and second compositions may each independently comprise a composition of Formula 2:



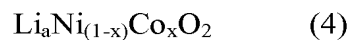
wherein M^2 is Al, V, Ti, B, Zr, Mn, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.2$, and $1.7 \leq b \leq 2.3$, provided that x in the second composition is greater than x in the first composition. In an embodiment M^2 is Al, V, Ti, B, Zr, or Mn. An embodiment in which M^2 is Al or B is specifically mentioned. In Formula 2, a, x, and y may be independently selected so long as Formula 2 is satisfied, and a of Formula 2 may satisfy $0.2 \leq a \leq 1.1$, specifically $0.3 \leq a \leq 1$, x of Formula 2 may satisfy $0.02 \leq x \leq 0.4$, specifically $0.04 \leq x \leq 0.3$, and y of Formula 2 may satisfy $0.01 < y \leq 0.15$, specifically $0.05 < y \leq 0.1$.

[0049] In an embodiment, the first and second compositions each independently comprise a composition of Formula 3:



wherein M^3 is Al, V, Ti, B, Zr, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.1$, $0.1 \leq z \leq 0.6$, and $1.7 \leq b \leq 2.3$. In an embodiment, M^3 is Al, V, Ti, B, or Zr. An embodiment in which M^3 is Al or B is specifically mentioned. In Formula 3, a, x, y, z, and b may be independently selected so long as Formula 3 is satisfied, and a of Formula 3 may satisfy $0.2 \leq a \leq 1.1$, specifically $0.3 \leq a \leq 1$, x of Formula 3 may satisfy $0.02 \leq x \leq 0.4$, specifically $0.04 \leq x \leq 0.3$, y of Formula 3 may satisfy $0.01 < y \leq 0.09$, specifically $0.05 < y \leq 0.08$, z of Formula 3 may satisfy $0.15 \leq z \leq 0.5$, specifically $0.2 \leq z \leq 0.4$, and b of Formula 3 may satisfy $1.8 \leq b \leq 2.2$, specifically $1.9 \leq b \leq 2.1$.

[0050] In an embodiment, the first and second compositions may each independently comprise a composition of Formula 4:



wherein $0.1 \leq a \leq 1.3$ and $0 < x < 0.2$. In an embodiment, a of Formula 4 may satisfy $0.2 \leq a \leq 1.1$, specifically $0.3 \leq a \leq 1$, and x of Formula 4 may satisfy $0.02 < x < 0.18$, specifically $0.04 < x < 0.16$. In another embodiment, the first composition, the second composition, or a combination thereof, comprises a composition of Formula 4 wherein $0.1 \leq a \leq 1.3$ and $0.2 < x < 0.5$. In an embodiment, x of Formula 4 may satisfy $0.25 < x < 0.45$, specifically $0.3 < x < 0.4$.

[0051] In an embodiment, the first composition comprises a composition of Formula 4 wherein $0 < x < 0.2$ and the second composition comprises a composition of Formula 4 wherein $0.2 < x < 0.5$.

[0052] As is further discussed above, in an embodiment a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallite. A concentration of cobalt in the crystallite may be 0 to about 17 atomic percent, specifically about 0.25 to about 17 atomic percent, more specifically about 1 to about 15 atomic percent, or about 2 to about 13 atomic percent, based on a total atomic composition of the crystallite. Also, a concentration of cobalt in the grain boundary may be about 0.5 to about 32 atomic percent, specifically about 1 to about 30 atomic percent, more specifically about 2 to about 28 atomic percent, based on a total atomic composition of the grain boundary. The concentration of cobalt in the grain boundary may be about 0.01 to about 30 atomic percent, specifically about 0.1 to about 20 atomic percent, more specifically about 1 to about 15 atomic percent greater than a concentration of cobalt in the crystallite, based on an average composition of the secondary particle. The atomic concentration of cobalt in the grain boundary and in the crystallite may be determined by energy dispersive X-ray (EDX) analysis of a center of a grain boundary and a center of an adjacent crystallite for a thinly sliced (e.g., 100-150 nm thick) section of the secondary particle prepared by a sectioning technique such as focused ion beam milling, for example.

[0053] The secondary particle may be prepared by contacting a lithium compound, a cobalt compound, and a nickel compound to form a mixture; heat treating the mixture at about 30 to about 200°C to form a dried mixture; heat treating the dried mixture at about 200 to about 500°C for about 0.1 to about 5 hours; then heat treating at 600 to about 800°C for about 0.1 to about 5 hours to manufacture the particle.

[0054] The lithium compound may comprise a lithium salt, such as lithium nitrate, lithium carbonate, lithium hydroxide, or a combination thereof. The cobalt compound may be a cobalt nitrate such as $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a cobalt chloride such as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, or cobalt isopropoxide, or a combination thereof. Also, the nickel compound may be a lithium nickel oxide comprising lithium in an amount of about 0.1 to about 1.3 moles, nickel in an amount of about 0.1 to about 0.79 mole, cobalt in an amount of about 0.01 to about 0.5 mole, and oxygen in an amount of about 1.7 to about 2.3 moles, each per mole of the lithium nickel oxide. In another embodiment, the lithium nickel oxide comprises nickel in an amount of about 0.91 to about 0.99 mole, per mole of the lithium nickel oxide. In an embodiment, the lithium nickel oxide comprises a composition of Formulas 1 to 4, or a combination thereof.

The stoichiometric ratio of the lithium compound and the cobalt compound may be 0.0 to about 1.2, specifically about 0.1 to about 1, more specifically about 0.2 to about 0.8.

[0055] To form the mixture, the lithium compound, the cobalt compound, and the nickel compound may be contacted in a liquid, and the liquid evaporated to form a mixture. The liquid may comprise water, an alcohol such as ethanol, propanol, isopropanol, butanol, or isobutanol, an acetate such as methyl acetate, ethyl acetate, or butyl acetate, acetonitrile, a ketone such as acetone, a glycol such as ethylene glycol, hexylene glycol, diethylene glycol, or ethylene glycol monoethyl ether, xylene, or a halogenated hydrocarbon such as methylene dichloride, chloroform, carbon tetrachloride, or ethylene dichloride, or a combination thereof. Water is specifically mentioned. The mixture may then be heat treated at about 30 to about 200°C, specifically about 40 to about 180°C, more specifically about 50 to about 160°C to form a dried mixture. The dried mixture may be heated at about 5 to about 20°C per minute to about 200 to about 500°C, specifically about 250 to about 450°C, and heat treated at about 200 to about 500°C, specifically about 250 to about 450°C, for about 0.1 to about 5 hours, specifically about 1 to about 4 hours. The material may then be heated at about 5 to about 100°C per minute to about 600 to about 900°C, specifically about 650 to about 850°C for about 0.1 to about 10 hours, specifically about 1 to about 9 hours, to manufacture the secondary particle.

[0056] Optionally a layer 30, such as a passivation layer or a protective layer, may be disposed on an outer surface of the secondary particle to provide a coated secondary particle. The coating may fully or partially cover the secondary particle. The layer may be amorphous or crystalline. The layer may comprise an oxide, a phosphate, a pyrophosphate, a fluorophosphate, a carbonate, a fluoride, an oxyfluoride, or a combination thereof, of a metal such as Zr, Al, Ti, Al, B, or Si, or a combination thereof. An embodiment in which the layer comprises a borate, an aluminate, a silicate, a fluoroaluminate, or a combination thereof is specifically mentioned. In an embodiment the layer comprises a carbonate. In an embodiment, the layer comprises ZrO_2 , Al_2O_3 , TiO_2 , AlPO_4 , AlF_3 , B_2O_3 , SiO_2 , Li_2O , Li_2CO_3 , or a combination thereof. A layer comprising AlPO_4 or Li_2CO_3 is specifically mentioned. The layer may be disposed by any process or technique that does not adversely affect the desirable properties of the secondary particle. Representative methods include spray coating and immersion coating, for example.

[0057] Also disclosed is cathode for a lithium-ion battery comprising the secondary particle. The cathode comprises the secondary particle disclosed above as an active material, and may further comprise a conductive agent and a binder. The conductive agent may

comprise any conductive agent that provides suitable properties and may be amorphous, crystalline, or a combination thereof. The conductive agent may comprise a carbon black, such as acetylene black or lamp black, a mesocarbon, graphite, carbon fiber, carbon nanotubes such as single wall carbon nanotubes or multi-wall carbon nanotubes, or a combination thereof. The binder may comprise any binder that provides suitable properties and may comprise polyvinylidene fluoride, a copolymer of polyvinylidene fluoride and hexafluoropropylene, poly(vinyl acetate), poly(vinyl butyral-co-vinyl alcohol-co vinyl acetate), poly(methylmethacrylate-co-ethyl acrylate), polyacrylonitrile, polyvinyl chloride-co-vinyl acetate, polyvinyl alcohol, poly(l-vinylpyrrolidone-co-vinyl acetate), cellulose acetate, polyvinylpyrrolidone, polyacrylate, polymethacrylate, polyolefin, polyurethane, polyvinyl ether, acrylonitrile-butadiene rubber, styrene-butadiene rubber, acrylonitrile-butadiene-styrene, tri-block polymer of sulfonated styrene/ethylene-butylene/styrene, polyethylene oxide, or a combination thereof, for example.

[0058] The cathode may be manufactured by combining the secondary particle, the conductive agent, and the binder in a suitable ratio, e.g., about 80 to about 98 weight percent of the secondary particle, about 2 to about 20 weight percent of the conductive agent, and about 2 to about 10 weight percent of the binder, based on a total weight of the secondary particle, the conductive agent, and the binder. The secondary particle, the conductive agent, and the binder may be suspended in a suitable solvent, such as N-methylpyrrolidinone, and disposed on a suitable substrate, such as aluminum foil, and dried in air.

[0059] Also disclosed is a battery comprising the cathode. The battery may be a lithium-ion battery, a lithium-polymer battery, or a lithium battery, for example. As shown in Fig. 2, the battery 100 may include a cathode 101; an anode 102; and a separator 103 interposed between the cathode 101 and the anode 102. The separator may be a microporous membrane, and may comprise a porous film comprising polypropylene, polyethylene, or a combination thereof, or may be a woven or non-woven material such as a glass-fiber mat. The anode 102 may comprise a coating on a current collector. The coating may comprise a suitable carbon, such as graphite, coke, a hard carbon, or a mesocarbon such as a mesocarbon microbead, for example. The current collector may be copper foil, for example.

[0060] The battery also comprises an electrolyte which contacts the positive electrode 101, the negative electrode 102, and the separator 103. The electrolyte may comprise an organic solvent and a lithium salt. The organic solvent may be a linear or cyclic carbonate. Representative organic solvents include ethylene carbonate, propylene carbonate, butylene

carbonate, trifluoropropylene carbonate, γ -butyrolactone, sulfolane, 1,2-dimethoxyethane, 1,2-diethoxyethane, tetrahydrofuran, 3-methyl-1,3-dioxolane, methyl acetate, ethyl acetate, methylpropionate, ethylpropionate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dipropyl carbonate, methylpropyl carbonate, or a combination thereof. In another embodiment the electrolyte is a polymer electrolyte.

[0061] Representative lithium salts include LiPF_6 , LiBF_4 , LiAsF_6 , LiClO_4 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, LiSbF_6 , $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiC}_4\text{F}_9\text{SO}_3$, and LiAlCl_4 . The lithium salt may be dissolved in the organic solvent. A combination comprising at least one of the foregoing can be used. The concentration of the lithium salt can be 0.1 to 2.0M in the electrolyte.

[0062] The battery may have any suitable configuration or shape, and may be cylindrical or prismatic.

[0063] While not wanting to be bound by theory, it is understood that the disclosed secondary particle is a dense polycrystalline agglomerate of submicron-sized primary crystallites. It has been shown that in polycrystalline materials having the layered α - NaFeO_2 -type structure, electrochemical cycling induces the layers of the transition metal atoms at the grain boundaries (e.g., edges of the crystallites) to reorganize into a NiO -type rock salt structure and/or to be reduced in oxidation state. These transformations are also associated with the appearance of cracks between adjacent crystallites. While not wanting to be bound by theory, it is understood that the resulting NiO -type phase and cracks in the grain boundaries between crystallites significantly degrade the electrochemical performance of these materials. It is also understood that whereas Ni atoms at the grain boundaries undergo reduction in oxidation state as part of these transformations, Co atoms in the grain boundaries do not, suggesting that it is primarily the Ni atoms that are mobile and drive the undesirable structural rearrangements in the grain boundaries.

[0064] The above observations indicate that Co substitution in lithium nickel oxides having the layered α - NaFeO_2 -type structure enhances electrochemical performance by stabilizing the grain boundaries of the secondary particle. Therefore Co-substituted lithium nickel oxides with Co preferentially disposed at the grain boundaries (and relatively less Co in the crystallites) can provide improved cycling stability with less overall cobalt content than a lithium nickel oxide with uniformly distributed Co, or Co disposed in a location other than in the grain boundaries. Materials with Co-enriched grain boundaries can thus provide improved stability, such as improved capacity, cycle life, coulombic efficiency, rate

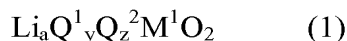
capability, and safety, while minimizing the detrimental impacts of Co substitution on capacity, rate capability, and cost by providing Co where it is most effective, e.g., in the grain boundaries, and avoiding use of Co where it is less effective, e.g., in the crystallites.

[0065] The grain boundary of the secondary particle disclosed herein is distinguished from a “shell” of a “core/shell” material or a “coating” of a coated particle in which a lithium nickel oxide secondary particle is coated with a Co-containing material, such as LiCoO_2 , to provide a LiCoO_2 coated $\text{LiNi}_{(1-x)}\text{Co}_x\text{O}_2$ core/shell or coated material, for example. In the core/shell material, the secondary particle is coated with the Co-containing material to provide cobalt on the outer surface of the secondary particle, ostensibly to reduce the interaction between the lithium nickel oxide secondary particle and an electrolyte in a battery.

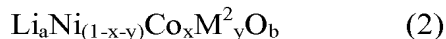
[0066] In an embodiment disclosed is a particle, comprising: a plurality of crystallites comprising a first composition having a layered $\alpha\text{-NaFeO}_2$ -type structure and comprising lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel in an amount of about 0.1 to about 0.79 mole, per mole of the first composition, cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having the layered $\alpha\text{-NaFeO}_2$ -type structure, a cubic structure, or a combination thereof, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

[0067] In various embodiments, (i) the grain boundary is substantially rectilinear in cross-section; and/or (ii) a direction of a surface of the grain boundary is different than a direction of a tangent of a nearest outer surface of the particle; and/or (iii) the particle comprises a first grain boundary and a second grain boundary, wherein the first grain boundary and the second grain boundary are each directly on a crystallite of the plurality of crystallites, and wherein the first grain boundary and second grain boundary intersect at an angle determined by a crystal structure of the first composition; and/or (iv) the grain boundary has a length of about 50 to about 1000 nanometers, wherein the length is parallel to a surface of an adjacent crystallite; and/or (v) the grain boundary has a thickness of about 1 to about 200 nanometers, wherein the thickness is perpendicular to the crystallite surface; and/or (vi) the particle has an average grain boundary length of about 50 to about 1000 nanometers; and/or (vii) the particle has an average grain boundary thickness of about 5 to about 200 nanometers; and/or (viii) the second composition comprises lithium in an amount of about 0.1 to about 1.3 moles, per mole of the second composition, nickel in an amount of about 0.1 to

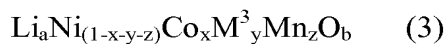
about 0.95 mole, per mole of the second composition, cobalt in an amount of about 0.02 to about 0.99 mole, per mole of the second composition, and oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the second composition; and/or (ix) the second composition comprises nickel in an amount of about 0.1 to about 0.79 mole, per mole of the second composition, and cobalt in an amount of about 0.02 to about 0.5 mole, per mole of the second composition; and/or (x) the first composition may further comprise an additional metal, wherein the additional metal is present in an amount of about 0.01 to about 0.9 mole, per mole of the first composition; and the second composition further comprises a second metal, wherein the second metal is present in an amount of about 0.01 to about 0.9 mole, per mole of the second composition; and/or (xi) the additional metal is present in an amount of about 0.01 to about 0.2 mole, per mole of the first composition, and the second metal is present in an amount of about 0.01 to about 0.2 mole, per mole of the second composition; and/or (xii) the additional metal and the second metal each independently comprise Mg, Sr, Ca, Cu, Zn, Mn, Al, V, Ba, Zr, Ti, Cr, Fe, Mo, B, or a combination thereof; and/or (xiii) the additional metal and the second metal are a same metal, and each consist of Mg, Al, V, Ti, B, Zr, or Mn; and/or (xiv) the additional metal and the second metal are each Mg; and/or (xv) the first composition comprises Mn, and the Mn is present in the first composition in an amount of about 0.01 to about 0.6 mole, per mole of the first composition, and the second composition comprises Mn, and the Mn is present in the second composition in an amount of about 0.01 to about 0.6 mole, per mole of the second composition; and/or (xvi) the first and second compositions each independently comprise a composition of Formula 1:



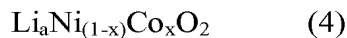
wherein Q^1 is Mg, Sr, Ca, Cu, Zn, or a combination thereof, Q^2 is Mn, Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga, or B, or a combination thereof, M^1 is Ni and Co, $0.1 \leq a \leq 1.2$, $0 < y \leq 0.2$, and $0 \leq z \leq 0.6$; and/or (xvii) the first and second compositions each independently comprise a composition of Formula 2



wherein M^2 is Al, V, Ti, B, Zr, Mn, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.2$, and $1.7 \leq b \leq 2.3$; and/or (xviii) the first and second compositions each independently comprise a composition of Formula 3:



wherein M^3 is Al, V, Ti, B, Zr, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.1$, $0.1 \leq z \leq 0.6$, and $1.7 \leq b \leq 2.3$; and/or (xix) the first and second compositions each independently comprise a composition of Formula 4:



wherein $0.1 \leq a \leq 1.3$, and $0 < x < 0.2$ or $0.2 < x < 0.5$; and/or (xx) the first composition comprises a composition of Formula 4 wherein $0 < x < 0.2$, and the second composition comprises a composition of Formula 4 wherein $0.2 < x < 0.5$; and/or (xxi) a concentration of cobalt in the crystallites is about 0.25 to about 17 atomic percent, and a concentration of cobalt in the grain boundary is about 0.5 to about 32 atomic percent, each based on a total atomic composition of the particle; and/or (xxii) further comprising a layer on a surface of the particle, wherein the layer comprises an oxide, a phosphate, a pyrophosphate, a fluorophosphate, a carbonate, a fluoride, an oxyfluoride, or a combination thereof, of Zr, Al, Ti, Al, B, or Si, or a combination thereof; and/or (xxiii) the layer comprises ZrO_2 , Al_2O_3 , TiO_2 , $AlPO_4$, AlF_3 , B_2O_3 , SiO_2 , Li_2O , Li_2CO_3 , or a combination thereof; and/or (xxiv) the layer comprises a borate, an aluminate, a silicate, a fluoroaluminate, or a combination thereof.

[0068] Also disclosed is a particle, comprising: a plurality of crystallites comprising a first composition having a layered α - $NaFeO_2$ -type structure and comprising lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel in an amount of about 0.91 to about 0.99 mole, per mole of the first composition, cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having a layered α - $NaFeO_2$ -type structure, a cubic structure, or a combination thereof, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

[0069] Also disclosed is an electrode for a lithium-ion battery, the electrode comprising the particle, and a lithium-ion battery comprising the particle.

[0070] Also disclosed is a method of manufacturing a particle, the method comprising: combining a lithium compound, a cobalt compound, and a nickel compound to form a mixture; heat treating the mixture at about 30 to about 200°C to form a dried mixture; heat treating the dried mixture at about 200 to about 500°C for about 0.1 to about 5 hours; then heat treating at 600 to about 900°C for about 0.1 to about 10 hours to manufacture the particle, wherein the particle comprises a plurality of crystallites comprising a first composition having a layered α - $NaFeO_2$ -type structure and comprising Li, Ni, Co, and O,

wherein the Li is present in an amount of about 0.1 to about 1.3 moles, per mole of the first composition, nickel is present in an amount of about 0.1 to about 0.79 mole or about 0.91 to about 0.99 mole, per mole of the first composition, cobalt is present in an amount of 0 to about 0.5 mole, per mole of the first composition, and oxygen is present in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof, wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

[0071] The disclosed embodiment is further illustrated in the following Examples.

EXAMPLES

Example 1. Preparation of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}_{2.05}$

[0072] A material having the composition $\text{Li}_{1.05}\text{Mg}_{0.025}\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}_{2.05}$ was prepared dry mixing 242.9 g Li(OH)₂ (anhydrous fine powder available from Sigma-Aldrich, Inc., St. Louis, Mo.), 14.8 g Mg(OH)₂ (fine powder available from Alfa Aesar, Ward Hill, Mass.), and 35.0 g LiNO₃ (crystals available from Alfa Aesar, Ward Hill, Mass.). To the mixture of Li(OH)₂, Mg(OH)₂, and LiNO₃ was added 940.3 g Ni_{0.92}Co_{0.08}(OH)₂ (available from OM Group, Inc.) in a 1 liter jar. The compounds were mixed by shaking the jar.

[0073] The mixed compounds were placed in an alumina crucible and sintered. Sintering was performed by heating at a rate of about 5 °C per minute to about 450 °C, and held at about 450 °C for about two hours. The temperature was then raised at about 2 °C per minute to about 700°C, and held for about six hours. The sample was then allowed to cool naturally to room temperature. The cooled sample was ground for about five minutes to break up any agglomerates to provide $\text{Li}_{1.05}\text{Mg}_{0.025}\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}_{2.05}$.

Example 2. $\text{Li}_{1.01}\text{Mg}_{0.024}\text{Ni}_{0.88}\text{Co}_{0.12}\text{O}_{2.03}$ with Co-enriched grain boundaries.

[0074] 0.3 grams (g) of LiNO₃ and 117.4 g of Co(NO₃)₂·6H₂O were dissolved in 1000 g of H₂O heated to 60 °C, and 1000 g of the $\text{Li}_{1.05}\text{Mg}_{0.025}\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}_{2.05}$ of Example 1 was added thereto and the resulting slurry was stirred for 30 minutes. The slurry was then spray-dried to yield a powder. The resulting powder was placed in an alumina crucible and heated at a rate of about 5 °C per minute to about 450 °C, and held at about 450 °C for about one hour. The temperature was then raised at about 2 °C per minute to about 700°C, and held for about two hours. The sample was then allowed to cool naturally to room temperature to

provide a material having the overall composition $\text{Li}_{1.01}\text{Mg}_{0.024}\text{Ni}_{0.88}\text{Co}_{0.12}\text{O}_{2.03}$. X-ray diffraction (XRD) confirmed the material as having the layered $\alpha\text{-NaFeO}_2$ -type structure with lattice parameters $a=2.872 \text{ \AA}$ and $c=14.192 \text{ \AA}$.

[0075] A thin (approximately 100 to 150 nanometer, nm) section of a secondary particle was prepared by focused ion beam milling for scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) analysis.

[0076] FIG. 3 is a low-resolution STEM image of secondary particle having a diameter of about $7 \mu\text{m}$. The secondary particle is comprised of densely agglomerated primary crystallites.

[0077] FIG. 4 is a higher resolution STEM image of the particle shown in Fig. 3, and FIG. 5 an enlarged view of a portion of FIG. 4. Indicated in FIGS. 4 and 5 is the location of the EDX spot analyses, the results of which are shown in FIGS. 6 and 7. A total of 25 spots (each indicated with an "s" and arranged in a line), were analyzed. The line began at position 1 the center of a first crystallite 201, traversed a grain boundary 203, and ended at position 25 at the center of an adjacent second crystallite 202.

[0078] FIG. 6 is a graph of concentration (arbitrary units) versus position showing the concentration of the elements O, Mg, Co, and Ni for each spot of the EDX analysis. The results of FIG. 6 show that a concentration of cobalt in the grain boundary 203 is greater than a concentration of cobalt in either of the first and second crystallites 201 and 202.

[0079] FIG. 7 is a graph of the concentration of cobalt (as a percentage of non-Lithium atoms) versus position for each spot of the EDX analysis. FIG. 7 also shows that the concentration of cobalt in the grain boundary 203 is greater than the concentration of cobalt in either of the first and second crystallites 201 and 202.

Example 3. $\text{Li}_{1.05}\text{Mg}_{0.025}\text{Ni}_{0.88}\text{Co}_{0.12}\text{O}_{2.05}$ with uniform Co distribution

[0080] A material having the overall composition $\text{Li}_{1.05}\text{Mg}_{0.025}\text{Ni}_{0.88}\text{Co}_{0.12}\text{O}_{2.05}$ was prepared using the same method as provided in Example 1, except that 940.3 g of $\text{Ni}_{0.88}\text{Co}_{0.12}(\text{OH})_2$ was used in place of $\text{Ni}_{0.92}\text{Co}_{0.08}(\text{OH})_2$, thus yielding a material having substantially the same overall composition as that of example 2, but with Co uniformly distributed as opposed to having the Co enriched grain boundaries of example 2. XRD confirmed the material as having the layered $\alpha\text{-NaFeO}_2$ -type structure with lattice parameters $a=2.869 \text{ \AA}$ and $c=14.182 \text{ \AA}$.

Example 4. Electrochemical analyses of Examples 2 and 3

[0081] The materials of Examples 2 and 3 were each blended with PVdF (Kureha KF-1120) and carbon (Denka black) in N-methylpyrrolidinone to form a slurry, and each slurry coated on an aluminum foil current collector. Cathodes were punched from the coated aluminum foil and were assembled into half cells with lithium foil, a glass fiber separator (Whatman 934-AH) and an electrolyte of 1 M LiPF_6 in 1/1/1 (vol.) EC/DMC/EMC with 1 wt. % VC (Kishida Chemical) in a 2025 coin cell. The capacity of each cell was determined by calculation from the electrode weight, assuming a capacity of 200 mAh/g cathode material. The cells were then charged to 4.3 V at C/20, and discharged at rates from C/20 to 5C. With respect to charge or discharge rates, C refers to the C-rate, which is the rate to charge or discharge the cell in one hour. The results of the half-cell analysis are shown in Table 1.

Table 1: Half Cell results

Cathode Type	Discharge Capacity (mAh/g)			Ratio of 5C to C/5
	C/20	C/5	5C	
Example 2	214	201	168	84%
Example 3	207	196	144	73%

[0082] As shown in Table 1, the material of Example 2, in which a concentration of cobalt in grain boundaries was greater than in the crystallites, provided higher capacity at all discharge rates evaluated, and a higher 5C to C/5 ratio, than the material of Example 3, which had a uniform cobalt content.

[0083] Cathodes of the example 2 and 3 materials were also assembled in lithium-ion coin cells (size 2025) opposite graphitic carbon anodes (MCMB 25-28, Osaka Gas) with a microporous polyolefin separator (Celgard 2325) and electrolyte of 1 M LiPF_6 in 1/1/1 (vol.) EC/DMC/EMC with 1 wt. % VC (Kishida Chemical). These lithium-ion cells underwent extended 1C charge, 1C discharge cycling between 4.2 V and 2.75 V. FIG. 8 graphs the results of this 1C/1C cycling, showing that the material of example 2 having Co-enriched grain boundaries obtains higher capacity and higher cycling capacity retention than does the material of example 3 having the same overall Co content as the material of example 2, but with the Co uniformly distributed.

Example 5. Preparation of $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_{2.05}$.

[0084] A material having the composition $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_{2.05}$ was prepared using the same method as provided in Example 1, except that 940.3 g of $\text{Ni}(\text{OH})_2$ (#543 high density spherical powder available from OM Group, Inc., Cleveland, Ohio) was used in place of $\text{Ni}_{0.92}\text{Co}_{0.08}(\text{OH})_2$.

Example 6. $\text{Li}_{1.01}\text{Mg}_{0.023}\text{Ni}_{0.93}\text{Co}_{0.07}\text{O}_{2.03}$ with Co-enriched grain boundaries.

[0085] A material having the overall composition $\text{Li}_{1.01}\text{Mg}_{0.023}\text{Ni}_{0.93}\text{Co}_{0.07}\text{O}_{2.03}$ was prepared using the same method as provided in Example 2, except that 28.4 g of LiNO_3 , 234.8 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 1000 g of the $\text{Li}_{1.05}\text{Mg}_{0.025}\text{NiO}_{2.05}$ of Example 5 were used. XRD confirmed the material as having the layered $\alpha\text{-NaFeO}_2$ -type structure with lattice parameters $a=2.876 \text{ \AA}$ and $c=14.200 \text{ \AA}$. A particle of the material was sectioned by focused ion beam milling and was analyzed by STEM with EDX.

[0086] Shown in FIG. 9 is a STEM image of a particle of the $\text{Li}_{1.01}\text{Mg}_{0.023}\text{Ni}_{0.93}\text{Co}_{0.07}\text{O}_{2.03}$. The area A in FIG. 9 indicates the area analyzed by high resolution STEM with energy dispersive X-ray analysis, the results of which are shown in FIGS. 10-13.

[0087] FIG. 10 is a high-resolution STEM image of area A of the particle shown in FIG. 9. The image of FIG. 10 shows crystallites and grain boundaries between the crystallites.

[0088] FIG. 11 is an energy dispersive X-ray (EDX) spectrum of the area shown in FIG. 10, showing the presence of cobalt and nickel. The overall cobalt to nickel ratio, determined by integrating the area of the cobalt and nickel peaks in the broad-area EDX spectrum, respectively, is 0.079.

[0089] FIGS. 12 and 13 are, respectively, cobalt and nickel high-resolution EDX maps of the area shown in FIG. 10. FIG. 12 shows that nickel is uniformly distributed and is present in the crystallites and in the grain boundaries. FIG. 13 shows that the cobalt is concentrated at the grain boundaries. An average thickness of the grain boundaries in FIG. 13 is about 100 nm, and the thickness of the grain boundaries range from 50 nm to 150 nm.

[0090] While this disclosure describes exemplary embodiments, it will be understood by those skilled in the art that various changes can be made and equivalents can be substituted for elements thereof without departing from the scope of the disclosed embodiments. In addition, many modifications can be made to adapt a particular situation or material to the teachings of this disclosure without departing from the scope thereof.

Therefore, it is intended that this disclosure not be limited to the particular embodiments disclosed as the best mode contemplated for carrying out this disclosure. It should also be understood that the embodiments disclosed herein should be considered in a descriptive sense only and not for purposes of limitation. Descriptions of features or aspects of each embodiment should be considered as available for other similar features or aspects of other embodiments

WHAT IS CLAIMED IS:

1. A particle, comprising:
a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising
lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,
nickel in an amount of about 0.1 to about 0.79 mole, per mole of the first composition,
cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and
oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and
a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having the layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof,
wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.
2. The particle of claim 1, wherein the grain boundary is substantially rectilinear in cross-section.
3. The particle of any of claims 1 to 2, wherein a direction of a surface of the grain boundary is different than a direction of a tangent of a nearest outer surface of the particle.
4. The particle of any of claims 1 to 3, wherein the particle comprises a first grain boundary and a second grain boundary, wherein the first grain boundary and the second grain boundary are each directly on a same crystallite of the plurality of crystallites, and wherein the first grain boundary and second grain boundary intersect at an angle determined by a crystal structure of the first composition.
5. The particle of any of claims 1 to 4,
having an average grain boundary length of about 50 to about 1000 nanometers,
having an average grain boundary thickness of about 1 to about 200 nanometers,
wherein the grain boundary has a length of about 50 to about 1000 nanometers,
wherein the length is parallel to a surface of an adjacent crystallite, and
wherein the grain boundary has a thickness of about 1 to about 200 nanometers,
wherein the thickness is perpendicular to the crystallite surface.
6. The particle of any of claims 1 to 5, wherein
the second composition comprises

lithium in an amount of about 0.1 to about 1.3 moles, per mole of the second composition,

nickel in an amount of about 0.1 to about 0.95 mole, per mole of the second composition,

cobalt in an amount of about 0.02 to about 0.99 mole, per mole of the second composition, and

oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the second composition.

7. The particle of any of claims 1 to 6, wherein

the first composition may further comprise an additional metal, wherein the additional metal of the first composition is present in an amount of about 0.01 to about 0.9 mole, per mole of the first composition;

the second composition further comprises an additional metal, wherein the additional metal of the second composition is present in an amount of about 0.01 to about 0.9 mole, per mole of the second composition; and

the additional metal of the first and second compositions each independently comprise Mg, Sr, Ca, Cu, Zn, Mn, Al, V, Ba, Zr, Ti, Cr, Fe, Mo, B, or a combination thereof.

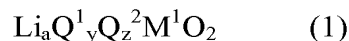
8. The particle of any of claims 1 to 7, wherein

the first composition comprises Mn, and the Mn is present in the first composition in an amount of about 0.01 to about 0.6 mole, per mole of the first composition, and

the second composition comprises Mn, and the Mn is present in the second composition in an amount of about 0.01 to about 0.6 mole, per mole of the second composition.

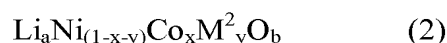
9. The particle of any of claims 1 to 8, wherein

the first and second compositions each independently comprise a composition of Formula 1:



wherein Q^1 is Mg, Sr, Ca, Cu, Zn, or a combination thereof, Q^2 is Mn, Al, Mg, Ca, Sr, Ba, Zn, Ti, Zr, Cr, Mo, Fe, V, Si, Ga, or B, or a combination thereof, M^1 is Ni and Co, $0.1 \leq a \leq 1.2$, $0 < y \leq 0.2$, and $0 \leq z \leq 0.6$; or

the first and second compositions each independently comprise a composition of Formula 2



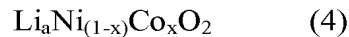
wherein M^2 is Al, V, Ti, B, Zr, Mn, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.2$, and $1.7 \leq b \leq 2.3$; or

the first and second compositions each independently comprise a composition of Formula 3:



wherein M^3 is Al, V, Ti, B, Zr, or a combination thereof, $0.1 \leq a \leq 1.3$, $0.01 \leq x \leq 0.5$, $0 < y \leq 0.1$, $0.1 \leq z \leq 0.6$, and $1.7 \leq b \leq 2.3$; or

the first and second compositions each independently comprise a composition of Formula 4:



wherein $0.1 \leq a \leq 1.3$ and $0 < x < 0.2$ or $0.2 < x < 0.5$.

10. The particle of any of claims 1 to 9,

wherein the first composition comprises a composition of Formula 4 wherein $0 < x < 0.2$, and the second composition comprises a composition of Formula 4 wherein $0.2 < x < 0.5$.

11. The particle of any of claims 1 to 10, wherein

a concentration of cobalt in the crystallites is about 0.25 to about 17 atomic percent, and

a concentration of cobalt in the grain boundary is about 0.5 to about 32 atomic percent, each based on a total atomic composition of the particle.

12. The particle of any of claims 1 to 11, further comprising a layer on a surface of the particle, wherein the layer comprises an oxide, a phosphate, a pyrophosphate, a fluorophosphate, a carbonate, a fluoride, an oxyfluoride, or a combination thereof, of Zr, Al, Ti, Al, B, or Si, or a combination thereof.

13. A particle, comprising:

a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising

lithium in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,

nickel in an amount of about 0.91 to about 0.99 mole, per mole of the first composition,

cobalt in an amount of 0 to about 0.5 mole, per mole of the first composition, and

oxygen in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and

a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof,

wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

14. A lithium-ion battery, the battery comprising an electrode comprising the particle of any of claims 1 to 13.

15. A method of manufacturing a particle, the method comprising:
combining a lithium compound, a cobalt compound, and a nickel compound to form a mixture;

heat treating the mixture at about 30 to about 200°C to form a dried mixture;

heat treating the dried mixture at about 200 to about 500°C for about 0.1 to about 5 hours; then

heat treating at 600 to about 900°C for about 0.1 to about 10 hours to manufacture the particle, wherein the particle comprises a plurality of crystallites comprising a first composition having a layered α -NaFeO₂-type structure and comprising Li, Ni, Co, and O, wherein

the Li is present in an amount of about 0.1 to about 1.3 moles, per mole of the first composition,

nickel is present in an amount of about 0.1 to about 0.79 mole or about 0.91 to about 0.99 mole, per mole of the first composition,

cobalt is present in an amount of 0 to about 0.5 mole, per mole of the first composition, and

oxygen is present in an amount of about 1.7 to about 2.3 moles, per mole of the first composition; and

a grain boundary between adjacent crystallites of the plurality of crystallites and comprising a second composition having a layered α -NaFeO₂-type structure, a cubic structure, or a combination thereof,

wherein a concentration of cobalt in the grain boundary is greater than a concentration of cobalt in the crystallites.

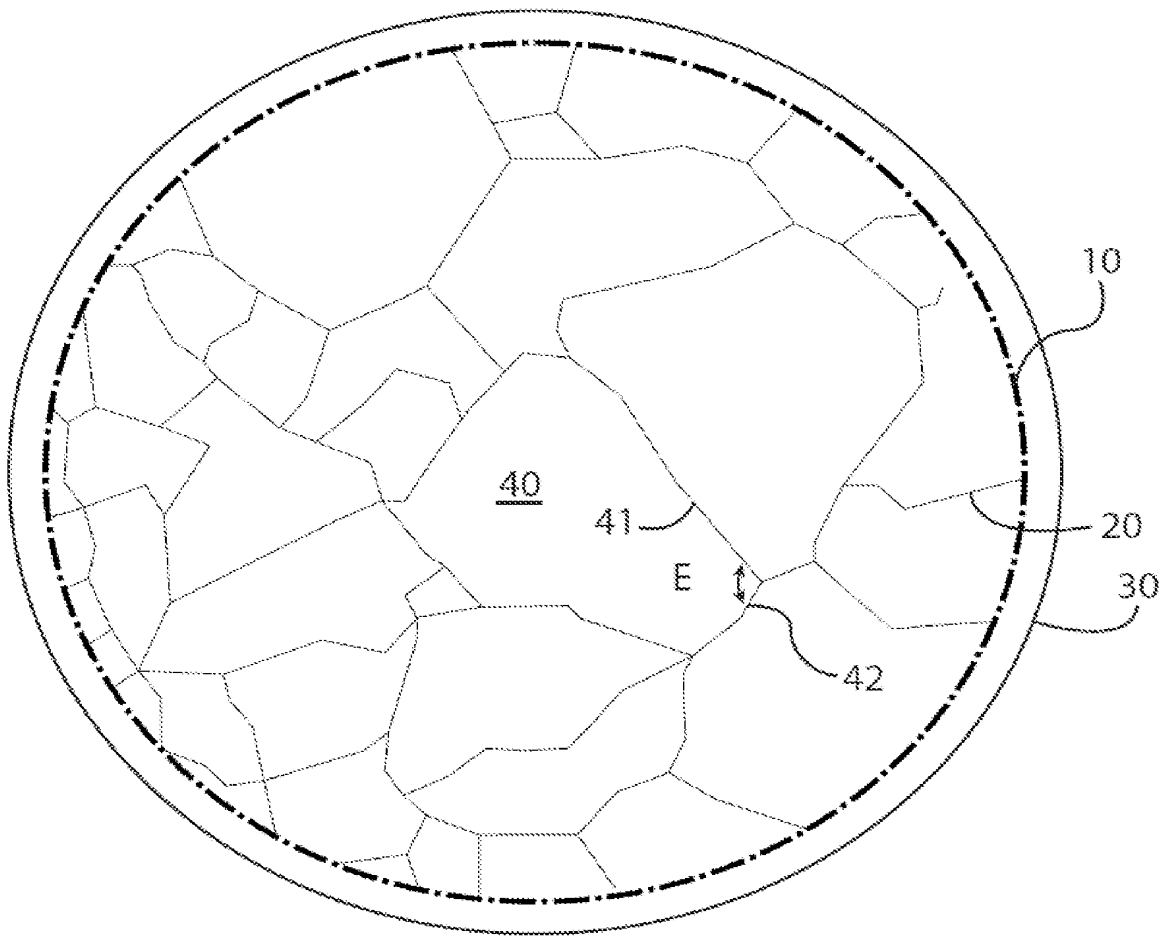


FIG. 1

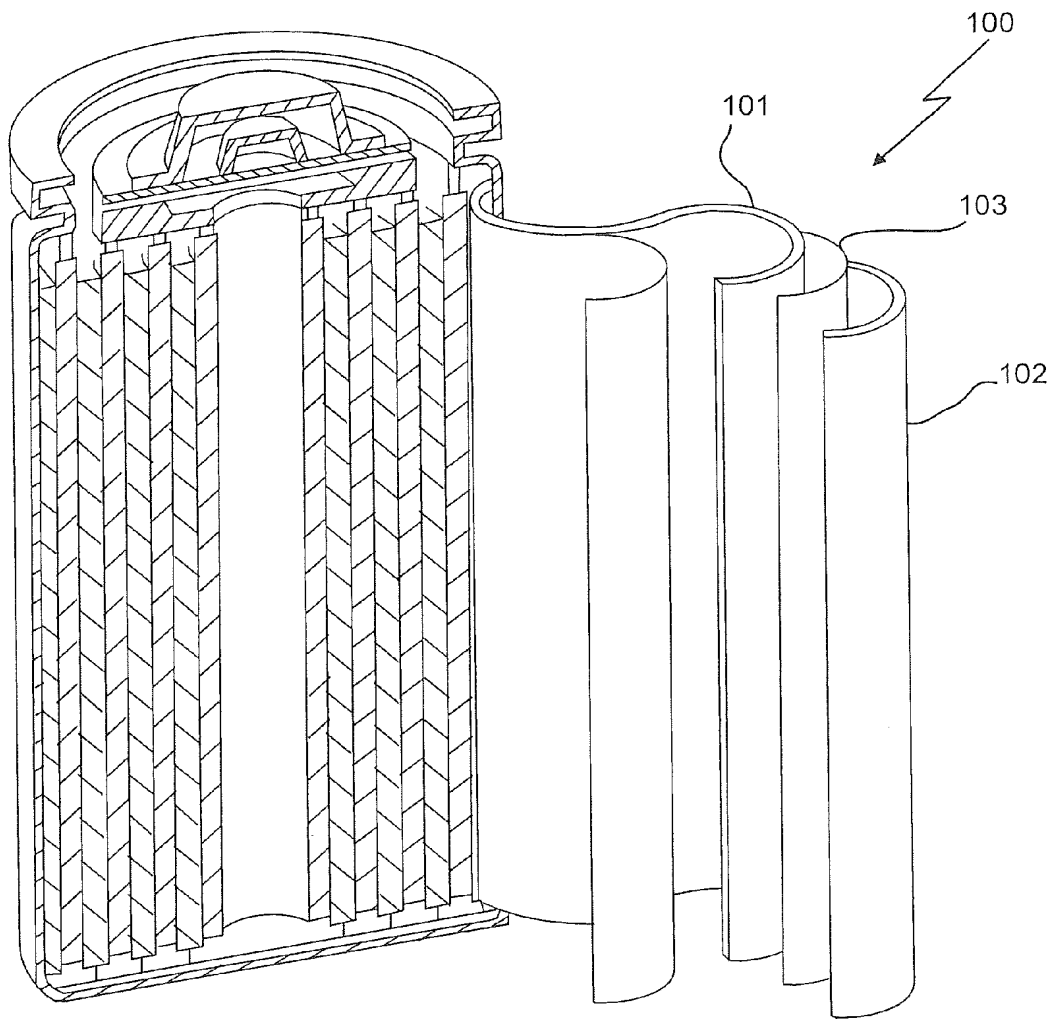


FIG. 2

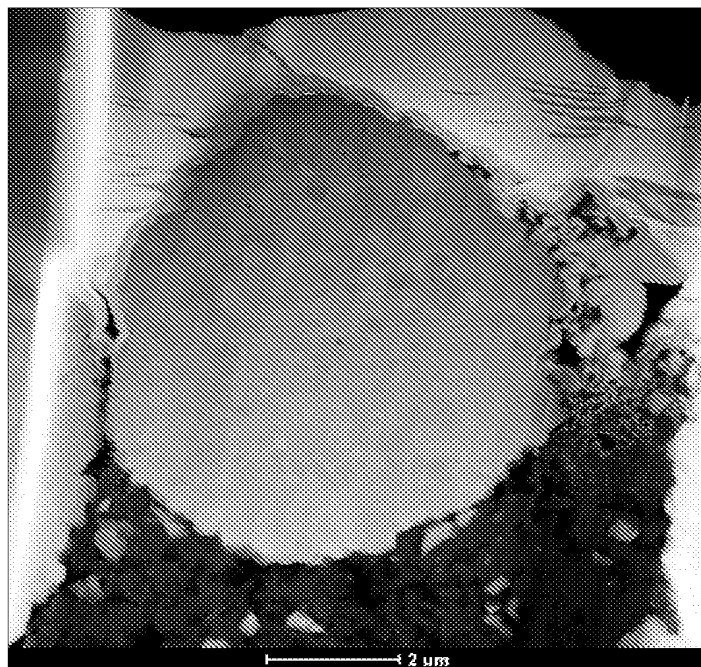


FIG. 3

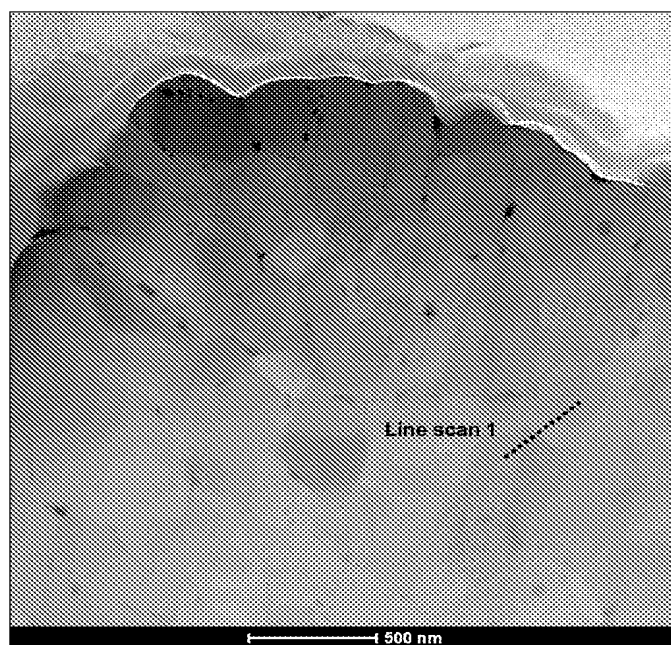


FIG. 4

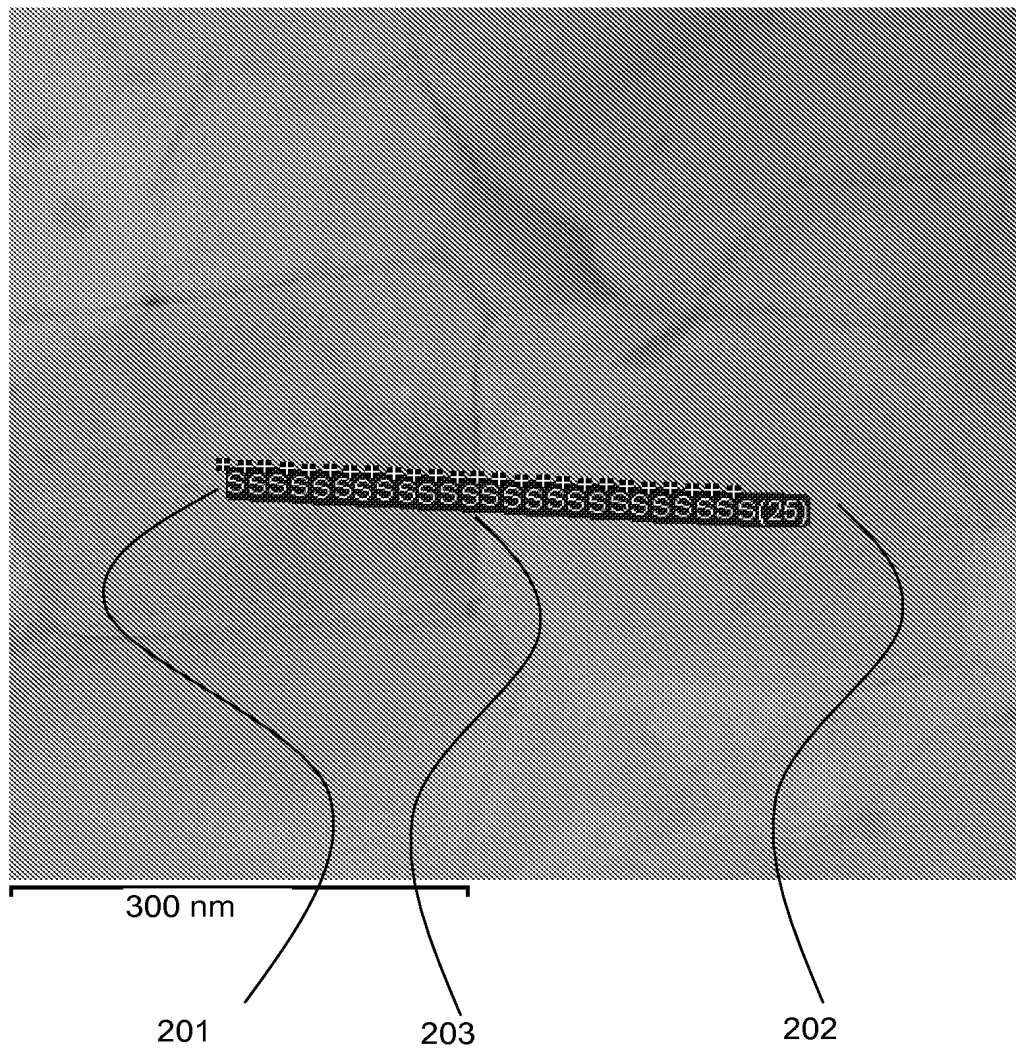


FIG. 5

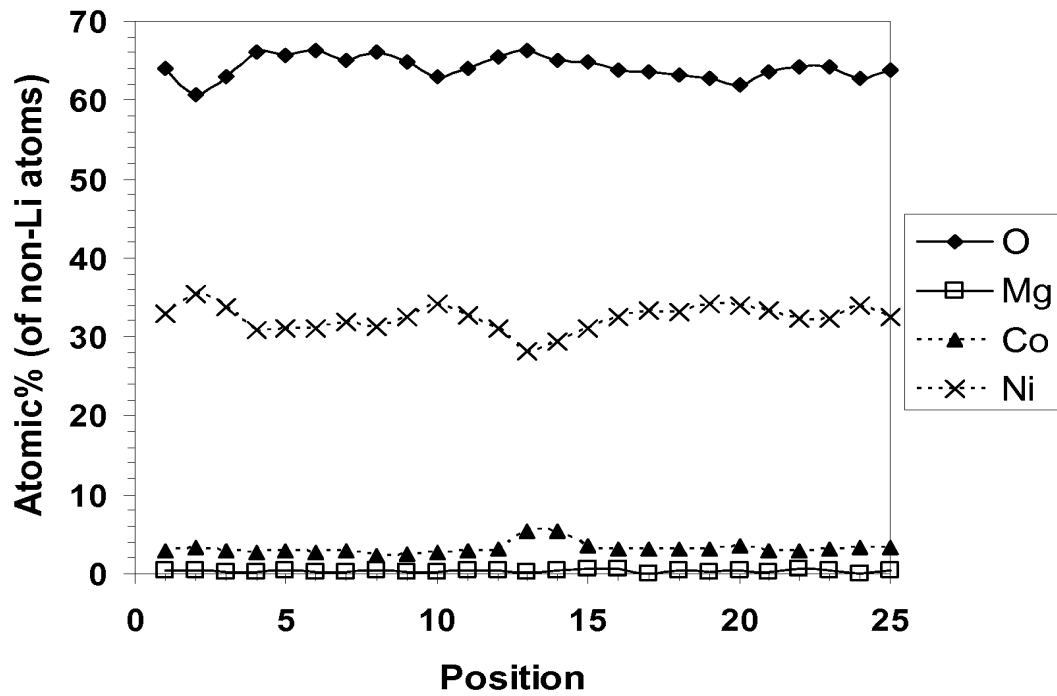


FIG. 6

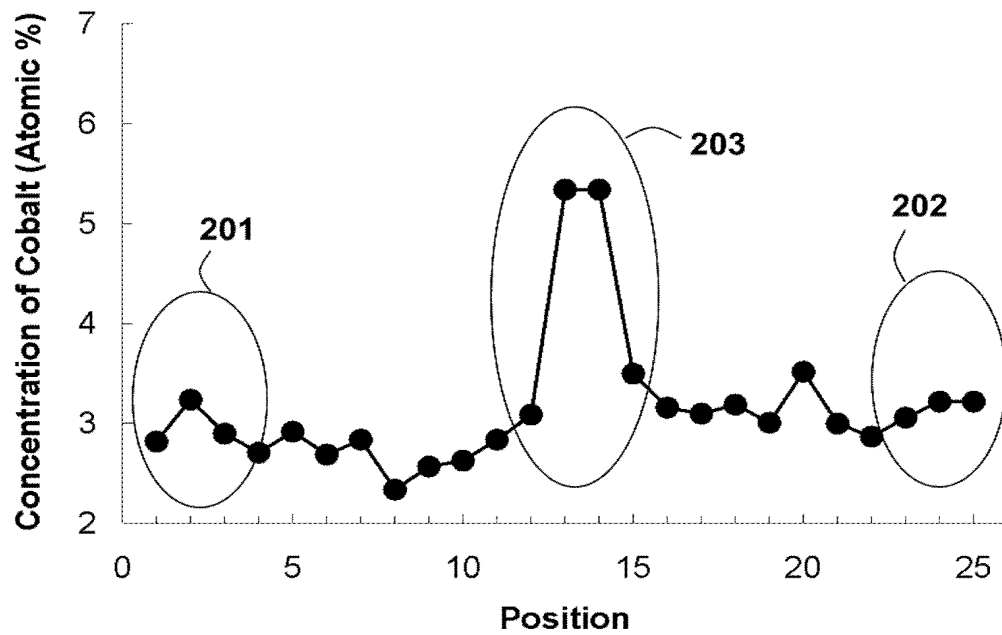


FIG. 7

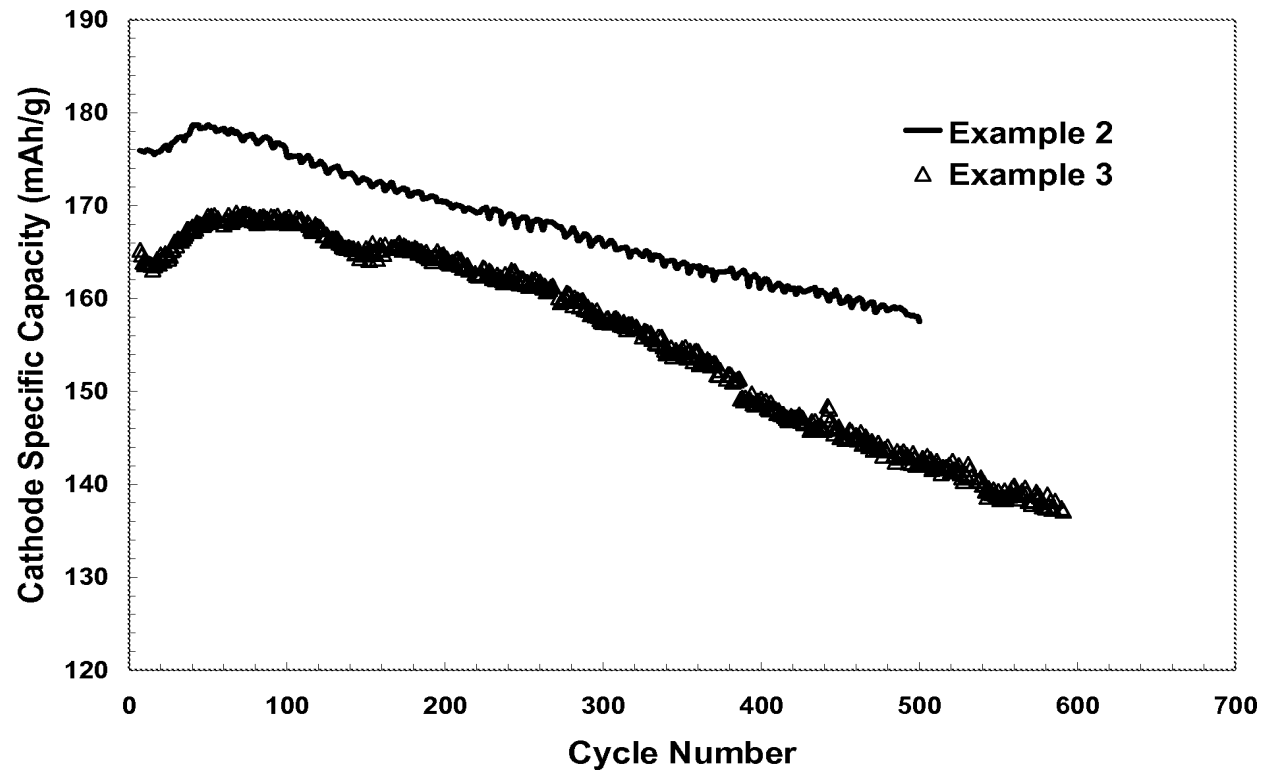


FIG. 8

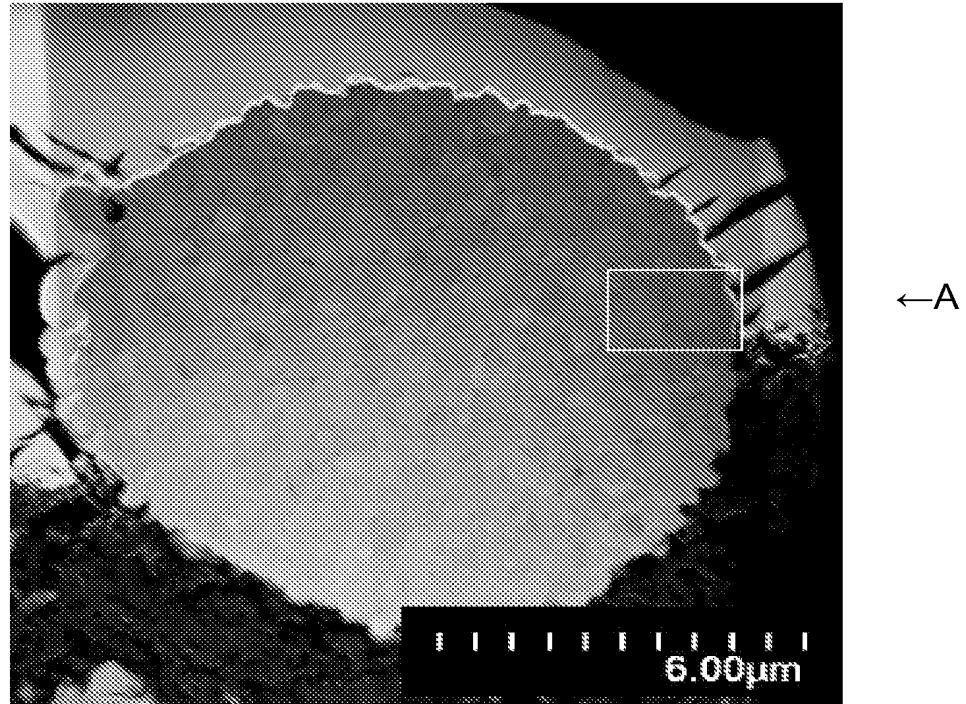


FIG. 9

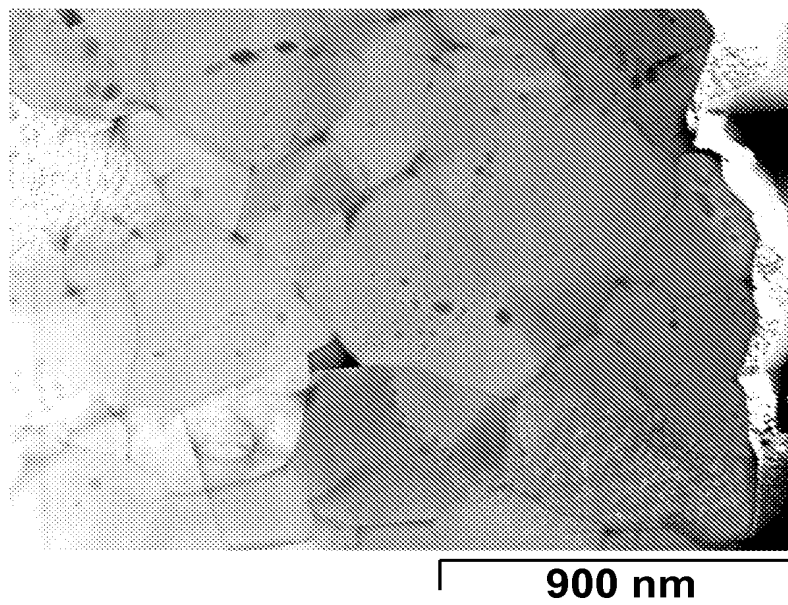


FIG. 10

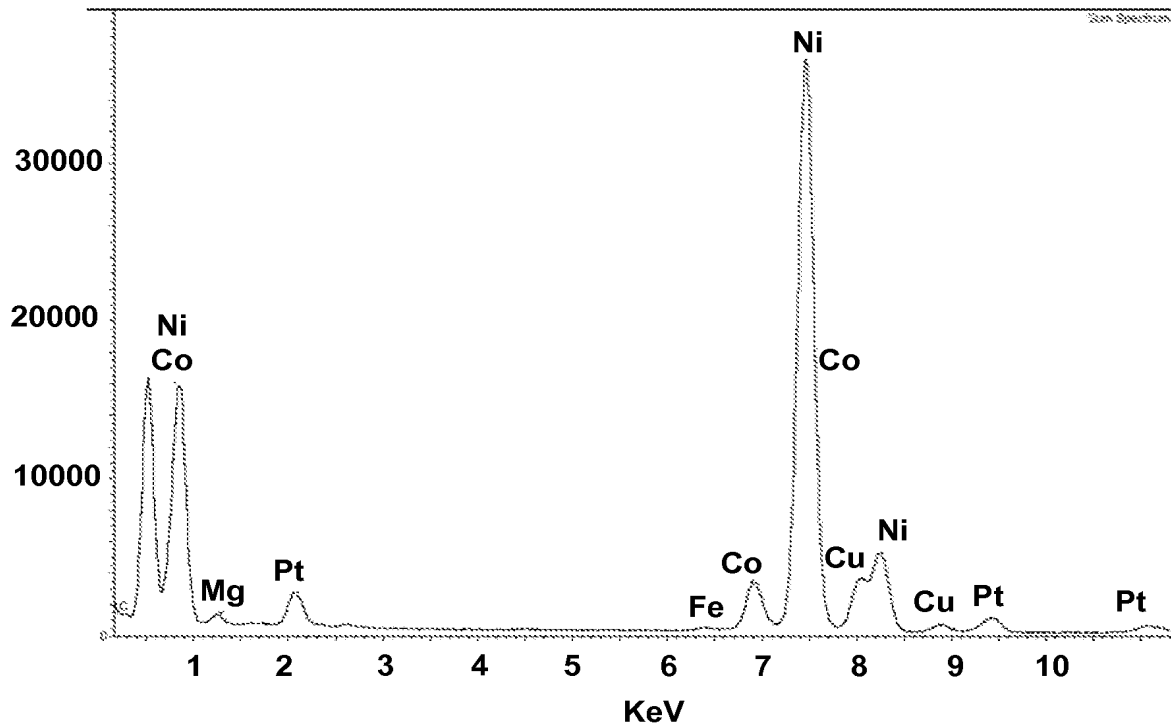


FIG. 11

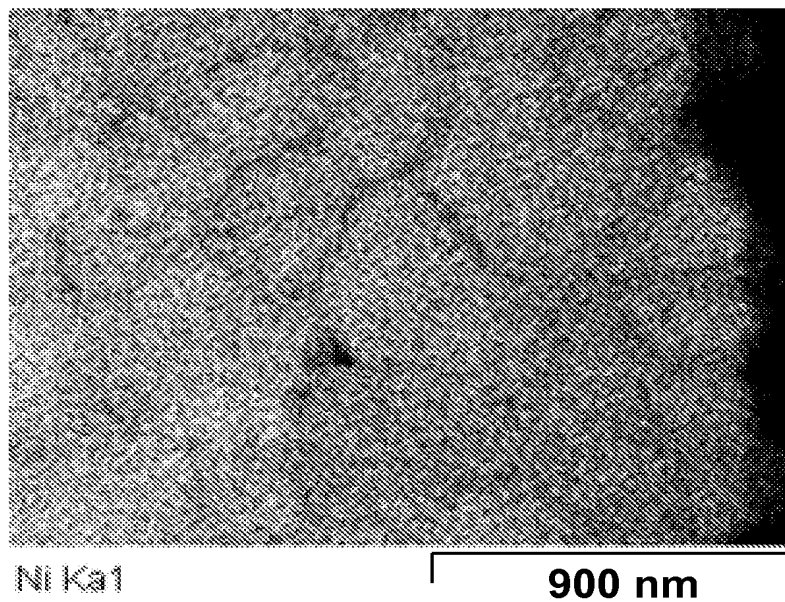


FIG. 12

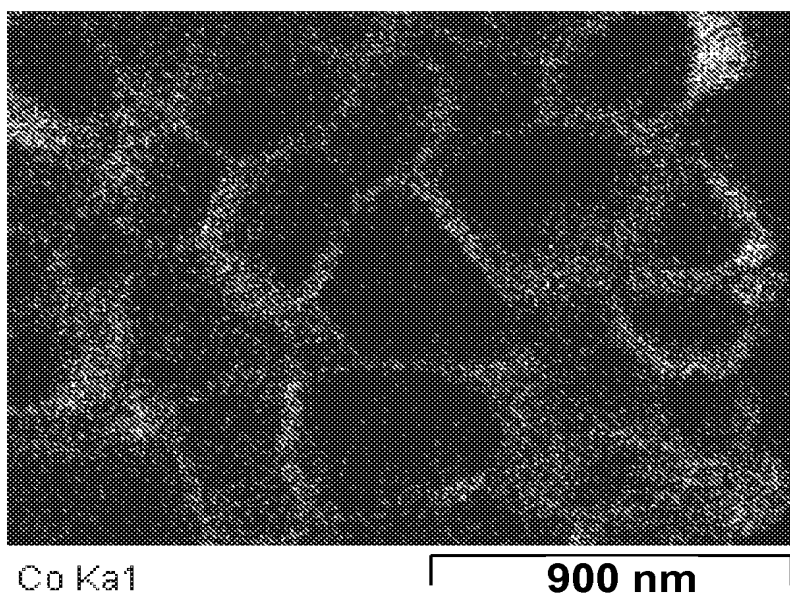


FIG. 13